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Surface Engineering

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The Volume Chairpersons were Catherine M. Cotell, James A. Sprague, and Fred A. Smidt, Jr.

Authors and Contributors

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Foreword

Improving the performance, extending the life, and enhancing the appearance of materials used for engineering components are fundamental--and increasingly important--concerns of ASM members. As the performance demands placed on materials in engineering applications have increased, the importance of surface engineering (cleaning, finishing, and coating) technologies have increased along with them.

Evidence of the growing interest in (and complexity of) surface engineering processes can be found in the expansion of their coverage in ASM handbooks through the years. The classic 1948 Edition of *Metals Handbook* featured a total of 39 pages in three separate sections on surface treating and coating. In the 8th Edition, surface technologies shared a volume with heat treating, and the number of pages jumped to over 350. The 9th Edition of *Metals Handbook* saw even further expansion, with a separate 715-page volume devoted to cleaning, finishing, and coating.

Surface Engineering, the completely revised and expanded Volume 5 of *ASM Handbook,* builds on the proud history of its predecessors, and it also reflects the latest technological advancements and issues. It includes new coverage of testing and analysis of surfaces and coatings, environmental regulation and compliance, surface engineering of nonmetallic materials, and many other topics.

The creation of this Volume would not have been possible without the early leadership of Volume Chairperson Fred A. Smidt, who passed away during the editorial development of the handbook. Two of his colleagues at the Naval Research Laboratory, Catherine M. Cotell and James A. Sprague, stepped in to see the project through to completion, and they have done an excellent job of shaping the content of the book and helping to ensure that it adheres to high technical and editorial standards. Special thanks are also due to the Section Chairpersons, to the members of the ASM Handbook Committee, and to the ASM editorial and production staffs. Of course, we are especially grateful to the hundreds of authors and reviewers who have contributed their time and expertise to create this outstanding information resource.

Jack G. Simon
President
ASM International

Edward L. Langer
Managing Director
ASM International

Preface

In the 9th Edition of *Metals Handbook,* the title of this Volume was *Surface Cleaning, Finishing, and Coating;* for the new *ASM Handbook* edition, the title has been changed to *Surface Engineering.* A useful working definition of the term *surface engineering* is "treatment of the surface and near-surface regions of a material to allow the surface to perform functions that are distinct from those functions demanded from the bulk of the material." These surface-specific functions include protecting the bulk material from hostile environments, providing low- or high-friction contacts with other materials, serving as electronic circuit elements, and providing a particular desired appearance.

Although the surface normally cannot be made totally independent from the bulk, the demands on surface and bulk properties are often quite different. For example, in the case of a turbine blade for a high-performance jet engine, the bulk of the material must have sufficient creep resistance and fatigue strength at the service temperature to provide an acceptably safe service life. The surface of the material, on the other hand, must possess sufficient resistance to oxidation

and hot corrosion under the conditions of service to achieve that same component life. In many instances, it is either more economical or absolutely necessary to select a material with the required bulk properties and specifically engineer the surface to create the required interface with the environment, rather than to find one material that has both the bulk and surface properties required to do the job. It is the purpose of this Volume to guide engineers and scientists in the selection and application of surface treatments that address a wide range of requirements.

Scope of Coverage. This Volume describes surface modifications for applications such as structural components, in which the bulk material properties are the primary consideration and the surface properties must be modified for aesthetics, oxidation resistance, hardness, or other considerations. It also provides some limited information on surface modifications for applications such as microelectronic components, in which the near-surface properties are paramount and the bulk serves mainly as a substrate for the surface material.

The techniques covered may be divided broadly into three categories:

- Techniques to prepare a surface for subsequent treatment (e.g., cleaning and descaling)
- Techniques to cover a surface with a material of different composition or structure (e.g., plating, painting, and coating)
- Techniques to modify an existing surface topographically, chemically, or microstructurally to enhance its properties (e.g., glazing, abrasive finishing, and ion implantation)

Two significant surface-modification techniques that are not covered extensively in this Volume are conventional carburizing and nitriding. Detailed information on these processes is available in *Heat Treating,* Volume 4 of the *ASM Handbook.*

The materials that are suitable for surface engineering by the techniques addressed in this Volume include metals, semiconductors, ceramics, and polymers. Coverage of the classes of surfaces to be engineered has been broadened in this edition, reflecting the trend toward the use of new materials in many applications. Hence, this Volume provides information on topics such as high-temperature superconducting ceramics, organic-matrix composites that are substituted for metals in many automotive parts, diamond coatings that are used for either their hardness or their electronic properties, and surfaces that are implanted on medical prostheses for use in the human body. While a number of new materials and processes have been added to the coverage of this Volume, every attempt has been made to update, expand, and improve the coverage of the established surface treatments and coatings for ferrous and nonferrous metals.

In this edition, a section has been added that specifically addresses the environmental protection issues associated with the surface treatment of materials. These issues recently have become extremely important for surface treatment technology, because many surface modification processes have the potential to create major environmental problems. For some technologies, such as cadmium and chromium plating, environmental concerns have prompted intensive research efforts to devise economical alternative surface treatments to replace the more traditional but environmentally hostile methods. This Volume presents the current status of these environmental protection concerns and the efforts underway to address them. This is a rapidly developing subject, however, and many legal and technological changes can be expected during the publication life of this Volume.

Organization. Depending on the specific problem confronting an engineer or scientist, the most useful organization of a handbook on surface engineering can be by technique, by material being applied to the surface, or by substrate material being treated. The choice of an appropriate technique may be limited by such factors as chemical or thermal stability, geometrical constraints, and cost. The choice of material applied to a surface is typically dictated by the service environment in which the material will be used, the desired physical appearance of the surface, or, in the case of materials for microelectronic devices, the electrical or magnetic properties of the material. The substrate material being treated is usually chosen for its mechanical properties. Although the surface modification technique and the material being applied to the surface can be changed, in many cases, to take advantage of benefits provided by alternative techniques or coatings, the choice of a substrate material is generally inflexible. For example, if the problem confronting the materials engineer is the corrosion protection of a steel component, the most direct approach is to survey the processes that have been successfully applied to that particular base material. Once candidate processes have been identified, they can be examined in more detail to determine their suitability for the particular problem.

To serve as wide a range of needs as possible, this Volume is organized by both treatment technique and base material. Wherever possible, efforts have been made to cross-reference the technique and material sections to provide the reader with a comprehensive treatment of the subject.

The first several sections are organized by technique, covering surface cleaning, finishing, plating, chemical coating, vapor deposition, ion implantation, and diffusion treatment. The first of the process-oriented sections, "Surface Cleaning," covers techniques for removing various types of foreign substances. In addition to the mature technologies that have been applied routinely for decades, this section describes a number of processes and innovations that have been developed recently, prompted by both technological demands and environmental concerns. The section "Finishing Methods" addresses processes used to modify the physical topography of existing surfaces. These processes also have a lengthy history, but they continue to evolve with the development of new materials and applications. New information has been added to this section on methods used to assess the characteristics of finished surfaces.

The section "Plating and Electroplating" describes processes used for electrolytic and nonelectrolytic deposition of metallic coatings. Coverage of these techniques has been significantly expanded in this edition to include a larger number of metals and alloys that can be plated onto substrate materials. This section also contains an article on electroforming, a topic that spans surface and bulk material production. The next section, "Dip, Barrier, and Chemical Conversion Coatings," contains articles on physically applied coatings, such as paints and enamels, as well as on coatings applied by chemical reactions, which are similar in many cases to plating reactions. The final technique-related section, "Vacuum and Controlled-Atmosphere Coating and Surface Modification Processes," covers techniques that apply coatings from the vapor and liquid phases, plus ion implantation, which modifies the composition near the surface of materials by injecting energetic atoms directly into the substrate. Several new technologies involving deposition of energetic atoms have been added to this section. Reflecting the rapid development of electronic materials applications since the last edition was published, articles have been added on processes specifically applicable to semiconductors, superconductors, metallization contacts, and dielectrics.

Following the technique-oriented sections, a new section has been added for this edition specifically to address methods for the testing and characterization of modified surfaces. This information is similar to that provided in *Materials Characterization,* Volume 10 of *ASM Handbook,* but it is extrapolated to surface-specific applications. Because of the functions performed by engineered surfaces and the limited thickness of many coatings, materials characterization techniques must be specifically tailored to obtain information relevant to these problems.

The next four sections of the book focus on then selection and application of surface modification processes for specific bulk or substrate materials. The section "Surface Engineering of Irons and Steels" is new to this edition and provides a convenient overview of applicable processes for these key materials. The articles in the section "Surface Engineering of Nonferrous Metals" provide updated information on the selection and use of surface treatments for widely used nonferrous metals. Reflecting the increased importance of a variety of materials to engineers and scientists and the integration of different classes of materials into devices, a section entitled "Surface Engineering of Selected Nonmetallic Materials" has been added to this edition.

The final section of this Volume, "Environmental Protection Issues," deals with regulatory and compliance issues related to surface engineering of materials. In recent years, concerns about the impact of many industrial processes on local environments and the global environment have joined economic and technological questions as significant drivers of manufacturing decisions. The surface engineering industry, with its traditional reliance on toxic liquids and vapors for many processes, has been especially affected by these concerns. Environmental protection in surface engineering of materials is a rapidly developing field, and this final section attempts to assess the current status of these issues and give some bases for predicting future trends.

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Staff

ASM International staff who contributed to the development of the Volume included Scott D. Henry, Manager of Handbook Development; Grace M. Davidson, Manager of Handbook Production; Steven R. Lampman, Technical Editor; Faith Reidenbach, Chief Copy Editor; Tina M. Lucarelli, Editorial Assistant; Randall L. Boring, Production Coordinator; Ann-Marie O'Loughlin, Production Coordinator. Editorial Assistance was provided by Kathleen S. Dragolich, Kelly Ferjutz, Nikki D. Wheaton, and Mara S. Woods. It was prepared under the direction of William W. Scott, Jr., Director of Technical Publications.

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Classification and Selection of Cleaning Processes

Revised by David B. Chalk, Texo Corporation

Introduction

CLEANING PROCESSES used for removing soils and contaminants are varied, and their effectiveness depends on the requirements of the specific application. This article describes the basic attributes of the most widely used surface cleaning processes and provides guidelines for choosing an appropriate process for particular applications.

The processing procedures, equipment requirements, effects of variables, and safety precautions that are applicable to individual cleaning processes are covered in separate articles that follow in this Section of the handbook. Additional relevant information is contained in the articles "Environmental Regulation of Surface Engineering," "Vapor Degreasing Alternatives," and "Compliant Wipe Solvent Cleaners" in this Volume. Information about considerations involved in cleaning of specific metals is available in the Sections

Cleaning Process Selection

In selecting a metal cleaning process, many factors must be considered, including:

- The nature of the soil to be removed
- The substrate to be cleaned (i.e., ferrous, nonferrous, etc.)
- The importance of the condition of the surface to the end use of the part
- The degree of cleanliness required
- The existing capabilities of available facilities
- The environmental impact of the cleaning process
- Cost considerations
- The total surface area to be cleaned
- Effects of previous processes
- Rust inhibition requirements
- Materials handling factors
- Surface requirements of subsequent operations, such as phosphate conversion coating, painting, or plating

Very few of these factors can be accurately quantified, which results in subjective analysis. Frequently, several sequences of operations may be chosen which together produce the desired end result. As in most industrial operations, the tendency is to provide as much flexibility and versatility in a facility as the available budget will allow. The size and shape of the largest predicted workpiece is generally used to establish the cleaning procedure, equipment sizes, and handling techniques involved.

Because of the variety of cleaning materials available and the process step possibilities, the selection of a cleaning procedure depends greatly on the degree of cleanliness required and subsequent operations to be performed. Abrasive blasting produces the lowest degree of cleanliness. Solvent, solvent vapor degrease, emulsion soak, alkaline soak, alkaline electroclean, alkaline plus acid cleaning, and finally ultrasonics each progressively produces a cleaner surface. In addition to these conventional methods, very exotic and highly technical procedures have been developed in the electronics and space efforts to produce clean surfaces far above the normal requirements for industrial use.

Cleaning Media. Understanding the mechanics of the cleaning action for particular processes can help guide the selection of an appropriate method.

Solvent cleaning, as the name implies, is the dissolution of contaminants by an organic solvent. Typical solvents are trichloroethylene, methylene chloride, toluene, and benzene. The solvent can be applied by swabbing, tank immersion, spray or solid stream flushing, or vapor condensation. Vapor degreasing is accomplished by immersing the work into a cloud of solvent vapor; the vapor condenses on the cooler work surface and dissolves the contaminants. Subsequent flushing with liquid solvent completes the cleaning process. Temperature elevation accelerates the activity.

One major drawback of solvent cleaning is the possibility of leaving some residues on the surface, often necessitating additional cleaning steps. Another more significant disadvantage is the environmental impact of solvent cleaning processes. In fact, much effort is being expended on replacing solvent-based processes with more environmentally acceptable aqueous-based processes (see the article "Vapor Degreasing Alternatives" in this Volume).

Emulsion cleaning depends on the physical action of emulsification, in which discrete particles of contaminant are suspended in the cleaning medium and then separated from the surface to be cleaned. Emulsion cleaners can be water or water solvent-based solutions; for example, emulsions of hydrocarbon solvents such as kerosene and water containing emulsifiable surfactant. To maintain stable emulsions, coupling agents such as oleic acid are added.

Alkaline cleaning is the mainstay of industrial cleaning and may employ both physical and chemical actions. These cleaners contain combinations of ingredients such as surfactants, sequestering agents, saponifiers, emulsifiers, and chelators, as well as various forms of stabilizers and extenders. Except for saponifiers, these ingredients are physically active and operate by reducing surface or interfacial tension, by formation of emulsions, and suspension or flotation of insoluble particles. Solid particles on the surface are generally assumed to be electrically attracted to the surface. During

the cleaning process, these particles are surrounded by wetting agents to neutralize the electrical charge and are floated away, held in solution suspension indefinitely, or eventually are settled out as a sludge in the cleaning tank.

Saponification is a chemical reaction that splits an ester into its acid and alcohol moieties through an irreversible base-induced hydrolysis. The reaction products are more easily cleaned from the surface by the surface-active agents in the alkaline cleaner. Excessive foaming can result if the alkalinity in the cleaner drops to the point where base-induced hydrolysis cannot occur; the reaction of the detergents in the cleaner with oil on the work surface can make soaps, which causes the characteristic foaming often seen in a spent cleaner.

Electrolytic cleaning is a modification of alkaline cleaning in which an electrical current is imposed on the part to produce vigorous gassing on the surface to promote the release of soils. Electrocleaning can be either anodic or cathodic cleaning. Anodic cleaning is also called "reverse cleaning," and cathodic cleaning is called "direct cleaning." The release of oxygen gas under anodic cleaning or hydrogen gas under cathodic cleaning in the form of tiny bubbles from the work surface greatly facilitates lifting and removing surface soils.

Abrasive cleaning uses small sharp particles propelled by an air stream or water jet to impinge on the surface, removing contaminants by the resulting impact force. A wide variety of abrasive media in many sizes is available to meet specific needs. Abrasive cleaning is often preferred for removing heavy scale and paint, especially on large, otherwise inaccessible areas. Abrasive cleaning is also frequently the only allowable cleaning method for steels sensitive to hydrogen embrittlement. This method of cleaning is also used to prepare metals, such as stainless steel and titanium, for painting to produce a mechanical lock for adhesion because conversion coatings cannot be applied easily to these metals.

Acid cleaning is used more often in conjunction with other steps than by itself. Acids have the ability to dissolve oxides, which are usually insoluble in other solutions. Straight mineral acids, such as hydrochloric, sulfuric, and nitric acids, are used for most acid cleaning, but organic acids, such as citric, oxalic, acetic, tartaric, and gluconic acids, occupy an important place in acid cleaning because of their chelating capability.

Phosphoric Acid Etching. Phosphoric acid is often used as an etchant for nonferrous metals (such as copper, brass, aluminum, and zinc) to enhance paint adhesion. A detergent-bearing iron phosphating solution is often ideal for this sort of combined cleaning and etching approach.

Molten salt bath cleaning is very effective for removing many soils, especially paints and heavy scale. However, the very high operating temperatures and high facility costs discourage widespread use of this process.

Ultrasonic cleaning uses sound waves passed at a very high frequency through liquid cleaners, which can be alkaline, acid, or even organic solvents. The passage of ultrasonic waves through the liquid medium creates tiny gas bubbles, which provide a vigorous scrubbing action on the parts being cleaned. Although the mechanism of this action is not completely understood, it yields very efficient cleaning. It is ideal for lightly soiled work with intricate shapes, surfaces, and cavities that may not be easily cleaned by spray or immersion techniques. A disadvantage of ultrasonic cleaning processes is the high capital cost of the power supplies and transducers that comprise the system. Therefore, only applications with the most rigorous cleaning requirements are suitable for this technique.

Substrate Considerations. The selection of a cleaning process must be based on the substrate being cleaned as well as the soil to be removed. Metals such as aluminum and magnesium require special consideration because of their sensitivity to attack by chemicals. Aluminum is dissolved rapidly by both alkalis and acids. Magnesium is resistant to alkaline solutions with pH values up to 11, but is attacked by many acids. Copper is merely stained by alkalis, yet severely attacked by oxidizing acids (such as nitric acid) and only slightly by others. Zinc and cadmium are attacked by both acids and alkalis. Steels are highly resistant to alkalis and attacked by essentially all acidic material. Corrosion-resistant steels, also referred to as *stainless steels*, have a high resistance to both acids and alkalis, but the degree of resistance depends on the alloying elements. Titanium and zirconium have come into common use because of their excellent chemical resistance. These two metals are highly resistant to both alkalis and acids with the exception of acid fluorides which attack them rapidly and severely.

Table 1 summarizes the comparative attributes of the principal cleaning processes.

Table 1 Comparative attributes of selected cleaning processes

Rated on a scale where 10 = best and 1 = worst

Attribute	Hand wiping	Immersion	Emulsion	Batch spray	Continuous conveyor	Ultrasonic
Handling	2	7	7	5	9	7
Cleanness	4	3	5	7	7	10
Process control	3	6	6	8	9	9
Capital cost	7	8	7	5	4	1
Operating cost	5	8	8	7	6	6

Types of soil may be broadly classified into six groups: pigmented drawing compounds, unpigmented oil and grease, chips and cutting fluids, polishing and buffing compounds, rust and scale, and miscellaneous surface contaminants, such as lapping compounds and residue from magnetic particle inspection. These six types of soil are dealt with separately in the order listed.

Removal of Pigmented Drawing Compounds

All pigmented drawing lubricants are difficult to remove from metal parts. Consequently, many plants review all aspects of press forming operations to avoid the use of pigmented compounds. Pigmented compounds most commonly used contain one or more of the following substances: whiting, lithopone, mica, zinc oxide, bentonite, flour, graphite, white lead (which is highly toxic), molybdenum disulfide, animal fat, and soaplike materials. Some of these substances are more difficult to remove than others. Because of their chemical inertness to acid and alkali used in the cleaners and tight adherence to metal surfaces, graphite, white lead, molybdenum disulfide, and soaps are the most difficult to solubilize and remove.

Certain variables in the drawing operation may further complicate the removal of drawing lubricants. For example, as drawing pressures are increased, the resulting higher temperatures increase the adherence of the compounds to the extent that some manual scrubbing is often an essential part of the subsequent cleaning operation. Elapsed time between the drawing and cleaning operations is also a significant factor. Drawing lubricants will oxidize and loosely polymerize on metal surfaces over time, rendering them even more resistant to cleaning.

Table 2 indicates cleaning processes typically selected for removing pigmented compounds from drawn and stamped parts such as Parts 1 through 6 in Fig. 1.

Table 2 Metal cleaning processes for removing selected contaminants

Type of production	In-process cleaning	Preparation for painting	Preparation for phosphating	Preparation for plating
Removal of pigmented drawing compounds[(a)]				
Occasional or intermittent	Hot emulsion hand slush, spray emulsion in single stage, vapor slush degrease[(b)]	Boiling alkaline blow off, hand wipe	Hot emulsion hand slush, spray emulsion in single stage, hot rinse, hand wipe	Hot alkaline soak, hot rinse (hand wipe, if possible) electrolytic alkaline, cold water rinse
		Vapor slush degrease, hand wipe		

Type of production	In-process cleaning	Preparation for painting	Preparation for phosphating	Preparation for plating
		Acid clean[c]		
Continuous high production	Conveyorized spray emulsion washer	Alkaline soak, hot rinse alkaline spray, hot rinse	Alkaline or acid[d] soak, hot rinse, alkaline or acid[d] spray, hot rinse	Hot emulsion or alkaline soak, hot rinse, electrolytic alkaline, hot rinse
Removal of unpigmented oil and grease				
Occasional or intermittent	Solvent wipe	Solvent wipe	Solvent wipe	Solvent wipe
	Emulsion dip or spray	Vapor degrease	Emulsion dip or spray, rinse	Emulsion soak, barrel rinse, electrolytic alkaline rinse, hydrochloric acid dip, rinse
	Vapor degrease	Phosphoric acid etch	Vapor degrease	
	Cold solvent dip		Alkaline spray	
	Alkaline dip, rinse, dry or dip in rust preventative			
Continuous high production	Automatic vapor degrease	Automatic vapor degrease	Emulsion power spray, rinse	Automatic vapor degrease, electrolytic alkaline rinse, hydrochloric acid dip, rinse[e]
	Emulsion, tumble, spray, rinse, dry		Vapor degrease	
			Acid clean[c]	
Removal of chips and cutting fluid				
Occasional or intermittent	Solvent wipe	Solvent wipe	Solvent wipe	Solvent wipe
	Alkaline dip and emulsion surfactant	Alkaline dip and emulsion surfactant	Alkaline dip and emulsion surfactant[f]	Alkaline dip, rinse, electrolytic alkaline[g], rinse, acid dip, rinse[h]
	Stoddard solvent or trichlorethylene	Solvent or vapor	Solvent or vapor	
	Steam			
Continuous high production	Alkaline (dip or spray) and emulsion surfactant	Alkaline (dip or spray) and emulsion surfactant	Alkaline (dip or spray) and emulsion surfactant	Alkaline soak, rinse, electrolytic alkaline[g], rinse, acid dip and rinse[h]

Type of production	In-process cleaning	Preparation for painting	Preparation for phosphating	Preparation for plating
Removal of polishing and buffing compounds				
Occasional or intermittent	Seldom required	Solvent wipe	Solvent wipe	Solvent wipe
		Surfactant alkaline (agitated soak), rinse	Surfactant alkaline (agitated soak), rinse	Surfactant alkaline (agitated soak), rinse, electroclean[i]
		Emulsion soak, rinse	Emulsion soak, rinse	Alkaline spray
Continuous high production	Seldom required	Surfactant alkaline spray, spray rinse	Surfactant alkaline spray, spray rinse	Surfactant alkaline soak and spray, alkaline soak, spray and rinse, electrolytic alkaline[i], rinse, mild acid pickle, rinse
		Agitated soak or spray, rinse[j]	Emulsion spray, rinse	

(a) For complete removal of pigment, parts should be cleaned immediately after the forming operation, and all rinses should be sprayed where practical.

(b) Used only when pigment residue can be tolerated in subsequent operations.

(c) Phosphoric acid cleaner-coaters are often sprayed on the parts to clean the surface and leave a thin phosphate coating.

(d) Phosphoric acid for cleaning and iron phosphating. Proprietary products for high-and low-temperature application are available.

(e) Some plating processes may require additional cleaning dips.

(f) Neutral emulsion or solvent should be used before manganese phosphating.

(g) Reverse-current cleaning may be necessary to remove chips from parts having deep recesses.

(h) For cyanide plating, acid dip and water rinse are followed by alkaline and water rinses.

(i) Other preferences: stable or diphase emulsion spray or soak, rinse, alkaline spray or soak, rinse, electroclean; or solvent presoak, alkaline soak or spray, electroclean.

(j) Third preference: emulsion spray rinse

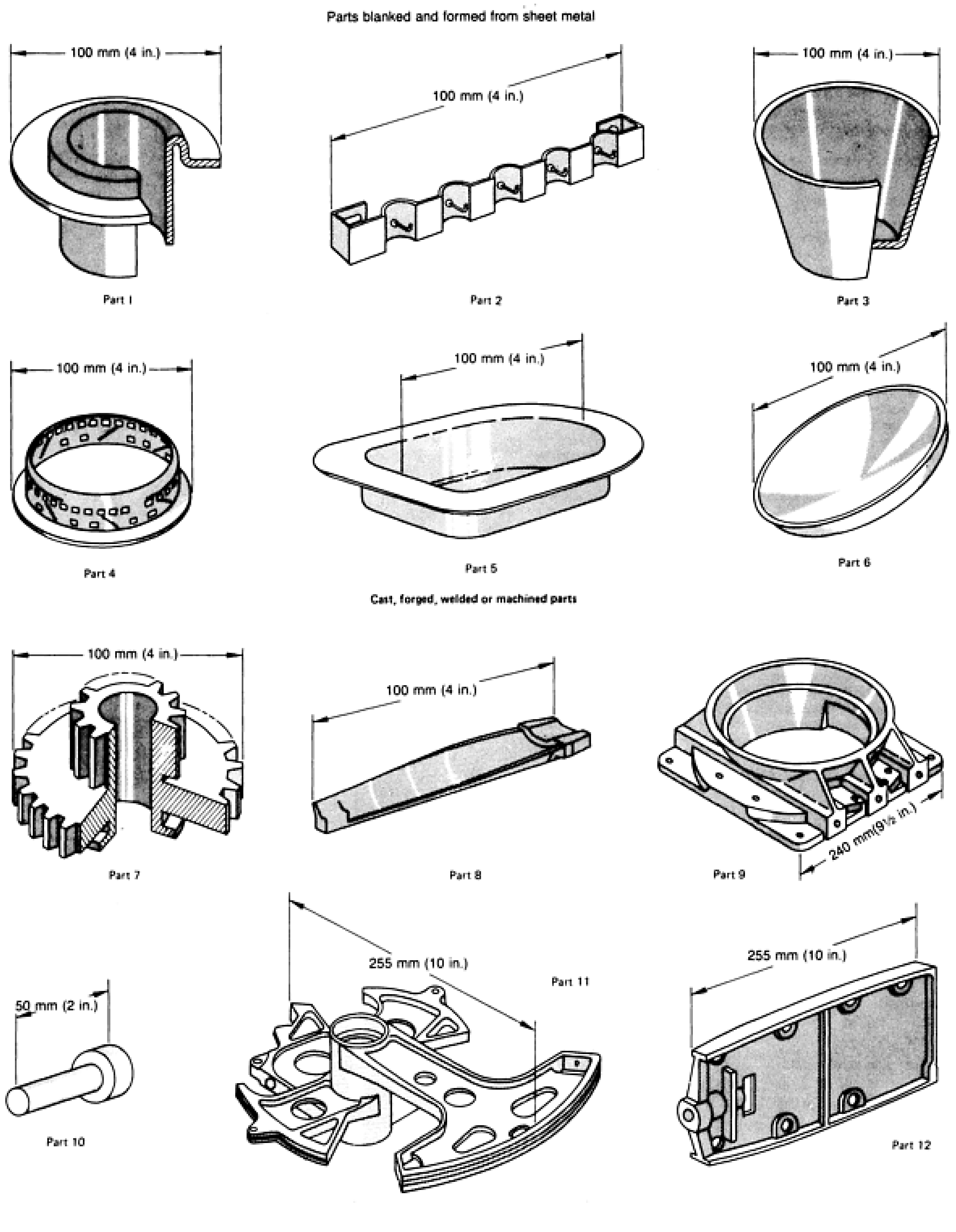

Fig. 1 Sample part configurations cleaned by various processes. See text for discussion.

Emulsion cleaning is one of the most effective methods for removing pigmented compounds, because is relies on mechanical wetting and floating the contaminant away from the surface, rather than chemical action which would be completely ineffective on such inert materials. However, emulsions alone will not do a complete cleaning job, particularly when graphite or molybdenum disulfide is the contaminant. Emulsion cleaning is an effective method of removing pigment because emulsion cleaners contain organic solvents and surfactants, which can dissolve the binders, such as stearates, present in the compounds.

Diphase or multiphase emulsions, having concentrations of 1 to 10% in water and used in a power spray washer, yield the best results in removing pigmented compounds. The usual spray time is 30 to 60 s; emulsion temperatures may range

from 54 to 77 °C (130 to 170 °F), depending on the flash point of the cleaner. In continuous cleaning, two adjacent spray zones or a hot water (60 to 66 °C, or 140 to 150 °F) rinse stage located between the two cleaner spraying zones is common practice.

Cleaning with an emulsifiable solvent, a combination of solvent and emulsion cleaning, is an effective technique for removing pigmented compounds. Emulsifiable solvents may either be used full strength or be diluted with a hydrocarbon solvent, 10 parts to 1 to 4 parts of emulsifiable solvent. Workpieces with heavy deposits of pigmented compound are soaked in this solution, or the solution is slushed or swabbed into heavily contaminated areas. After thorough contact has been made between the solvent and the soil, workpieces are rinsed in hot water, preferably by pressure spray. Emulsification loosens the soil and permits it to be flushed away. Additional cleaning, if required, is usually done by either a conventional emulsion or an alkaline cleaning cycle.

Most emulsion cleaners can be safely used to remove soil from any metal. However, a few highly alkaline emulsion cleaners with pH higher than 10 must be used with caution in cleaning aluminum or zinc because of chemical attack. Low alkaline pH (8 to 9) emulsion cleaners, safe on zinc and aluminum, are available. Emulsion cleaners with a pH above 11 should not be used on magnesium alloys.

Alkaline cleaning, when used exclusively, is only marginally effective in removing pigmented compounds. Success depends mainly on the type of pigmented compounds present and the extent to which they have been allowed to dry. If the compounds are the more difficult types, such as graphite or white lead, and have been allowed to harden, hand slushing and manual brushing will be required for removing all traces of the pigment. Hot alkaline scale conditioning solutions can be used to remove graphite and molybdenum disulfide pigmented hot forming and heat treating protective coatings. The use of ultrasonics in alkaline cleaning is also highly effective in removing tough pigmented drawing compounds.

The softer pigmented compounds can usually be removed by alkaline immersion and spray cycles (Table 2). The degree of cleanness obtained depends largely on thorough mechanical agitation in tanks or barrels, or strong impingement if a spray is used. A minimum spray pressure of 0.10 MPa (15 psi) is recommended.

Parts such as 1 to 6 in Fig. 1 can be cleaned effectively by immersion or immersion and spray when the parts are no longer than about 508 mm (20 in.) across. Larger parts of this type can be cleaned more effectively by spraying. Operating conditions and the sequence of processes for a typical alkaline cleaning cycle are listed in Table 3. This cycle has removed pigmented compounds effectively from a wide variety of stampings and drawn parts. Energy saving low-temperature solventized-alkaline cleaners are available for soak cleaning. Similarly low-temperature electro-cleaners also are effectively employed in industry, operating at 27 to 49 °C (80 to 120 °F).

Table 3 Alkaline cleaning cycle for removing pigmented drawing compounds

Process sequence	Concentration		Time, min	Temperature		Anode current		Remarks
	g/L	oz/gal		°C	°F	A/dm^2	A/ft^2	
Alkaline soak clean								
Barrel[(a)]	65 to 90	9 to 12	3 to 5	Boiling	Boiling	. . .	. . .	. . .
Rack[(b)]	65 to 90	9 to 12	3 to 5	Boiling	Boiling	. . .	. . .	. . .
Hot water rinse, immersion, and spray								
Barrel[(a)]	. . .	. . .	3[(c)]	43	110	. . .	. . .	Spray jet if barrel is open type

Process sequence	Concentration		Time, min	Temperature		Anode current		Remarks
	g/L	oz/gal		°C	°F	A/dm^2	A/ft^2	
Rack[b]	. . .	. . .	2[c]	43	110	. . .	. . .	Spray rinse, immerse, and spray rinse
Electrolytic alkaline clean								
Barrel[a]	55 to 65	7 to 9	2	82 to 99	180 to 210	4 to 6	40 to 60	. . .
Rack[b]	65 to 90	9 to 12	2	82 to 99	180 to 210	4 to 6	40 to 60	. . .
Hot water rinse, immersion, and spray[d]								
Barrel[a]	. . .	. . .	3[c]	43	110	. . .	. . .	Spray jet if barrel is open type
Rack[b]	. . .	. . .	2[c]	43	110	. . .	. . .	Spray rinse, immerse, and spray rinse
Cold water rinse, immersion, and spray[e]								
Barrel[a]	. . .	. . .	2[c]	. . .	. . .	. . .	. . .	Spray jet if barrel is open type
Rack[b]	. . .	. . .	1[c]	. . .	. . .	. . .	. . .	Spray rinse, immerse, and spray rinse

(a) Rotate during entire cycle.

(b) Agitate arm of rack, if possible.

(c) Immersion time.

(d) Maintain overflow at approximately 8 L/min (2 gal/min).

(e) Clean in cold running water.

Electrolytic alkaline cleaning is seldom used as a sole method for the removal of pigmented compounds. Although the generation of gas at the workpiece surface provides a scrubbing action that aids in removal of a pigment, the cleaner becomes contaminated so rapidly that its use is impractical except for final cleaning before plating (Table 2).

Copper alloys, aluminum, lead, tin, and zinc are susceptible to attack by uninhibited alkaline cleaners (pH 10 to 14). Inhibited alkaline cleaners (pH below 10), which have reduced rates of reaction, are available for cleaning these metals. These contain silicates and borates.

Acid Cleaning. Acid cleaners, composed of detergents, liquid glycol ether, and phosphoric acid have proved effective in removing pigmented compounds from engine parts, such as sheet rocker covers and oil pans, even after the pigments have dried. These acid compounds, mixed with water and used in a power spray, are capable of cleaning such parts without hand scrubbing.

A power spray cycle used by one plant is given in Table 4. A light blowoff follows the rinsing cycle. Parts with recesses should be rotated to allow complete drainage. This cleaning procedure suitably prepares parts for painting, but for parts to be plated, the acid cleaning cycle is conventionally followed by electrolytic cleaning which is usually alkaline, but sometimes done with sulfuric or hydrochloric acid. Phosphoric acid cleaners will not etch steel, although they may cause some discoloration.

Table 4 Power spray acid cleaning for removing pigmented compounds

Steel parts cleaned by this method are suitable for painting, but electrolytic cleaning normally follows if parts are to be electroplated; solventized, phosphoric acid-based, low-temperature (27 to 49 °C, or 80 to 120 °F) products are successfully used for power spray cleaning.

Cycle	Phosphoric acid		Solution temperature		Cycle time, min
	g/L	oz/gal	°C	°F	
Wash	15-19	2-2.5	74-79	165-175	3-4

Aluminum and aluminum alloys are susceptible to some etching in phosphoric acid cleaners. Chromic acid or sodium dichromate with either nitric or sulfuric acid is used to deoxidize aluminum alloys. Nonchromated deoxidizers are preferred environmentally. Ferric sulfate and ferric nitrate are used in place of hexavalent chromium. However, nonchromated deoxidizers tend to produce smut on the workpiece, especially 2000- and 7000-series alloys, when the deoxidizer etch rate is maintained (normally with fluoride) above 0.003 μm/side per hour (0.1 μin./side per hour). For more information on removing smut from aluminum, see the article "Surface Engineering of Aluminum and Aluminum Alloys" in this Volume.

Vapor degreasing is of limited value in removing pigmented compounds. The solvent vapor will usually remove soluble portions of the soil, leaving a residue of dry pigment that may be even more difficult to remove by other cleaning processes. However, modifications of vapor degreasing, such as slushing, spraying, ultrasonic, or combinations of these, can be utilized for 100% removal of the easier-to-clean pigments, such as whiting, zinc oxide, or mica.

The latter practice is often used for occasional or intermittent cleaning (Table 2). However, when difficult-to-clean pigments such as graphite or molybdenum disulfide are present, it is unlikely that slush or spray degreasing will remove 100% of the soil.

Vapor degreasing of titanium should be limited to detailed parts and should not be used on welded assemblies that will see later temperatures in excess of 290 °C (550 °F) because degreasing solvents are known to cause stress-corrosion cracking of titanium at these temperatures. Subsequent pickling in nitric-fluoride etchants may relieve this concern.

Solvent cleaning, because of its relatively high cost, lack of effectiveness, rapid contamination, and health and fire hazards, is seldom recommended for removing pigmented compounds, except for occasional preliminary or rough cleaning before other methods. For example, parts are sometimes soaked in solvents such as kerosene or mineral spirits immediately following the drawing operation to loosen and remove some of the soil, but the principal effect of the operation is to condition parts for easier cleaning by more suitable methods, such as emulsion or alkaline cleaning.

Removal of Unpigmented Oil and Grease

Common shop oils and greases, such as unpigmented drawing lubricants, rust-preventive oils, and quenching and lubricating oils, can be effectively removed by several different cleaners. Selection of the cleaning process depends on production flow as well as on the required degree of cleanness, available equipment, and cost. For example, steel parts in a clean and dry condition will rust within a few hours in a humid atmosphere. Thus, parts that are thoroughly clean and dry must go to the next operation immediately, be placed in hold tanks, or be treated with rust preventatives or water displacing oils. If rust preventatives are used, the parts will probably require another cleaning before further processing. Accordingly, a cleaner that leaves a temporary rust-preventive film might be preferred.

Table 2 lists cleaning methods frequently used for removing oils and greases from the 12 types of parts in Fig. 1. Similar parts that are four or five times as large would be cleaned in the same manner, except for methods of handling. Variation in shape among the 12 parts will affect racking and handling techniques.

Advantages and disadvantages of the cleaners shown in Table 2, as well as other methods for removing common unpigmented oils and greases, are discussed in the following paragraphs.

Emulsion Cleaning. Emulsion cleaners, although fundamentally faster but less thorough than alkaline cleaners, are widely used for intermittent or occasional cleaning, because they leave a film that protects the steel against rust. Emulsion cleaners are most widely used for inprocess cleaning, preparation for phosphating, and precleaning for subsequent alkaline cleaning before plating (Table 2).

Vapor degreasing is an effective and widely used method for removing a wide variety of oils and greases. It develops a reproducible cleanliness because the degreasing fluid is distilled and filtered.

Vapor degreasing has proved especially effective for removing soluble soil from crevices, such as rolled or welded seams that may permanently entrap other cleaners. Vapor degreasing is particularly well adapted for cleaning oil-impregnated parts, such as bearings, and for removing solvent-soluble soils from the interiors of storage tanks.

Solvent cleaning may be used to remove the common oils and greases from metal parts. Methods vary from static immersion to multistage washing. Eight methods of solvent cleaning listed in increasing order of their effectiveness are as follows:

- Static immersion
- Immersion with agitation of parts
- Immersion with agitation of both the solvent and the parts
- Immersion with scrubbing
- Pressure spraying in a spray booth
- Immersion scrubbing, followed by spraying
- Multistage washing
- Hand application with wiper

A number of solvents and their properties are found in the articles on vapor degreasing and solvent cleaning in this Volume. Solvent cleaning is most widely used as a preliminary or conditioning cleaner to degrease both the time required in and contamination of the final cleaner.

Shape of the part influences the cycle and method selected. For example, parts that will nest or entrap fluids (Parts 3 and 6 in Fig. 1) are cleaned by dipping in a high-flash naphtha, Stoddard solvent, or chlorinated hydrocarbon for 5 to 30 s at room temperature. Time depends on the type and amount of soil. Parts that are easily bent or otherwise damaged, such as Part 2 in Fig. 1, are now sprayed for 30 s to 2 min at room temperature. Complex parts, such as Part 9 in Fig. 1, are soaked at room temperature for 1 to 10 min.

Acid Cleaning. Acid cleaners such as the phosphoric acid-ethylene glycol monobutyl ether type are efficient in the removal of oil and grease. Also, they remove light blushing rust and form a thin film of phosphate that provides temporary protection against rusting and functions as a suitable base for paint (Table 2).

Acid cleaners are usually used in a power spray washer. The cycle shown for removing pigmented compounds in Table 4 also removes unpigmented compounds.

Although acid cleaners are comparatively high in cost, they are often used on large ferrous components, such as truck cabs, before painting. Acid cleaners will etch aluminum and other nonferrous metals.

Alkaline Cleaning. Alkaline cleaners are efficient and economical for removing oil and grease and are capable of cleaning to a no-water-break surface. They remove oil and grease by saponification or emulsification, or both. The types that saponify only are quickly exhausted.

Mineral, lard, and synthetic unpigmented drawing compounds are easily removed by alkaline cleaners. Silicones, paraffin, and sulfurized, chlorinated, oxidized, or carbonized oils are difficult, but can be removed by alkaline cleaners. Alkaline cleaners will etch aluminum and other nonferrous metal parts unless inhibitors are used, and aqueous solutions of alkaline cleaners cannot be tolerated on some parts or assemblies. On assemblies comprised of dissimilar metals, this presence of alkaline solution in crevices may result in galvanic corrosion, and even a trace of alkali will contaminate paint and phosphate coating systems; therefore, rinsing must be extremely thorough. However, very hot rinsing will promote flash drying and flash rusting of work. Parts should be kept wet between stages, and delays before subsequent processing should be kept to a minimum. Cold water rinsing is recommended.

Electrolytic alkaline cleaning is effective as a final cleaning process for removing oil and grease from machined surfaces when extreme cleanness is required. It is almost always used for final cleaning before electroplating of items such as precision steel parts (fitted to ±0.0076 mm, or ±0.0003 in.) in refrigeration and air conditioning equipment. Electrolytic alkaline cleaning provided a cleanness of 0.0005 g/10 parts on the small plate assembly (Part 13) in Fig. 2, and of 0.003 g/10 parts on the 165 mm (6.5 in.) diameter part (Part 14). This degree of cleanness was obtained by using a conveyor system and the following cycle:

1. Soak in alkali, 45 to 60 g/L (6 to 8 oz/gal) at 77 to 88 °C (170 to 190 °F) for 1 to 2 min. Energy saving, solventized-alkaline low-temperature soak cleaners, suitable for ferrous and nonferrous metals are available. Similarly, low-temperature electrocleaners are also used. Both operate at 27 to 49 °C (80 to 120 °F).
2. Alkaline clean with reverse current, using current density of 5 A/dm^2 (50 A/ft^2), same time, concentration, and temperature as in step 1. Avoid making the part cathodic when cleaning high-strength steels or titanium to avoid hydrogen embrittlement.
3. Rinse in cold water containing chromic acid for rust prevention.
4. Rinse in cold water containing ammonia.
5. Rinse in hot water containing 0.1% sodium nitrate.
6. Dry in hot air.
7. Place parts in solvent emulsion prior to manganese phosphate coating.

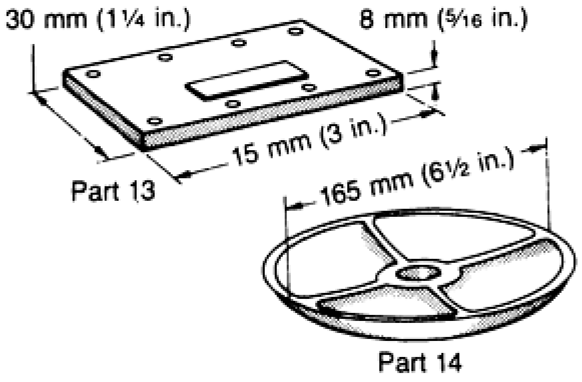

Fig. 2 Parts for refrigerators or air conditioners that are cleaned using electrolytic alkaline processes

Removal of Chips and Cutting Fluids from Steel Parts

Cutting and grinding fluids used for machining may be classified into three groups, as follows:

- Plain or sulfurized mineral and fatty oils (or combination of the two), chlorinated mineral oils, and sulfurized chlorinated mineral oils.
- Conventional or heavy-duty soluble oils with sulfur or other compounds added and soluble grinding oils with wetting agents.
- Chemical cutting fluids, which are water-soluble and generally act as cleaners. They contain soaps, amines, sodium salts of sulfonated fatty alcohols, alkyl aromatic sodium salts of sulfonates, or other types of soluble addition agents.

Usually, all three types of fluids are easily removed, and the chips fall away during cleaning, unless the chips or part become magnetic. Plain boiling water is often suitable for removing these soils, and in some plants, mild detergents are added to the water to increase its effectiveness. Steam is widely used for in-process cleaning, especially for large components. Table 2 indicates cleaning processes typically used for removing cutting fluids to meet specific production requirements.

Emulsion cleaning is an effective and relatively inexpensive means of removing all three types of cutting fluids. Attendant fire hazard is not great if operating temperatures are at least 8 to 11 °C (15 to 20 °F) below the flash temperature of the hydrocarbon used. Parts may be cleaned by either dipping or spraying. Many parts are immersed and then sprayed, particularly parts with complex configurations, such as Part 9 in Fig. 1.

It is has often proved economical to remove a major portion of the soil by alkaline cleaning first and then to use an emulsion surfactant, an emulsion containing surface-activating agent. This sequence prevents the possible contamination of painting or phosphating systems with alkaline solution.

Most emulsion cleaners can be safely used for removing these soils from nonferrous metals. Only the emulsions having pH values higher than 10 are unsafe for cleaning nonferrous metals.

Alkaline Cleaners. Alkaline cleaners are effective for removing all three types of cutting and grinding fluids. Alkaline cleaning is usually the least expensive process and is capable of delivering parts that are clean enough to be phosphate coated or painted. Inhibited alkaline cleaners are required for removing cutting and grinding fluids from aluminum and zinc and their alloys.

Electrolytic alkaline cleaning, which invariable follows conventional alkaline cleaning for parts that are to be plated, is also recommended for removing cutting fluids when extra cleanness is required. For example, Parts 7 and 9 in Fig. 1 would be cleaned electrolytically before scaleless heat treating.

Vapor degreasing will remove cutting fluids of the first group easily and completely, but fluids of the second and third groups may not be completely removed and are likely to cause deterioration of the solvent. Water contained in these soluble fluids causes the hydrolysis of the degreasing solvent and produces hydrochloric acid, which will damage steel and other metals. Vapor degreasing solvents have inhibitors to reduce corrosion by stabilizing the pH. A potential fire hazard exists when water or moisture and aluminum chips are allowed to accumulate in a vapor degreaser.

If vapor degreasing is used to remove water-containing soils, perchloroethylene may be the preferred solvent because its higher boiling point (120 °C or 250 °F) causes most of the water to be driven off as vapor. However, prolonged immersion at 120 °C (250 °F) may also affect the heat treated condition of some aluminum alloys. Used exclusively, the vapor phase will not remove chips or other solid particles. Therefore, combination cycles, such as warm liquid and vapor, are ordinarily used. An air blowoff also aids in removing chips.

Solvent cleaning by soaking (with or without agitation), hand wiping, or spraying is frequently used for removing chips and cutting fluids. Solvents preferentially remove cutting fluids of the first group. Solvent cleaning is commonly used for cleaning between machining operations, to facilitate inspection or fixturing.

Acid Cleaning. Phosphoric or chromic acid cleaners used in a power spray or soak cleaning when followed by pressure spray rinsing are effective in removing most types of cutting fluids. However, they are expensive and are seldom used for routine cleaning. In some applications, acid cleaners have been used because they also remove light rust from ferrous metals and oxide and scale from aluminum alloys.

Removal of Polishing and Buffing Compounds

Polishing and buffing compounds are difficult to remove because the soil they deposit is composed of burned-on grease, metallic soaps, waxes, and vehicles that are contaminated with fine particles of metal and abrasive. Consequently, cleaning requirements should be considered when selecting polishing and buffing compounds. Compounds used for obtaining buffed and polished finishes may be classified by cleaning requirements:

- *Liquids:* mineral oils and oil-in-water emulsions or animal and vegetable oils with abrasives
- *Semisolids:* oil based, containing abrasives and emulsions, or water based, containing abrasives and dispersing agents
- *Solids:* greases containing stearic acid, hydrogenated fatty acid, tallow, hydrogenated glycerides, petroleum waxes, and combinations that produce either saponifiable or unsaponifiable materials, in addition to abrasives

Table 2 lists preferred and alternate methods for removing polishing and buffing compounds from sheet metal parts. However, some modification may be required for complete removal of all classes of these soils. Characteristics of polishing compounds and their effects on cleaning for the three broad classifications of soil are described in the following paragraphs.

Liquid compositions are oil based and flow readily, leaving a thin film of oil that contains particles of metal and abrasive on the work. Under extreme heat and pressure, some oils polymerize and form a glaze that is difficult to remove.

Mineral oils are usually unsaponifiable and are not readily removable by conventional alkaline cleaners. Solvent wiping, alkaline, or emulsion cleaning, using surfactant cleaners containing surface-activating agents, are more effective in removing residues from mineral oils.

Most animal and vegetable oils can be saponified at a slow rate. These oils are insoluble in water, but can be removed by soaking or spraying in hot alkaline solutions (82 °C, or 180 °F). Spraying is preferred because it removes adhering particles more effectively. Surfactants are suitable also, but their higher cost cannot always be justified.

Semisolid compounds are mixtures of liquid binders and abrasives that contain emulsifying or dispersing agents to keep the abrasive in suspension. When subjected to heat and pressure, these compounds usually form a heavy soil on the surface and may cake and fill in depressions and corners. Such compounds vary from unsaponifiable to completely saponifiable. Hand wiping with solvent or emulsion cleaner is effective in removing these compounds. Impingement from power washers usually removes most of the soil, regardless of the cleaner used. If power washers are not available, soak in agitated solutions containing surfactants, followed by a thorough rinsing, for satisfactory results.

Solid Compounds. The oil phases of solid compounds are easily removed, but the remaining residues cling tenaciously to metal surfaces and must be dislodged by scrubbing action. Power washers are the most effective. Most agitated surfactant cleaners are also effective, but the agitation must be strong enough to dislodge the soils.

Removal Methods

Solvent cleaning is effective for precleaning but is more costly than alkaline or emulsion methods. Cleaning with chlorinated solvents in a mechanical degreaser or brushing or spraying with petroleum solvents quickly removes most of the gross soil after buffing or polishing.

Emulsion Cleaning. Emulsion cleaners containing one part of emulsion concentrate to 50 to 100 parts of water, and operated at 54 to 60 °C (130 to 140 °F) are effective for removing mineral oils and other unsaponifiable oils from polished work. To effectively remove semisolid compounds, the temperature must be raised to 66 to 71 °C (150 to 160 °F) and the concentration increased to one part concentrate to 10 to 20 parts water. Agitation helps dislodge soil from corners or grooves. Table 5 describes cleaning cycles for removing polishing and buffing compounds. Thickened emulsion cleaners may be applied with an airless spray pump. Allow 5 to 10 min dwelling time before cold water rinsing. Emulsion cleaners applied manually at ambient temperature are suitable for many applications, especially for buffed aluminum parts.

Table 5 Emulsion cleaning cycles for removing polishing and buffing compounds

All workpieces were rinsed using water spray.

Type of compound	Temperature		Time, min	Concentration, emulsion to water	Agitation
	°C	°F			
Oil	66-71	150-160	3-5	1:10-20	Soak
Semisolid	54-60	130-140	3-5	1:50-100	Solution movement
Solid	71-82	160-180	$1\frac{1}{2}$	1:20-50	Spray wash

Note: All emulsion cleaned parts should be subsequently cleaned by alkaline soaking and electrolytic alkaline cleaning before

Removal of solid soils or those containing grit requires the use of higher temperature (71 to 82 °C, or 160 to 180 °F) and increased concentration (one part concentrate to ten parts water). If the soil is heavy, caked, or impacted in corners, a spray washer is required, and the proper ratio of concentrate to water is between 1 to 20 and 1 to 50 (Table 5).

All emulsion methods must be followed by a thorough water spray rinse. The cleaner will loosen and remove most of the soil, but only a strong water spray can remove the remainder. Warm water is preferred, but cold water can be used. A rust inhibitor additive may be required in the rinse after emulsion cleaning to control flash rusting.

In spray equipment, concentration must be controlled to avoid foaming or breaking the emulsion. When soil removal requires a critical concentration, a foam depressant may be added to the cleaner. Polishing compounds containing soap or soap-forming material will cause excessive foaming during agitation, which may reduce the efficiency of the cleaner and the washer. The performance of emulsion cleaners can sometimes be improved by using them in conjunction with alkaline solutions, particularly in spray washers. Alkaline cleaning compounds at a concentration of about 4 g/L ($\frac{1}{2}$ oz/gal) may be used, but the surface being cleaned will still have an oily film after rinsing.

Although the preceding information is applicable primarily to ferrous metal parts, it can be applied also to brass and to zinc-based die castings. The following is a cycle that proved successful for removing polishing and buffing soil from zinc-based die castings in high-volume production:

1. Preclean by soaking for 4 min in diphase cleaner, using kerosene as the solvent; temperature, 71 °C (160 °F); concentration, 1 to 50; plus a 75 mm (3 in.) layer of kerosene. Parts are sprayed with a solution as they are being withdrawn from the tank.
2. Fog spray rinse.
3. Alkaline spray cleaner, 7.5 g/L (1 oz/gal), 71 °C (160 °F), for $1\frac{1}{2}$ min.
4. Alkaline soak cleaner, 30 to 45 g/L (4 to 6 oz/gal), 71 °C (160 °F), for 4 min.
5. Spray rinse.
6. Transfer to automatic plating machine or electrolytic alkaline cleaning.

Alkaline cleaning, or one of its modifications, is an effective and usually the least expensive method for removing soils left by polishing and buffing. Mineral oils and other saponifiable oils are difficult to remove by soak cleaning. Oil that floats to the surface redeposits on the work unless the bath is continually skimmed. Agitation of the bath to minimize oil float and proper rinsing of parts as there are withdrawn from the tank minimizes the retention of oil by cleaned parts.

Removing liquid or solid compounds that contain abrasives requires agitation. Most soak cleaners foam if agitated sufficiently to dislodge hardened soil from recesses or pockets. A mildly agitated surfactant cleaner, followed by a strong water spray, can loosen these soils (Table 2).

Operating conditions for soak, spray, and electrolytic alkaline cleaning methods for removing polishing and buffing compounds are listed in Table 6. When the soil is charged with abrasive, alkaline cleaners must be renewed more frequently to prevent the accumulation of dirt that will clog screens and nozzles.

Table 6 Alkaline cleaning for removing polishing and buffing compounds

Soak and spray cleaning are followed by electrolytic cleaning if parts are to be electroplated; electrolytic cleaning is usually preceded by soak or spray cleaning.

Method of cleaning	**Concentration**		**Temperature**		**Time, min**
	g/L	**oz/gal**	**°C**	**°F**	
Soak[(a)]	30-90	4-12	82-100	180-212	3-5
Spray[(b)]	4-15	$\frac{1}{2}$ -2	71-82	160-180	1-2
Electrolytic[(c)]	30-90	4-12	82-93	180-200	1-3

Note: Use great care in cleaning brass and zinc die cast, because these materials are easily attacked at high concentration, temperature, and current density of alkaline cleaners. Anodic cleaning is best, using a concentration of 30 to 45 g/L (4 to 6 oz/gal) at a temperature

(a) For removing light oils, semisolid compounds, and solid compounds if not impacted or burned on work; must be followed by a strong spray rinse.

(b) For removing light mineral oils, semisolids, and solids if impacted or caked on work; followed by a rinse.

(c) For removing light oil films and semisolids. Solids are difficult to remove, especially if combined with grit or metal particles.

Electrolytic alkaline cleaning provides a high level of agitation close to the work surface because of the gas generated and is an effective method for removing polishing and buffing residues. Electrocleaners can be easily contaminated by polishing and buffing compounds as well as steel particles which may be attracted to the work and cause surface roughness during plating. Precleaning is necessary. Parts on which mineral oil has been used as a polishing compound should always be precleaned before being electrocleaned. Use of both heavy duty alkaline soak cleaners and electrocleaners is often necessary to provide a water-break-free surface necessary for good plating quality and adhesion. The presence of large amounts of animal or vegetable oils or fatty acids and abrasives in the polishing and buffing compounds will react with free caustic and form soaps in the electrocleaner and shorten its life.

Acid Cleaning. Acid cleaners are chemically limited in their ability to remove polishing and buffing compounds. Soaps and other acid-hydrolyzable materials present in these compounds are decomposed by acid cleaners into insoluble materials, which precludes the use of acid cleaners in most instances.

Acid cleaners can be used alone for the more easily removed polishing and buffing compounds, such as fresh and unpolymerized liquids. In these applications, the acid cleaner must be used at the maximum operating temperature recommended for the specific cleaner in conjunction with the maximum agitation obtainable by spraying or scrubbing.

Acid cleaners may be desirable for removing acid-insensitive soils in special instances such as: where slight surface attack (short of pickling) is needed for dislodging particles or smut, and in conjunction with alkaline or alkaline emulsion cleaners, when successive reversal of pH proves to be advantageous. A light pickle in dilute hydrochloric, hydrofluoric, or sulfuric acid may be added to the cleaning sequence to remove fine metal particles, tarnish, or light scale to activate the surface for electroplating.

Removal of Rust and Scale

The seven basic methods used for removing rust and scale from ferrous mill products, forgings, castings, and fabricated metal parts are:

- Abrasive blasting (dry or wet)
- Tumbling (dry or wet)
- Brushing
- Acid pickling
- Salt bath descaling
- Alkaline descaling
- Acid cleaning

The most important considerations in selecting one of the above methods are:

- Thickness of rust or scale
- Composition of metal
- Condition of metal (product form or heat treatment)
- Allowable metal loss
- Surface finish tolerances
- Shape and size of workpieces
- Production requirements
- Available equipment
- Cost
- Freedom from hydrogen embrittlement

Combinations of two or more of the available processes are frequently used to advantage.

Abrasive blast cleaning is widely used for removing all classes of scale and rust from ferrous mill products, forgings, castings, weldments, and heat treated parts. Depending on the finish requirements, blasting may be the sole means of scale removal, or it may be used to remove the major portion of scale, with pickling employed to remove the remainder. Glass bead cleaning (blasting) is used for cleaning threaded or precision parts, high-strength steel, titanium, and stainless steel.

Tumbling is often the least expensive process for removing rust and scale from metal parts. Size and shape of parts are the primary limitations of the process. Tumbling in dry abrasives (deburring compounds) is effective for removing rust and scale from small parts of simple shape, such as Part 10 in Fig. 1. However, parts of complex shape with deep recesses and other irregularities cannot be descaled uniformly by tumbling and may require several hours of tumbling if that method is used. Adding descaling compounds rather than deburring compounds often decreases the required tumbling time by 75%.

Brushing is the least used method of descaling parts, although it is satisfactory for removing light rust or loosely adhering scale. It is better suited for workpieces formed from tubing than for castings or forgings.

Pickling in hot, strong solutions of sulfamic, phosphoric, sulfuric, or hydrochloric acid is used for complete removal of scale from mill products and fabricated parts. However, pickling is declining in use as a single treatment for scale removal. With increasing frequency, pickling, at acid concentrations of about 3% and at temperatures of about 60 °C (140 °F) or lower, is being used as a supplementary treatment following abrasive blasting or salt bath descaling. Use of

deoxidizing aluminum alloys in room-temperature chromic-nitric-sulfuric acid solutions to remove heat treat scale is common practice.

Electrolytic pickling, although more expensive than conventional pickling, can remove scale twice as fast and may prove economical where the time is limited. In an automatic plating installation, electrolytic pickling removes light scale and oxidizes during the time allowed in the pickling cycle and eliminates a preliminary pickling operation. For this purpose, a solution of 30% hydrochloric acid is used at 55 °C (130 °F) and 3 to 6 V for 2 to 3 min. Cathodic current is used.

Sulfuric acid formulas also are used electrolytically. A cycle for removing light scale from spot-welded parts is a solution of 10% sulfuric acid at 82 °C (180 °F) and 3 to 6 V for 5 to 20 s.

The main objection to electrolytic pickling is high cost. In addition to the requirement for more elaborate equipment, all workpieces must be racked.

Salt bath descaling is an effective means of removing or conditioning scale on carbon, alloy, stainless, and tool steels, heat-resisting alloys, copper alloys, nickel alloys, titanium, and refractory metals. Several types of salt baths either reduce or oxidize the scale. Various baths operate within a temperature range of 400 to 525 °C (750 to 975 °F).

Except in the descaling of pure molybdenum, molten salt baths are seldom used alone for scale removal. Usually, salt bath descaling and quenching are followed by acid pickling as a final step in removing the last of the scale. The supplementary pickling is done with more dilute acids at lower temperatures and for shorter times than are used in conventional pickling. A solution of 3% sulfuric acid at a maximum temperature of about 60 °C (140 °F) is commonly used for pickling after salt bath descaling. Other acids are used at comparable concentrations. Metal loss and the danger of acid embrittlement are negligible in this type of pickling.

Alkaline descaling or alkaline derusting is used to remove rust, light scale, and carbon smut from carbon, alloy, and stainless steels and from heat-resisting alloys. Alkaline descaling is more costly and slower in its action than acid pickling of ferrous alloys, but no metal is lost using the alkaline method, because chemical action stops when the rust or scale is removed. Alkaline descaling also allows complete freedom from hydrogen embrittlement. Alkaline etch cleaning of aluminum alloys is less expensive than acid pickling solutions for descaling, removing shot peen residue, removing smeared metal prior to penetrant inspection, chemical deburring, and decorative finishing of nonclad surfaces.

A number of proprietary compounds are available. They are composed mainly of sodium hydroxide (60% or more) but also contain chelating agents.

Immersion baths are usually operated from room temperature to 71 °C (160 °F), but can be used at 93 to 99 °C (200 to 210 °F) with concentrations of about 0.9 kg (2 lb) of compound to 4 L (1 gal) of water. Required immersion time depends on the thickness of the rust or scale.

The rate of removal of oxide can be greatly increased by the use of current in the bath, either continuous direct or periodically reversed. In one instance, an electrolyzed bath descaled steel parts in $1\frac{1}{2}$ min, as compared to 15 min for a nonelectrolytic bath doing the same job. However, parts must be racked for electrolytic descaling, increasing cost because of the additional equipment, increased power requirement, and decreased bath capacity.

The addition of about 0.5 kg (1 lb) of sodium cyanide per 4 L (1 gal) of water increases the effectiveness of electrolyzed baths. However, when cyanide is used, the bath temperature should be kept below 54 °C (130 °F) to prevent excessive decomposition of the cyanide. One manufacturer descales heat treated aircraft parts in an alkaline descaling bath, using direct current and cyanide additions. Another manufacturer descales similar work in an alkaline bath operated at 82 to 93 °C (180 to 200 °F) with a lower concentration of descaling compound, 60 to 90 g/L (8 to 12 oz/gal), and no cyanide. The latter bath is operated at a current density of 2 to 20 A/dm^2 (20 to 200 A/ft^2) and with periodic current reversal (55 s anodic, followed by 5 s cathodic). Alkaline permanganate baths are also used for descaling. Proprietary products available are used at about 120 g/L (1 lb/gal), 82 to 93 °C (180 to 200 °F), 30 min or longer, depending on scale thickness and condition

Despite the high cost of alkaline descaling baths, they can be economical. Because alkaline descaling baths are compounded for detergency as well as derusting, chemical cleaning and derusting are accomplished simultaneously.

Paint, resin, varnish, oil, grease, and carbon smut are removed along with rust and scale. Thus, in a single operation, work is prepared for phosphating, painting, or electroplating. If parts are to be plated, the cost of electrolytic descaling may be comparable to that of the nonelectrolytic process, because in either case workpieces must be racked before final cleaning and plating. An electrolytic descaling bath may serve as the final cleaner.

Alkaline descalers are used for applications on critical parts such as turbine blades for jet engines where risk of hydrogen embrittlement, loss of metal, or etched surfaces cannot be tolerated. Alkaline descaling may also be chosen for parts made of high-carbon steel or cast iron, because acid pickling will leave smut deposits on these metals. Because of the time required, alkaline descaling is seldom used for removing heavy scale from forgings.

Acid Cleaning. Acid cleaners more dilute than acid pickling solutions are effective for removing light, blushing rust, such as the rust that forms on ferrous metal parts in storage under conditions of high humidity or short-time exposure to rain. Acid deoxidizing solutions specifically designed for use on aluminum remove oxides and should be used before electroplating or chemical coating. Various organic acid-based solutions, such as citric acid, are used to remove rust from stainless steels, including the 400 series and the precipitation hardening steels.

The following examples illustrate the considerations that influence the choice of process for removing rust and scale. Additional criteria for selection of process are included in Table 7, which compares advantages and disadvantages of abrasive blast cleaning, pickling, and salt bath descaling.

Table 7 Advantages and disadvantages of the three principal processes for removing scale and rust from steel parts

Advantages

Abrasive blast cleaning
A variety of equipment and abrasives is available
Does not interfere with properties established by heat treatment
Size of workpiece is limited only by available equipment
A wide variety of shapes can be blasted
All metals can be safely blasted
Adaptable to either intermittent low or continuous high production
Pickling
Formulations can be adjusted to meet individual requirements in removing scale from various ferrous and nonferrous alloys
Equipment required is simple and relatively inexpensive
Materials are relatively low in cost, and process control usually is not difficult
Adaptable to products of virtually any size or shape
Installations can be adapted to either low or high, intermittent or continuous production
Temperatures used will not affect properties of heat treated steel
Salt bath descaling
Reduction or oxidation of the scale is almost instantaneous after workpieces reach bath temperature
No loss of metal and no danger of hydrogen embrittlement
Preliminary cleaning is unnecessary unless there is so much oil on the work that a fire hazard is involved as workpieces enter the bath
Different metals can be descaled in the same bath
Workpieces of complex shape can be processed, although special handling may be required to obtain complete removal of salt
Processing temperature may provide useful stress relieving
For some heat-resisting and refractory metals, molten salt is the only satisfactory method
Will not damage sensitized stainless steels, whereas acid pickling would be harmful

Disadvantages

Abrasive blast cleaning
Some of the metal will be abraded from workpieces, especially from corners
May alter dimensions of machined parts or damaged corners
If sufficiently drastic to remove scale, process may cause more surface etching or roughness than can be tolerated

Complex configurations will not receive equal blasting on all surfaces without special handling, which may be too costly

Pickling

Potential source of hydrogen embrittlement in some metals such as carbon and alloy steels of high carbon content, especially if these materials have been heat treated to high strength levels

Up to 3% of the metal may be lost in pickling--particularly significant for the more costly metals such as stainless steels or heat-resisting alloys

Fume control and disposal of spent acids are major problems

Process is likely to deposit smut on cast iron

Excessive pitting may occur in the pickling of cast steels and irons

Salt bath descaling

Not economical for intermittent production, because high operating temperatures necessitate special heating and handling equipment, and because the bath must be kept molten between production runs

The required water quenching may cause cracking or excessive warping of complex workpieces

The process is not suitable for metals (such) as some grades of stainless steel) that precipitation harden at the temperature of the salt bath

Operating temperature of the bath can cause carbide precipitation in unstabilized stainless steels

Properties of heat treated workpieces may be impaired if their tempering temperature is below that of the salt bath

Subsequent acid cleaning is usually required to neutralize remaining salts, complete the descaling, and brighten the finished product

Example 1:

Barrel or vibratory tumbling is probably the most economical method for removing scale or rust from steel parts like Part 10 in Fig. 1, if they are no larger than about 50 to 75 mm (2 to 3 in.). For similar but larger parts, abrasive blasting is usually a better choice.

However, if such parts are close to finished dimensions and these dimensions are critical, a nonabrasive method of cleaning should be chosen. If parts are made of low-carbon steel and are not heat treated, pickling in inhibited hydrochloric or sulfuric acid is satisfactory and less expensive, and hydrogen embrittlement is not a factor. However, if such parts are made of high-carbon (or carburized) steel and are heat treated, acid pickling would be hazardous and alkaline descaling would be preferred.

Example 2:

The gear illustrated as Part 7 in Fig. 1 is made of 8620 steel, carburized, and hardened to about 56 to 58 HRC. Although the part is processed in a controlled atmosphere, a descaling operation is required. Abrasive blasting with fine steel grit or chilled iron shot (SAE G40 or S170) proved the most economical method for cleaning large tonnages of such parts used in the manufacture of trucks, tractors, and similar vehicles. Acid pickling was precluded because of hydrogen embrittlement, and descaling in molten salt was unsuitable because of the softening effect of the high-temperature bath.

Conventional abrasive blasting may deleteriously affect the dimensions of precision gears or pinions. In these special applications, alkaline descaling or wet blasting with a fine abrasive, such as glass beads, under carefully controlled conditions, is indicated.

Example 3:

The turbine blade shown as Part 8 in Fig. 1 is made of type 403 stainless steel. If such parts are made in continuous production, molten salt bath descaling would be the preferred cleaning method. If production is intermittent, the molten salt method would be too costly, and alkaline descaling would be more practical. Abrasive blasting is unsuitable for this application because of close dimensional requirements; pickling cannot be used because of metal loss and the risk of hydrogen embrittlement.

Example 4:

Scale resulting from welding of the low-carbon steel component shown as Part 12 in Fig. 1 could be removed satisfactorily and economically by either abrasive blasting or acid pickling. Because the part is phosphated and painted, surfaces are not critical. Acid pickling would probably be preferred, because it would make more uniform contact with all areas without the need for special handling. Even if a large quantity of parts were to be cleaned, salt bath descaling would

not be used, because the water quench from about 425 °C (800 °F) would cause excessive warpage. The cost of alkaline descaling in an aqueous solution would not be justified for this class of work.

Example 5:

Normally, abrasive blasting would be the preferred method for removing rust and scale from a rough ferrous metal casting like Part 11 in Fig. 1. Chilled iron shot or steel abrasives are usually the most economical abrasives for this purpose.

Pickling is seldom used for descaling castings, such as cast iron, because smut is deposited and must be removed by another cleaning operation. Severe pitting is also likely to result.

Salt baths have been successfully used for descaling ferrous castings, but there is danger of cracking and excessive distortion for configurations such as Part 11.

Removal of Residues from Magnetic Particle and Fluorescent Penetrant Inspection

Successful removal of the iron oxide particles deposited on ferrous parts during magnetic particle inspection requires complete demagnetization of the part. After demagnetization, emulsion cleaning is an effective and practical means of removing both the iron oxide residues and oil. Fluorescent pigments used for similar inspection of aluminum parts can be removed with hot alkaline cleaners.

For low-to-moderate production, an efficient procedure consists of immersing parts in a light, undiluted, oil-based emulsion cleaner at room temperature or slightly above. Parts are then drained to remove excess cleaner and rinsed in water, using either agitation or forced spray at room temperature or slightly above. For higher-volume production, power washers are successful. Parts can be handled singly or in baskets or carriers.

Parts with complex configurations such as Part 9 in Fig. 1, fine threads, or serrations are difficult to clean thoroughly. As-cast or as-forged surfaces also cause the magnetic oxide particles to cling tenaciously. However, immersion in a cleaning emulsion with sufficient agitation or the use of a power washer, with properly placed nozzles and with suitable handling equipment, will clean almost any part. All oxide particles must be removed before the part is dried, or hand wiping or brushing will be required.

A type of emulsion cleaner that incorporates a rust preventative is usually preferred, because it provides protection until the next operation is performed. If rust-preventive films are objectionable in the next operation, they can be removed easily with alkaline cleaners.

Special Procedures for the Removal of Grinding, Honing, and Lapping Compounds

Residues remaining on parts after honing or grinding are usually mixtures of metallic and abrasive particles with oil-based or water-based cutting fluids. Thus, the methods recommended earlier in this article for the removal of chips and cutting fluids are applicable also for the removal of grinding residues in a majority of instances.

Lapped parts are usually more difficult to clean than honed or ground parts. Lapping residues are composed of extremely fine particles of various abrasives, minute metal particles, semi-solid greases and oils, and some graphite. Even if graphite is not a part of the original lapping compound, it accumulates from the wear of cast iron laps. Allowing compounds to dry increases cleaning difficulty. In many instances, methods used for removing polishing and buffing compounds are applicable also for removing lapping compounds. However, parts that are precision ground, honed, or lapped present special cleaning problems because: such parts are commonly used in precision machinery, and consequently the degree of cleanness required is higher than for most commercial work; they are frequently intricate in design (an example in Part 15 in Fig. 3); and they are commonly susceptible to damage and frequently require special handling.

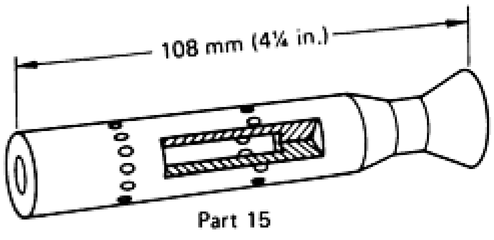

Fig. 3 Part for fuel control mechanism that requires special modification of solvent cleaning to remove grinding and lapping compounds

An extremely high degree of cleanness without damage is required on some expensive delicate parts (e.g., fuel injection equipment). Ultrasonic cleaning with alkaline solution, followed by spray with alkaline and immersion/spray rinsing is ideal for this application. Ultrasonic cleaning is rapidly replacing the old pressure solvent spray/agitated immersion technologies, which were only partially effective. Parts which normally took an hour or more to clean using solvent cleaning processes are now effectively cleaned in just a few minutes of ultrasonic cleaning. Other inherent advantages of this approach are that it is nondestructive to the parts; it uses more environmentally friendly cleaning solutions, and it is much safer with respect to the explosion dangers that are characteristic of many solvent cleaning technologies. As always, the primary drawback to ultrasonic cleaning is the comparative high up-front capital cost.

Room-Temperature Cleaning

Room-temperature or cold cleaners are aqueous solutions for removing soil without the aid of heat other than that resulting from pumping and circulating the solution or being transferred from the surrounding atmosphere. The operating range of such cleaners is usually from 21 to 46 °C (70 to 115 °F). For additional information, see the article "Alkaline Cleaning" in this Volume.

Cold alkaline cleaners, such as the silicate or phosphate types (orthosilicate or tetrasodium pyrophosphate), are chiefly used for cleaning where heat is not available, where heated solutions are not permitted, or when heating the parts above about 46 °C (115 °F) is not desirable. In a cold process for iron phosphating, for example, parts that have been cleaned in a heated solution and have not cooled sufficiently before entering the phosphate solution will yield an unacceptable phosphate coat. In some applications, an unheated cleaning solution is preferred in order to facilitate the checking of part dimensions at room temperature without the delay involved in cooling the parts after cleaning. This procedure is used for cam shafts, honed cylinder walls, and valve-guide holes in engine heads. One automotive plant utilizes a cold alkaline cleaner for removing soil from engine blocks in a power washer at the rate of 300 per hour. In another application, carburetor parts are cleaned at a rate of 600 to 700 per hour. Table 8 provides several detailed examples of the application of cold alkaline cleaners.

Table 8 Examples of application of room-temperature alkaline cleaners

Part	Surface from last operation	Relative amount of original soil on part	Residual soil on part after cleaning, mg
Aluminum alloy piston	Ground	Heavy, up to 0.75 g per part	0.1
Pinion gear, ferrous	Ground and lapped	Heavy	0.1
Ring gear, ferrous	Ground and lapped	Heavy	0.1

Part	Surface from last operation	Relative amount of original soil on part	Residual soil on part after cleaning, mg
Engine heads, ferrous	Fully machined	Heavy	1.5
Engine intake manifold, ferrous	Fully machined	Heavy	10
Carburetor throttle body, ferrous	Fully machined	Medium to heavy	0.5
Automatic transmission pump, ferrous	Fully machined	Medium to heavy	6

Cold cleaners may also reduce costs by using simpler equipment, eliminating the expense of energy for heating, and reducing maintenance requirements.

Cold acid cleaners, such as monosodium phosphate containing a detergent, are also available. Their chief use is for cleaning immediately before iron phosphating, where the advantage of a lower pH is significant. These acid cleaners have a pH of about 6 and thus impart a surface compatible with the iron phosphate bath, which has a pH of 4.5 to 5.5.

Some proprietary products now offer simultaneous cleaning and iron phosphating at room or low temperatures. In a few other isolated applications, cold acid cleaners perform satisfactorily, but in most instances heated solutions are much more efficient.

Ultrasonic Cleaning

Ultrasonic energy can be used in conjunction with several types of cleaners, but it is most commonly applied to chlorinated hydrocarbon solvents, water, and water with surfactants. Ultrasonic cleaning, however, is more expensive than other methods, because of higher initial cost of equipment and higher maintenance cost, and consequently the use of this process is largely restricted to applications in which other methods have proved inadequate. Areas of application in which ultrasonic methods have proved advantageous are:

- Removal of tightly adhering or embedded particles from solid surfaces
- Removal of fine particles from powder-metallurgy parts
- Cleaning of small precision parts, such as those for cameras, watches, or microscopes
- Cleaning of parts made of precious metals
- Cleaning of parts with complex configurations, when extreme cleanness is required
- Cleaning of parts for hermetically sealed units
- Cleaning of printed circuit cards and electronic assemblies

Despite the high cost of ultrasonic cleaning, it has proved economical for applications that would otherwise require hand operations.

Part size is a limitation, although no definite limits have been established. The commercial use of ultrasonic cleaning has been limited principally to small parts. The process is used as a final cleaner only, after most of the soil is removed by another method. Ultrasonic cleaning, in some cases, has resulted in fatigue failure of parts. Proper racking and isolation from tank wall will often solve this problem.

Surface Preparation for Phosphate Coating

Because the chemical reaction that results in the deposit of a phosphate coating depends entirely on good contact between the phosphating solution and the surface of the metal being treated, parts should always be sufficiently clean to permit the phosphating solution to wet the surface uniformly. Soil that is not removed can act as a mechanical barrier to the phosphating solution, retarding the rate of coating, interfering with the bonding of the crystals to the metal, or, at worst, completely preventing solution contact. Some soils can be coated with the phosphate crystals, but adherence of the coating will be poor, and this will in turn affect the ability of a subsequent paint film to remain continuous or unbroken in service.

Soils such as cutting oils, drawing compounds, coolants, and rust inhibitors can react with the substrate metal and form a film that substantially changes the nature of the coating. Precautions must be taken to avoid carryover of cleaning materials into phosphating tanks. This is particularly true for alkaline cleaners, which can neutralize the acid phosphating solutions, rendering them useless. Additional information can be found in the article "Phosphate Coatings" in this Volume.

Surface Preparation for Painting

Surface preparation has a direct effect on the performance of paint films. The best paint available will fail prematurely if applied to a contaminated or improperly prepared surface. The surface will also influence the final appearance of the paint film. Surface irregularities may not be hidden by the paint, but they may instead be reflected as apparent irregularities of the paint film. The principal surface contaminants that are deleterious to the performance of paint films include oil, grease, dirt, weld spatter, alkaline residues, rust, mill scale, water, and salts such as chlorides and sulfides.

Mechanical and chemical cleaning operations may be used in combination to meet a rigid requirement of surface cleanliness. For example, on scale-bearing steel intended for an application involving exposure to chemical environments, complete removal of all oil, grease, rust, mill scale, and any other surface contaminants is mandatory. Nonferrous alloys such as aluminum require chemical conversion pretreatment plus chromated primers for maximum life and corrosion protection.

Further discussion can be found in the article "Painting" in this Volume.

Surface Preparation for Electroplating

Preparation for plating is one of the most critical of all cleaning operations, because maximum adhesion of the plated coating to the substrate is the major requirement for quality work. Maximum adhesion depends on both the elimination of surface contaminants in order to induce a metallurgical bond whenever possible and the generation of a completely active surface to initiate plating on all areas. In addition to pickling or other descaling operations, adequate cleaning requires multistage cycles, usually comprised of the following steps: (1) precleaning with a solvent to remove most of the soil; (2) intermediate cleaning with alkaline cleaners; (3) electrocleaning to remove the last traces of solids and other contaminants that are especially adherent; (4) acid treatment and surface conditioning to remove light oxide films formed during previous cleaning processes and to microetch the surface; and (5) electrolytic (anodic) desmutting to remove any smut formed during acid pickling of heat treated high-carbon steel parts. Low-carbon steels do not require this desmutting step. Anodic electrocleaning also offers oxidation or conditioning of scale. The oxidized or softened scale is easily removed in subsequent acid pickling. The types of cleaning usually employed in the above steps are:

- *Precleaning:* cold solvent, vapor degreasing, emulsifiable solvent, solvent emulsion spray, or alkaline spray with or without solvent emulsion
- *Intermediate alkaline cleaning:* soak cleaning with 30 to 90 g/L (4 to 12 oz/gal) of cleaner at 82 °C (180 °F) to boiling, spray cleaning with 4 to 15 g/L (0.5 to 2 oz/gal) at 66 to 82 °C (150 to 180 °F), and barrel cleaning with 7.5 to 45 g/L (1 to 6 oz/gal) at temperatures below 82 °C (180 °F)
- *Electrocleaning:* cathodic, anodic, or periodic-reverse
- *Acid treatment:* practice is highly specific for the metal being processed
- *Anodic desmutting:* necessary to remove carbon smut

ASTM recommended practices for cleaning various metals prior to plating are given below:

A 380	Descaling and cleaning of stainless steel surfaces
B 183	Preparation of low-carbon steel for electroplating
B 242	Preparation of high-carbon steel for electroplating
B 252	Preparation of zinc-based die castings for electroplating
B 253	Preparation of and electroplating on aluminum alloys
B 254	Preparation of and electroplating on stainless steel
B 281	Preparation of copper and copper-based alloys for electroplating
B 319	Preparation of lead and lead alloys for electroplating
B 480	Preparation of magnesium and magnesium alloys for electroplating
B 322	Cleaning metals before electroplating

Process sequences and operating details in surface preparation for electroplating are presented in articles in this Volume on cadmium plating, finishing of stainless steel, finishing of aluminum alloys, finishing of copper alloys, finishing of magnesium alloys, and finishing of titanium alloys. The procedures used for preparing the surfaces of high-carbon and low-alloy steels, low-carbon steel, and zinc-base die castings are discussed below.

Steels may be cleaned and otherwise prepared for electroplating according to the procedures outlined by the flow charts in Fig. 4 and operating conditions in Table 9. The preparation of low-carbon steel for electroplating consists essentially of cleaning to remove oil and caked-on grease, pickling to remove scale and oxide films, cleaning to remove smut left on the surface, and reactivating the surface for plating.

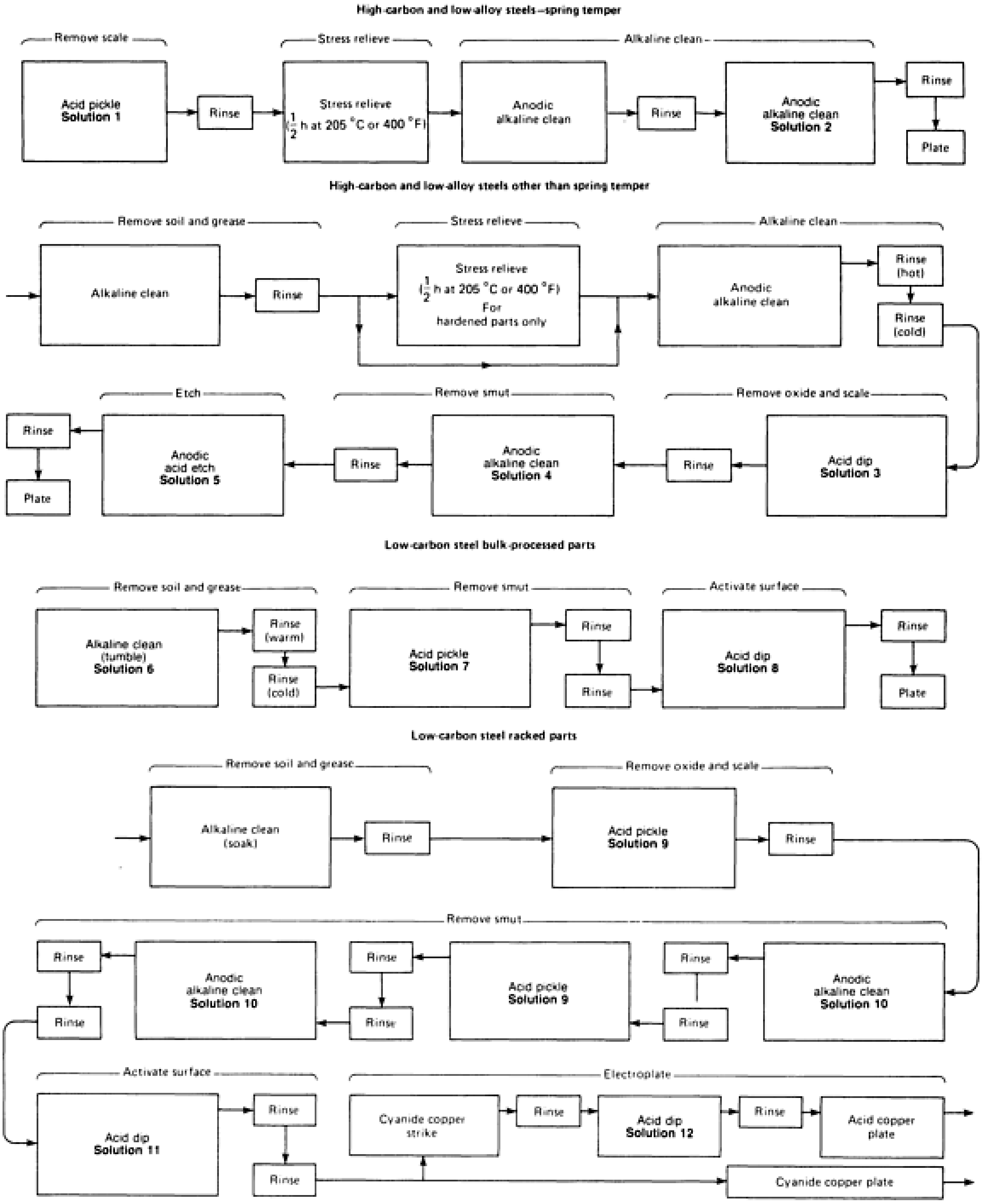

Fig. 4 Process flow charts for preparation of steels for electroplating. See Table 9 for operating conditions.

Table 9 Solutions and operating conditions for preparation of steels for electroplating

See Fig. 4.

Solution no.	Type of Solution	Composition	Amount	Operating temperature		Cycle time, s
				°C	°F	
High-carbon and low-alloy steels, spring tempter						

1	Acid pickle	HCl HNO_3	20-80 vol% 1-5 vol%	Room temperature		[a]
2	Anodic alkaline cleaner[b]	NaCN	20-45 g/L (3-6 oz/gal)	49-54	120-130	30-60
High-carbon and low-alloy steels other than spring temper						
3	Acid dip	HCl	1-10 vol%	Room temperature		[a]
4	Anodic alkaline cleaner[b]	NaCN	20-45 g/L (3-6 oz/gal)	Room temperature		30-60
5	Anodic acid etch[c]	H_2SO_4	250-1005 g/L (33.5-134 oz/gal)	30 max	86 max	60 max
Low-carbon steel bulk-processed parts						
6	Alkaline cleaner[d]	Alkali	30-60 g/L (4-8 oz/gal)	82-99	180-210	60-120
7	Acid pickle	HCl	25-85 vol%	Room temperature		5-15
8	Acid dip	H_2SO_4	4-10 vol%	Room temperature		5-15
Low-carbon steel racked parts[e]						
9	Acid pickle	HCl	25-85 vol%	Room temperature		[a]
10	Anodic alkaline cleaner[f]	Alkali	60-120 g/l (8-16 oz/gal)	93-99	200-210	60-120
11	Acid dip	H_2SO_4	4-10 vol%	Room temperature		5-15
12	Acid dip	H_2SO_4	1 vol%	Room temperature		5-10

(a) Minimum time for removal of scale.

(b) Current density, 1.5 to 2.0 A/dm^2 (15 to 20 A/ft^2).

(c) Current density, 1.50 A/dm^2 (150 A/ft^2).

(d) Tumble, without current.

(e) Cycles for copper plating included in chart are applicable to all steels here, except that for high-carbon and low-alloy steels, a cyanide copper strike precedes cyanide copper plating.

(f) Current density, 5.0 to 10.0 A/dm^2 (50 to 100 A/ft^2)

Plating on low-carbon steels represents the bulk of industrial plating. The steps generally used before plating low-carbon steels are:

1. Vapor degrease, if necessary
2. Alkaline soak clean
3. Water rinse
4. Descale, if necessary
5. Water rinse
6. Alkaline electroclean
7. Water rinse
8. Acid activate
9. Water rinse
10. Plate, as required

These steps are a general guideline and should not be construed as firm recommendations. The actual required cycle would depend on extent of grease and oil contamination, type of scale, and facilities available for the plating operation. Some of the options available to the plater are:

- Emulsion cleaning may be used in place of vapor degreasing. In this case, additional water rinsing is required.
- Anodic electrocleaning is preferred over cathodic cleaning which can cause smut on parts because of plating of polar soils in the cleaner. Electrocleaners are generally used at 60 to 75 g/L (8 to 10 oz/gal) and at 8.0 to 10.0 A/dm^2 (80 to 100 A/ft^2). Temperature will depend on the type of cleaner. Low-temperature cleaners operate at 27 to 49 °C (80 to 120 °F); high-temperature cleaners operate at 82 to 93 °C (180 to 200 °F).
- If parts are not excessively dirty, soak cleaning can be used instead of electrocleaning. Specially compounded alkaline cleaners are sometimes used to remove slight amounts of oxides. Elevated temperatures are recommended for all alkaline cleaning.
- Alkaline cleaners are difficult to rinse. Carryover of residues can produce staining, skip plating, or loss of adhesion. Warm water is recommended in the first rinse along with good agitation. Two or more countercurrent (cascade) rinses are highly desirable both from the standpoint of good rinsing and conservation of water. If both alkaline soak cleaning and alkaline electrocleaning are used, the two cleaning steps should be separated with a thorough rinse.
- Plating is initiated on an active surface. A wide variety of activators is available, and most are acidic in nature. Hydrochloric, sulfuric, or fluoboric acids are commonly used.
- Water rinse after activation is critical to avoid contaminating the sensitive plating solution. Countercurrent rinsing with two or more rinse tanks is desirable.
- High-carbon and low-alloy steels are susceptible to hydrogen embrittlement.
- Proprietary inhibited acid pickles are available for the effective removal of scale and rust with reduced danger of hydrogen embrittlement and base metal attack.

Unless the acids used contain inhibiting agents, the acid treatments for surface preparation must be very mild and of short duration. If electrolysis is necessary, it should be used with anodic current. This is especially significant for spring-temper parts and parts that have been case hardened. Mechanical methods of descaling can often eliminate the need for pickling.

During the anodic etch, a high acid content, low solution temperature, and high current density will minimize smut formation. Carryover of water into the anodic etching solution should be held to a minimum, and long transfer times after the anodic etch should be avoided.

Cold rolled steel that has been subjected to deep drawing and certain prepickled hot rolled steels with glazed brownish-colored surfaces may be exceedingly difficult to clean. For these materials, a solution of 25 to 85 vol% nitric acid has proved effective.

Paint Stripping

Infrequently, parts have to be stripped and repainted. Possibly there is a problem with appearance; the wrong paint or color may have been used. Tools, fixtures, and automatic spray line fixtures must be periodically cleaned of old paint buildup as well. Some paints are easier to strip than others, and some paint stripping methods are incompatible with some metals. A hot alkaline cleaning bath, which is a part of a metal process line, should not be used as a paint stripping tank. Even if the cleaning bath works, the bath quality would be degraded and uncontrolled impurities introduced. Paint cannot be effectively removed from a soiled part, so any part should first be cleaned. Table 10 compares various stripping methods and lists appropriate financial considerations. Selection of strippers is summarized in Table 11. In paint stripping, two processes are widely used, hot stripping and cold stripping.

Table 10 Methods of stripping paint

Method	Facility	Cost factors
Immersion	One or more tanks, water rinse capability required	Slow removal rate, low labor, costly facility, disposal cost
Spray or brush-on	Area, ventilation, rinse capability required	Slow removal rate, higher labor, lesser cost facility, disposal cost
Abrasive	Sand or shot blast facility	Slow removal, high labor, may use existing facility, disposal cost
Molten salt	Specialized facility for steel only	Rapid removal rate, costly facility, low labor, very efficient, lower disposal cost, fume collection required

Table 11 Selection of strippers for removing organic coatings

Type of organic finish to be removed	Approved metal substrates	Means of application	Approved strippers and methods	Operating temperature		Remarks
				°C	°F	
Epoxy primer epoxies polyurethanes	All[(a)]	Spray or brush on	Proprietary phenolic chromated methylene chloride	10-38[(b)]	50-100[(b)]	Good ventilation and protective clothing. Must be approved for high-strength steels
All others	Steel	Immersion	Low viscosity[(c)]	10-38[(b)]	50-100[(b)]	Good ventilation and protective clothing
	All[(a)]	Spray or brush on	High viscosity[(c)]	10-38[(b)]	50-100[(b)]	Must be approved for high-strength steels

All	Steel[d]	Immersion	Proprietary molten salt	As specified by vendor		2-5 min follow with water quench and rinse. Smoke and fume control required
Primers, wax, overspray, and temporary coatings	All	Wipe or squirt on	Butyl cellosolve methyl isobutyl ketone, ethyl alcohol xylene, toluene	Room temperature[e]		Xylene and toluene are normally only effective on waxes and some temporary coatings
All except epoxy based	All	Immersion	Caustic stripper	10-38[b]	50-100[b]	Water base 10-12 pH
Epoxy	All	Dry abrasive blast	MIL-G-5634 Type III	Room temperature		Adjust pressure to part fragility
	Aluminum	Immersion	Chromic acid solution,360-480 g/L (3-4 lb/gal)	74 ± 3	165 ± 5	Maximum allowable immersion time is 15 min. Water rinse parts as soon as possible on removal from solution.
			Chromic acid plus nitric acid solution			CrO_3 360-480 g/L (3-4 lb/gal), HNO_3 5% total volume
All	Aluminum	Immersion	Nitric acid solution 50-78% HNO_3	34 ± 6	110 ± 10	Maximum allowable immersion time, 20 min

Note: Heavy metals plus stripping chemicals require appropriate means of disposal to meet EPA regulations.

(a) Except steel heat treated above 1500 kPa (220 psi).

(b) Optimum temperature range: 18 to 29 °C (65 to 85 °F).

(c) Proprietary: phenolic, chromated, methylene chloride.

(d) Except heat treated steel.

(e) Do not exceed 32 °C (90 °F)

Hot stripping uses high caustic level and high temperatures. Alkaline paint strippers contain caustic soda, sodium gluconate, phenols, or cresols. The bath is used at 80 to 95 °C (180 to 200 °F). Depending on the type of paint and coating thickness, stripping can be done in 30 min to 6 to 8 h. Hot stripping is slow, but economical and environmentally safe. Hot alkaline paint strippers will attack brass, zinc, and aluminum. These strippers are safe for steel and copper.

Cold stripping, as the name indicates, is done without any heating. The stripping bath consists of powerful organic solvents, such as methylene chloride; also organic acids, such as phenols or cresols. Many of the organic solvent strippers available in the market contain two layers. The heavier bottom layer is the organic solvent layer, in which the actual paint stripping takes place. The lighter top layer is the aqueous layer which prevents the evaporation of the highly volatile organic solvents from the bottom layer.

Cold solvent stripping, when applicable, is fast. The process, however, is very expensive and waste disposal could be a problem. Unlike hot strippers, the organic cold strippers can be used on all base metals such as steel, copper, aluminum, brass, and zinc.

Newer paint stripping technologies strive to combine advantages of both the hot and cold stripping techniques. These paint strippers, called *diphase* or *multiphase* strippers, allow hot alkaline stripping and solvent-based stripping to occur in the same tank via formation of a stable paint stripping emulsion. The emulsion stripper is best run hot with high agitation to keep the emulsion stable. This process is often able to strip paint that cannot be stripped by either hot alkaline or cold solvent methods, and it is comparatively fast.

Glass Bead Cleaning

Glass bead cleaning is a low energy, nonpolluting method for use with both small and delicate parts as well as large turbines and engines. Glass bead air systems equal or surpass the finish quality provided by liquid abrasive slurry. Other benefits include no measurable amount of metal removed from close tolerance surfaces (fine threaded screws) and noncontamination of work surfaces with wide range of bead sizes (170 to 400+ grit). Glass bead cleaning has been successfully applied to a wide diversity of uses such as: preparation of surfaces for painting, plating, brazing, welding, bonding; finishing of castings; production of matte finish on metal, glass, and plastics for decorative purposes; reclamation of tools such as files and saws; stripping of paint; and removal of solder from electrical assemblies.

Air pressures recommended for this procedure range from 70 to 415 kPa (10 to 60 psi). An angle of 40 to 60° for nozzle to work direction should be used to minimize bounce back and reduce bead consumption because of breakage. The selection of bead size should be based on the smallest particle that will give the desired surface. This provides the maximum number of impacts per pound. Working distances of 100 to 200 mm (4 to 8 in.) from nozzle to work will provide greatest impact (velocity) with the best pattern.

Pollution Control and Resource Recovery

The increasing cost of waste disposal has a great impact on process cost and should be considered in selecting cleaning processes. Treatment of waste within the plant should be considered to reduce cost, reduce liability, permit reuse of the raw material, and improve process control. A good example of closed-loop recycling is the distillation purification of vapor degreasing solvent. The federal EPA has established compliance guidelines, but state and local regulations are often more stringent. For more information, see the article "Environmental Regulation of Surface Engineering" in this Volume.

Safety

In the use of any metal cleaning process, there are possible safety, health, and fire hazards which need to be considered. The degree of hazard is dependent upon such factors as the specific materials and chemicals involved, the duration of employee exposure, and the specific operating procedures.

Information is presented in Table 12 on the types of hazards which may be associated with each cleaning process and the general control measures which would be used for each hazard.

Table 12 Safety and health hazards of cleaning processes

Cleaning process	Hazard/air contaminant	Control measures	OSHA/NFPA references
Abrasive blasting	Silica dust/total dust exposures	Local exhaust ventilation	(29 CFR)
		Respiratory protection	1910.94(a)
		Goggles or face shield	1910.95

Cleaning process	Hazard/air contaminant	Control measures	OSHA/NFPA references
	Noise exposures	Noise exposures	1910.133
		Hearing protective devices	1910.134
	Skin abrasion	Leather protection garments	1910.1000
			Table Z-3
Acid cleaning	Acid gas or mist exposure	Local exhaust ventilation	1910.94(L)
		Respiratory protection	1910.133
		Goggles or face shield	1910.134
	Skin contact	Impervious gloves and garments	1910.1000
			Table Z-1
Alkaline cleaning	Alkaline mist exposure	Local exhaust ventilation	1910.94(d)
		Respiratory protection	1910.133
		Goggles or face shield	1910.134
	Skin contact	Impervious gloves and garments	1910.1000
			Table Z-1
Emulsion cleaning	Petroleum or chlorinated hydrocarbons	Local exhaust ventilation	1910.94(d)
		Respiratory protection	1910.132
	Alkaline mist exposures	Local exhaust ventilation	1910.133
			1910.134
			1910.1000

Cleaning process	**Hazard/air contaminant**	**Control measures**	**OSHA/NFPA references**
			Tables Z-1, Z-2
Emulsion cleaning	Alkaline mist exposures	Respiratory protection	
		Goggles or face shield	
	Skin contact	Impervious gloves and garments,	
Pickling	Acid gas or mist exposures	Local exhaust ventilation	1910.94(d)
		Respiratory protection	1910.133
		Goggles or face shield	1910.134
	Skin contact	Impervious gloves and garments	1910.1000
			Table A
Salt bath descaling	Burns	Heat resistant gloves and garments	1910.132
		Face shield	1910.133
	Toxic gases	Local exhaust ventilation	1910.134
		Respiratory protection	1910.1000
			Table Z-1
	Fire/explosion	Proper facility design, construction, maintenance	NFPA 86C, Chapter 11
		Proper controls for tank	
		Proper work procedures	
Solvent cleaning	Petroleum or chlorinated hydrocarbon exposure	Local exhaust ventilation	1910.94(d)
			1910.132

Cleaning process	Hazard/air contaminant	Control measures	OSHA/NFPA references
			1910.133
		Respiratory protection	1910.134
			1910.1000
	Skin contact	Impervious gloves and garments	Tables Z-1, Z-2
Tumbling	Noise exposure	Noise enclosure for equipment	1910.95
		Hearing protective devices	
Vapor degreasing	Chlorinated hydrocarbon exposure	Condenser cooling system and appropriate thermostats	1910.94(d)
		Minimize dragout	
		Local exhaust ventilation	
	Solvent decomposition products	Eliminate hot surfaces above 400 °C (750 °F) in the vicinity	
		Eliminate sources of ultraviolet radiation in the vicinity	
		Proper monitoring of solvent for acid buildups to prevent exothermic decomposition	

The Occupational Safety and Health Administration has established in its General Industry Standards (29 CFR 1910) regulations pertaining to a variety of safety and health hazards. Those sections of the standards which may apply to each cleaning process are referenced in Table 12. Because of the unusual fire hazard associated with salt bath descaling, an applicable chapter of the NFPA standards has also been referenced.

Tests for Cleanliness

The final evaluation of the effectiveness of a cleaning process should come from a performance test. Eight well-known methods of determining the degree of cleanness of the work surface are discussed below.

Water-break test is a simple test, widely used in industry. It consists of dipping the work into clean water to reveal a break in the water film in the soiled area. However, because the test depends on the thickness of the applied water film, a factor which cannot be controlled, false results can be obtained because of bridging of residues. A mild acid dip before testing for water break has been found advantageous.

Nielson method requires that ten soiled panels be processed individually to determine the time required for each to be cleaned. Panels are checked by the water-break test and then by the acid copper test. In the acid copper test, the ferrous panel is immersed in a copper sulfate solution (typical composition, 140 g [5 oz] of copper sulfate and 30 cm^3 [1 fluid oz]

of sulfuric acid per gallon of water). On clean surface areas, copper will be deposited by chemical activity, forming a strongly adherent, semibright coating that is free of spots.

An average of the times required to clean the ten panels is taken as a measure of the effectiveness of the cleaning solution.

Atomizer Test. In the atomizer test, panels are cleaned, acid dipped, dried, placed in a vertical position, and sprayed with an atomizer containing a blue dye solution. Just before the droplets begin to run, the spray is stopped and the panel is placed in a horizontal position. Heat is applied to freeze the pattern. The cleaning index is the percentage of the total area that appears clean. This is determined by placing a grid over the panel, estimating the cleaning for several random squares, and then averaging for the reported value. The atomizer test is 10 to 30 times as sensitive as the water-break test.

Fluorescent method requires soiling with a fluorescent oil, cleaning, and inspecting under ultraviolet light. It is very slow and is less sensitive than the water-break and atomizer tests.

Weight of residual soil is also an evaluation of cleanness. The cleaned panel is washed with ether, the washings are evaporated, and the residue is then weighed. A modified method is to clean, dry, and weigh the test panel, then soil, clean, dry, and reweigh it. The increase in weight represents the amount of residual soil present.

Wiping method is a qualitative test. A panel is coated with pigmented soil, cleaned, and then wiped with a white cloth or paper. The presence of soil on the cloth or paper indicates poor cleaning.

In the residual pattern method, cleaned panels are dried at 49 °C (120 °F) for 20 min. After drying, the presence of a stained area indicates residual soil and incomplete cleaning.

Radioisotope tracer technique requires that radioactive atoms be mixed with the soil. Panels are coated uniformly with the soil, and their radioactivity is determined. The panels are then subjected to various cleaning cycles, after which their radioactivity is again determined. The cleaning ability of each of the various cycles can be evaluated by the amount of radioactivity remaining on the panels. This is the most sensitive test; however, dealing with radioactive materials requires an AEC license, trained personnel, and special types of equipment.

Alkaline Cleaning

Revised by Gerald J. Cormier, Parker+Amchem, Henkel Corporation

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Introduction

ALKALINE CLEANING is a commonly used method for removing a wide variety of soils from the surface of metals. Soils removed by alkaline cleaning include oils, grease, waxes, metallic fines, and dirt. Alkaline cleaners are applied by either spray or immersion facilities and are usually followed by a warm water rinse. A properly cleaned metal surface optimizes the performance of a coating that is subsequently applied by conversion coating, electroplating, painting, or other operations. The main chemical methods of soil removal by an alkaline cleaner are saponification, displacement, emulsification and dispersion, and metal oxide dissolution.

Alkaline Cleaner Composition

Alkaline cleaners have three major types of components: builders, which make up the bulk of the cleaner; organic or inorganic additives, which promote better cleaning or affect the rate of metal oxide dissolution of the surface; and surfactants.

Builders are the alkaline salts in an alkaline cleaner. Most cleaners use a blend of different salts chosen from:

- Orthophosphates, such as trisodium phosphate
- Condensed phosphates, such as sodium pyrophosphate and sodium tripolyphosphate
- Sodium hydroxide
- Sodium metasilicate
- Sodium carbonate

- Sodium borate

The corresponding (and more expensive) potassium versions of these salts are also commonly used, especially in liquid cleaner formulations. The choice of salts for a given cleaner is based on the metal being cleaned, the cleaning method, performance requirements, and economics. Table 1 shows a few common formulations for specific combinations of metals and cleaning methods.

Table 1 Alkaline cleaning formulas for various metals

Constituent	**Formula, wt%, for cleaning:**					
	Aluminum		**Steel**		**Zinc**	
	Immersion	**Spray**	**Immersion**	**Spray**	**Immersion**	**Spray**
Sodium hydroxide	. . .	. . .	38	50	. . .	. . .
Sodium carbonate	55	18	36	17	10	20
Sodium metasilicate, anhydrous	37	. . .	12	. . .	15	10
Sodium metasilicate, hydrated	. . .	60	. . .	. . .	. . .	. . .
Tetrasodium pyrophosphate	. . .	20	9	20	20	65
Sodium tripolyphosphate	. . .	. . .	. . .	. . .	50	. . .
Trisodium phosphate	. . .	. . .	. . .	10	. . .	. . .
Fatty acid esters	1	. . .	3	0.6	. . .	. . .
Ethoxylated alkylphenol	. . .	. . .	2	0.2	. . .	. . .
Ethoxylated alcohol	. . .	2	. . .	2	. . .	5
Sodium lauryl sulfonate	5	. . .	. . .	. . .	5	. . .

Phosphates are of great importance in the builder packages of alkaline cleaners. A key function of phosphates is their ability to complex with hard water salts. By "softening" these hard water salts, they eliminate the formation of flocculate precipitation caused by calcium, magnesium, and iron. Phosphates are also effective as dispersants for many types of soils. Additionally, they provide alkalinity and prevent large changes in the pH of the cleaning solution.

Silicates are also versatile as builders for cleaners. They provide alkalinity, aid detergency, and most importantly, protect metals such as aluminum and zinc from attack by other alkaline salts. However, silicates are difficult to rinse away and therefore may cause trouble in subsequent plating operations.

Carbonates are an inexpensive source of alkalinity and buffering. They are useful in powdered cleaners as adsorbents for liquid components. Hydroxides are relatively inexpensive and are the strongest form of alkalinity available.

Borates provide strong buffering at a moderately alkaline pH. They have been used extensively in the cleaning of aluminum. Borates provide a degree of metal inhibition and aid detergency.

Additives are organic or inorganic compounds that enhance cleaning or surface modification. Chemical compounds such as glycols, glycol ethers, corrosion inhibitors, and chelating agents should be considered additives.

- *Glycols and glycol ethers* are solvents that remove certain oily soils.
- *Corrosion inhibitors* can be incorporated into a cleaner to help decrease the occurrence of oxidation of the metal surface during water rinsing.
- *Chelating agents* are specialized chemicals for counteracting the negative effects of hard water salts and metal ions.

Some widely used chelating agents are sodium gluconate, sodium citrate, tetrasodium ethylenediaminetetraacetic acid (EDTA), trisodium nitrilotriacetic acid (NTA), and triethanolamine (TEA).

Surfactants are organic and are the workhorses of alkaline cleaners. They are key in displacing, emulsifying, and dispersing many of the soils found on a metal surface. Surfactants lower the surface tension of the cleaner at the metal surface, allowing it to cover the surface uniformly. There are four major types:

- *Anionic* (e.g., sodium alkylbenzene sulfonate)
- *Cationic* (e.g., quaternary ammonium chloride)
- *Amphoteric* (e.g., alkyl substituted imidazoline)
- *Nonionic* (e.g., ethoxylated long chain alcohol)

These major types differ in the type of charge found on the individual surfactant molecule, which has both a water-soluble portion and an oil-soluble portion. In anionic surfactants, the water-soluble portion of the molecule is negatively charged. Cationic surfactants have a positively charged entity. Amphoteric surfactants have both a positively and a negatively charged entity on each molecule. Nonionic surfactants are free of any charge; they are neutral.

For spray cleaners, nonionic surfactants are used almost exclusively, because in general this is the only type that can provide both low foaming and good cleaning ability. For immersion cleaning, anionic or nonionic surfactants are most often used. Alkaline immersion cleaners can use any of the four types, because the foaming properties of surfactants do not cause a problem. Amphoteric surfactants behave like anionic surfactants when used in an alkaline medium, so it is usually more cost-effective to use an anionic surfactant directly. Cationic surfactants are rarely used in the alkaline cleaning of metal because they are the weakest cleaners. In addition, certain cationics react with the metal surface and form a counterproductive film.

Cleaning Mechanisms

Cleaning is accomplished using saponification, displacement, emulsification and dispersion, and metal oxide dissolution. When a particular part is cleaned, any one or more of these mechanisms may be at work.

Saponification is limited to the removal of fats or other organic compounds that react chemically with alkaline salts. Fatty compounds, both animal and vegetable, react with the alkaline cleaner salts in the cleaning solution to form water-soluble soaps. The soap formed may be either beneficial or detrimental to the performance of the cleaner.

Displacement is the lifting of oily soils from a surface by the action of surfactants. By their chemical nature, surfactants have an affinity for metal surfaces that is stronger than the oil's affinity. The surfactant in the cleaning solution lifts the oil from the surface and replaces it with itself. Once the oil is in solution, dispersion and emulsification phenomena act on it.

Dispersion and emulsification hold oily materials in solution. These two mechanisms have the same goal: to allow mutually insoluble liquids, such as oil and water, to stay together.

Emulsification is the use of a surfactant as a connector to keep oil and water together as if they were one unit. As stated above, one portion of a surfactant molecule is water soluble, and this allows it to move freely in water-based cleaners. The oil-soluble portion of the surfactant molecule allows it to hold on to oil-soluble molecules. In a typical water-based cleaner, the surfactant captures and holds oil in solution.

Dispersion is the ability of the cleaner to break oil down into tiny droplets and prevent it from regrouping (reassembling). Both the surfactants and the alkaline salts of the cleaning solution aid in keeping the oil dispersed.

Metal Oxide Dissolution. Surface oxide dissolution is the direct reaction of the alkaline cleaner salts on the metal surface. Metal oxide dissolution targets the removal of undesirable oxides and inorganic contaminants (e.g., light mill scale, corrosion products, and superficial oxides) from a metal surface. The type of metal being cleaned and the concentration, composition, and temperature of the cleaner all play a role in the speed and degree of metal dissolution. The rate should be controlled to minimize the loss of base metal beneath the oxide. Excessive base metal removal will result in localized corrosion and pitting of the surface.

Rinsing

A good water rinse is essential for good cleaning. The temperature of the water rinse may be hot, warm, or cold, but regardless of the temperature the solution should be kept clean. Warm water is usually the best for rinsing. Cold rinses are less efficient than warm rinses, while hot rinses may promote the rapid formation of an oxide film commonly known as "flash rust."

The water rinse should contain no more than 3% of the concentration of the cleaner solution. For example, if the cleaner is prepared at 30 g/L (4 oz/gal), the rinse water should contain no more than 0.9 g/L (0.12 oz/gal). The water rinse is mainly responsible for removing residual cleaner, but it may also remove a small amount of soil. Water rinsing can be done by either immersion, spray, or a combination.

Method of Application

Immersion Cleaning. When an alkaline cleaner is applied by immersion, the parts to be cleaned are immersed in the solution and allowed to soak. As the alkaline cleaner acts on the parts, convection currents (due to heating or mechanical agitation) help to lift and remove soils from the metal surface. The efficiency of removal by the soak cleaner is greatly enhanced by agitation.

There are several approaches to immersion cleaning:

- *Barrel cleaning,* in which small parts are agitated inside a barrel that rotates in the cleaner solution
- *Moving conveyor cleaning,* in which solution flow is created as parts are dragged through the cleaner
- *Mechanical agitation,* in which the cleaner is circulated using pumps, mechanical mixers, or ultrasonic waves
- *Mechanical contact,* in which the cleaner is applied with external forces such as brushes or squeegees

Spray Cleaning. The effectiveness, low cost of equipment, and high degree of flexibility associated with spray cleaning has made this method popular for many years. Specialized methods of spray cleaning include *steam cleaning,* in which the cleaning solution is injected into a stream of high-pressure steam, and *flow cleaning,* in which the cleaning solution is flooded onto the part at high volume but at relatively low pressure.

Spray cleaning is accomplished by pumping the cleaning solution from a reservoir through a large pipe ("header"), through a series of smaller pipes ("risers"), and finally out of spray nozzles onto the part to be cleaned (Fig. 1). The

pressure at which the solution is applied to the part can vary from as low as 14 kPa (2 psi) to as much as 13,800 kPa (2,000 psi). On a typical cleaning line the application pressure will range from 70 to 210 kPa (10 to 30 psi). In general, higher spray pressure produces greater mechanical forces for removing soils from a metal surface. Mechanical effects are especially important for the removal of insoluble particles such as dust, metal fines, and carbon smut.

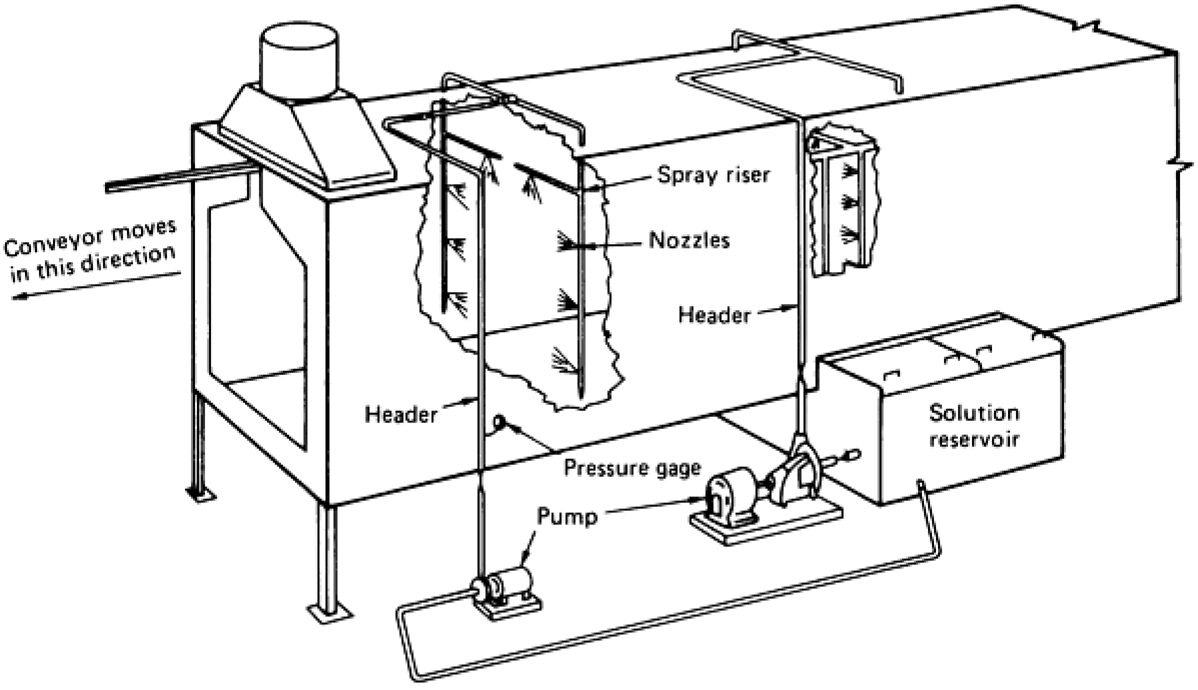

Fig. 1 Equipment for spray cleaning operation

Spray cleaners are prepared with low foaming surfactants that minimize foam formation, even at high spray pressure. Over the last few years, low-foaming surfactants designed for spray cleaning have achieved cleaning performance comparable to that of surfactants used for immersion cleaning.

While spray cleaning is effective on most parts, certain parts, such as the interior of an enclosed section, have soiled areas inaccessible to the sprayed cleaning solution. In these instances, immersion cleaning is more effective because all surfaces of the part can be brought in contact with the cleaning solution.

Operating Conditions

The operating conditions for applying an alkaline cleaner by spray are very different from those used for immersion cleaning. The following table shows typical operating conditions for spray and immersion cleaners.

Operating condition	Immersion cleaners	Spray cleaners
Concentration	7.5-90 g/L (1-12 oz/gal)	1.9-22.5 g/L (0.25-3 oz/gal)
Application temperature	50-100 °C (122-212 °F)	40-71 °C (140-160 °F)

Processing time	1-5 min	0.5-3 min
Spray pressure	. . .	35-210 kPa (5-30 psi)

Considerable progress has been made in recent years to lower the operating temperature of alkaline cleaners. Improved nonionic surfactants, especially for spray-applied cleaners, have allowed for a reduction in cleaner temperature of 15 °C (25 °F) or more without a loss in cleaning performance. A considerable cost savings results from this decrease in energy demand. For example, the cost of heating a solution by steam to 88 °C (190 °F) is about three times that of heating to 49 °C (120 °F). Research in this area is being directed at further reducing the temperature necessary to provide top-quality cleaning of metal surfaces in both spray and immersion applications.

Testing and Control of Cleaners

Alkaline cleaners lose strength through use and dilution, as well as through the necessity of replacing lost cleaning solution with water, so a reliable method of determining cleaner concentration is necessary. The most commonly used method is acid-base titration. In this procedure, an accurately measured amount of alkaline cleaner is placed in a container, and then an acid of specific concentration is slowly added (titrated) to the solution with stirring until a specific pH is achieved. The equipment to determine when the sample has reached the proper pH may be as exacting as a pH meter, or it may use a less precise method such as the addition of a colored indicator solution. (An indicator solution changes the color of the titrated solution at or near the desired pH.) The acid added to achieve the final test pH is generally measured in millimeters (commonly referred to as "points"). The amount of acid that must be added to the alkaline cleaner solution to achieve the proper pH relates directly to the cleaner's strength.

Cleaners age as they react with atmospheric carbon dioxide, as soils are removed, and as water is added due to cleaner dragout and evaporation. The increase in total alkalinity indicates the degree of contamination in the cleaner, and this can be determined by two titrations of the cleaning solution. The pH values used for measuring the age of a cleaner are 8.2 and 3.9. The amount of acid required to change the pH of an alkaline cleaner to 8.2 is called the *free alkalinity*. The amount of acid required to increase the pH of an alkaline cleaner to 3.9 is the *total alkalinity*. If indicators are used, phenolphthalein is used for pH 8.7 (changes from pink to clear) and methyl orange is used for pH 3.9 (changes from yellow to orange). The relationship between the free and total alkalinity will change as a cleaner ages. For instance, if the free alkalinity of a fresh cleaner sample was 5.0 and the total alkalinity was 6.0, the ratio of total alkalinity to free alkalinity would be 6:5, or 1.2. Cleaner manufacturer guidelines differ, but a rule of thumb for disposing of a cleaner is that a cleaner should be rebuilt when the ratio of total alkalinity to free alkalinity of the solution has doubled relative to its starting ratio.

Equipment for Alkaline Cleaners

All equipment for alkaline cleaners can be constructed of low-carbon steel. However, construction from 300 series stainless steel will significantly increase life and simplify maintenance. Stainless steel is recommended for areas that are exposed to highly corrosive environments, such as circulation pumps and heat exchangers. For cleaner stage piping, plastic is used increasingly often due to its excellent resistance to corrosion.

The simplest type of cleaning line is immersion, where the equipment consists of a tank, a source of heat (such as gas, electricity, steam, or a heat exchanger), and an exhaust system to draw off the steam being generated by the hot cleaner. For a spray system, additional equipment includes a spray pump, riser, nozzles, and a spray zone enclosure. Periodically, the cleaning tank and spray equipment must be cleaned in order to remove the scale and contaminants that build up during normal operations. The cleaning method consists of circulating an inhibited acid throughout the cleaning system until the scale and hard water deposits are removed. These deposits cause reduced spray pressures and inefficient heating. If not removed, they could permanently damage the equipment. After acidic cleaning, the tank is thoroughly rinsed and charged with fresh cleaner.

Safety and Environmental Concerns

The handling and use of alkaline cleaners follows general, common chemical handling rules. A person handling powdered cleaners should wear not only gloves and aprons, to prevent skin contact, but also appropriate goggles and a particle mask, to prevent eye contact and inhalation. Liquid cleaners are becoming more popular due to their ease of handling and increased safety. Alkaline cleaners are also becoming more popular as an alternative for hydrocarbon and fluorocarbon solvent degreasing operations.

Environmental regulations continue to affect the direction of cleaner development and cleaner use. Three major issues confront cleaner formulators: reducing or eliminating phosphate effluent; reducing the aquatic toxicity and increasing the biodegradability of cleaners; and "recycling" of cleaners to extend bath life and therefore reduce cleaner dump frequencies and their associated costs. These regulation-driven issues are being approached in a number of ways. For instance, the reduction of phosphate salt use is being addressed by partial or complete replacement of phosphate salts (e.g., with polyacrylic-acid-base polymers). These polymers provide good hard water control and are easy to waste treat. The pursuit of lowering aquatic toxicity and increasing biodegradability of alkaline cleaners is being accomplished by reformulating with biodegradable surfactants. Recycling of cleaners includes the use of ultrafiltration to remove dispersed oil, thereby extending bath life and decreasing the frequency of cleaner discharge. Thermal oil separators have also been useful for removing emulsified or dispersed oil in cleaner baths.

Solvent Cold Cleaning and Vapor Degreasing

Revised by Vicki L. Rupp and Ken Surprenant, Dow Chemical USA

Introduction

SOLVENT CLEANING is a surface preparation process that is especially adept at removing organic compounds such as grease or oil from the surface of a metal. Most organic compounds are easily solubilized by organic solvent and removed from the workpieces. In some cases, solvent cleaning before other surface preparations can extend the life of cleaning operations and reduce costs. In other cases, solvent cleaning prepares workpieces for the next operation, such as assembly, painting, inspection, further machining, or packaging. Before plating, solvent cleaning is usually followed by an alkaline wash or another similar process that provides a hydrophilic surface. Solvent cleaning can also be used to remove water from electroplated parts, a common procedure in the jewelry industry.

Solvent cleaning can be accomplished in room-temperature baths or by using vapor degreasing techniques. Room-temperature solvent cleaning is referred to as *cold cleaning. Vapor degreasing* is the process of cleaning parts by condensing solvent vapors of a solvent on workpieces.

Parts may also be degreased by immersion in the hot solvent, as well as by exposure to the solvent vapor. Drying is accomplished by evaporating the solvent from the parts as they are withdrawn from the hot solvent vapor. In cold cleaning, parts are dried at room temperature or by the use of external heat, centrifuging, air blowing, or an absorptive medium.

The use of many industrial solvents is being severely restricted because of health, safety, and environmental concerns. These concerns are discussed to some degree in this article; additional information is available in the articles "Environmental Regulation of Surface Engineering" and "Vapor Degreasing Alternatives" in this volume.

Cold Cleaning

Cold cleaning is a process for removing oil, grease, loose metal chips, and other contaminants from the surfaces of metal parts. Common organic solvents such as petroleum distillate fractions, chlorinated hydrocarbons, chlorofluorocarbons, hydrofluorocarbons, or blends of these classes of solvents are used. Cleaning is usually performed at, or slightly above, room temperature. Parts are cleaned by being immersed and soaked in the solvent, with or without agitation. Parts that are too large to be immersed are sprayed or wiped with the solvent. Ultrasonic agitation is sometimes used in conjunction with solvent cleaning to loosen and remove soils, such as abrasive compounds, from deep recesses or other difficult-to-reach areas. This reduces the time required for solvent cleaning of complex shapes.

Cold cleaning is chosen when one or more special conditions exist: water will not remove the soils, water would promote corrosion or rusting, or soil must be removed from temperature-sensitive parts. Equipment for cold cleaning can be as simple as a small tank or a pail with a cover. Thus, cold cleaning is a convenient choice for temporary operations,

operations where each machinist must be able to clean parts, or operations where capital intensive equipment cannot be justified.

Solvents

Table 1 lists aliphatic petroleums, chlorinated hydrocarbons, chlorofluorocarbons, alcohols, and other solvents commonly used in cold cleaning. Stoddard solvent, mineral spirits, and VM&P naphtha are widely used because of their low cost and relatively high flash points. The chlorinated hydrocarbons and chlorofluorocarbons exhibit a wide range of solvency and are nonflammable, but most are far more expensive than the aliphatic petroleums. Blends of solvents are offered to provide improved solvency, reduce cost, reduce fire hazard, adjust evaporation rates, and so on. The alcohols are used alone, or in conjunction with chlorocarbons or chlorofluorocarbons, for special cold cleaning applications such as removing activated soldering fluxes. Acetone and other solvents having low flash points are used for special purposes only, such as cleaning the components of precision instruments, but may pose a serious fire hazard. Their storage and use require strict observance of all safety precautions.

Table 1 Properties of cold cleaning solvents

Solvent	Flash point[a]		OSHA TWA, ppm[b]
	°C	°F	
Aliphatic petroleums			
Kerosene	63	145	. . .
Naphtha, hi-flash	43	110	. . .
Mineral spirits	14	57	500
Naphtha, VM&P	9	48	500
Stoddard solvent	41	105	100
Chlorinated hydrocarbons[c]			
Methylene chloride	None	None	500
Perchloroethylene	None	None	100
Trichloroethane (1,1,1)	None	None	350
Trichloroethylene	None	None	100
Trichlorotrifluoroethane	None	None	1000
Alcohols			

Ethanol, SD	14	57	1000
Isopropanol	10	50	400
Methanol	12	54	200
Other solvents			
Acetone	-18	0	750
Benzol	-11	12	10
Cellosolve(d)	40	104	50
Toluol	4	40	100

(a) Tag closed cup.

(b) OSHA exposure values expressed as parts of vapor or gas per million parts of air by volume at 25 °C (77 °F) and 760 mm Hg pressure. These values should not be regarded as precise boundaries between safe and dangerous concentrations. They represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect. The values refer to time-weighted average concentrations for a normal workday.

(c) Also used for vapor degreasing.

(d) 2-ethoxyethanol

In choosing an organic solvent for a particular operation, the most important characteristics to consider are its:

- Toxicity
- Solvency for soils, water, and salts
- Evaporation rate
- Purity
- Biodegradability
- Ease of conservation/recovery/distillation
- Compatibility with part or assembly materials
- Cost
- Ease of disposal
- Associated regulatory requirements

The importance of any specific characteristic is related to the cleaning required, the sophistication of the equipment engineering, and other properties of the candidate solvent. For example, a more toxic solvent might be acceptable if the equipment prevents overexposure of workers. Solvency for the soil to be removed is usually essential, but solubility of water may be preferred for drying parts. On the other hand, solubility of water could be a disadvantage if the discharge water contains excessive amounts of solvent. A low-vapor-pressure solvent is lost through evaporation more slowly, and

may be more easily controlled below its acceptable worker exposure standard, than a solvent with greater volatility. However, slow evaporation causes prolonged drying time. Removal of one soil only to have it replaced by a different soil from the solvent is normally not desirable. Therefore, initial solvent purity is important, and a means is required (usually distillation) of maintaining a level of purity to prevent redeposition of soil from previously cleaned parts. Highly biodegradable solvents may be more acceptable in discharge to public water treatment plants, but even so they could cause fish kills due to oxygen depletion in ponds or lakes. Tight equipment may conserve solvent to the extent that a preferred higher-price solvent may be a practical choice. Greater conservation results in less addition of fresh solvent to the system and increases the need for purification by distillation. Identification markings, paint, or plastic components may require a solvent that is selective in dissolving the soil without damaging the parts. Critical factors in cost control may be the use of a minimum of labor, elimination of reject parts, and reduction of disposal costs, rather than the price of the solvent. Disposal costs are another factor in the overall operating costs. Regulations have become another major consideration in the solvent selection process. The best illustration of this is the production ban on 1,1,1-trichloroethane and trichlorotrifluoroethane, beginning January 1, 1996, because they deplete stratospheric ozone. Table 1 provides some information that can be used in choosing a solvent.

Process Control Variables

Cold cleaning is chosen for its simplicity and the low capital cost for the great majority of its uses. It is not surprising that most operations are conducted in a simple tank or pail with a cover at room temperature. A course spray, mechanical agitation (usually manual), brushing, and ultrasound are used to speed cleaning and assist in the removal of insoluble matter. Increasing the solvent temperature will increase its solvency, but this option is infrequently used. Elevated temperatures can significantly increase the fire hazard of flammable solvents, and control of worker vapor exposures becomes difficult as the solvent evaporates more rapidly.

Cleanness of Solvent. As contamination of the solvent increases, cleaning efficiency and the cleanness of processed parts decrease correspondingly. Cleanness requirements prescribe the time at which the solvent must be replaced. For example, a service business that has become quite popular, especially in automotive repair shops, provides the tank equipment and solvent, periodically removes the dirty solvent, and replaces it with clean solvent.

Solvent Reclamation. All solvents can be reclaimed by either a factory-operated still or a licensed reclamation service. In general, the reclamation process is one of simple distillation. However, explosion-proof equipment is essential for the distillation of flammable solvents.

Factory distillation equipment must be selected on the basis of the volume of solvent used, whether the solvent is flammable, the boiling point of the solvent, the nature of the contaminants, and the degree of purity required. A still may service multiple cold cleaning locations, or it may be incorporated into the large sizes of dip or soak equipment on a semiautomated basis.

Standards for recovered solvent usually relate to color, clarity, moisture content, and neutrality, although tests for specific contaminants may be included. Chlorinated hydrocarbons contain stabilizers, added during manufacture; many times, distillation necessitates supplemental inhibition.

The time to replace dirty solvent with clean solvent is determined by the degree of redeposition. Each part placed in a dip solvent comes out of the solvent with a thin film of soil redeposited on its surface. The permissible degree of redeposition determines the practical limit of usefulness of a solvent and the rate at which fresh solvent must be introduced. Alternatively, immersion in sequentially cleaner solvent baths can prolong the useful life of the solvent. In spray wipe applications in which the solvent is aided by strong mechanical action, there is a nearly continuous use of fresh solvent, which is seldom reused.

Each solvent typically has a temperature range where ultrasonic energy optimally agitates it. If the solvent bath is heated too close to the boiling point of the solvent by the sonic energy, the mechanical action diminishes. Control of the bath temperature is important to effective use of ultrasonic cleaning, which is often employed to remove insoluble matter that would need to be filtered from the solvent to maintain cleaning effectiveness.

Tests of cleanness made directly on parts generally are more practical for determining the reclamation point than are measurements of soil buildup in the solvent. Although checking the cleaned item for satisfactory performance in subsequent operations is a practical method for determining whether a required degree of cleanness has been obtained,

various other methods of testing for cleanness are also available. In order of increasing degree of cleaning requirements, they are:

1. Visual observation of parts and solvent condition
2. Wiping parts with a clean dry white cloth and then examining the cloth for adhering soil
3. Applying tape to the cleaned surface, removing it, and examining it for adhering soil (Scotch tape test)
4. Tests for the adhesion of paints, ranging from special low-adhesion test paints to conventional paint
5. Microscopic examination of parts
6. Resoaking parts in fresh solvent and weighing the nonvolatile residue
7. Chemical analysis for specific soils
8. Electrical test (on combinations of conductors and nonconductors only)
9. Use of radioactive tracers

Methods from the above list generally are used for specific purposes according to the following table:

Method No.	Purpose of cleaning
1, 2, 3	Preclean only
4	Preparation for paint or adhesive
5, 6, 7, 8	Precision instrument parts
6, 7, 8, 9	Initial studies on precision parts

Drying the Work. Cold cleaning solvents are selected so that the evaporation of the solvent film on parts does not require an excessively long time. In all drying operations, solvent fumes must be exhausted to prevent the possibility of fire, explosion, or health hazards.

Equipment

Pails, tanks, and spray equipment are used in solvent cleaning. Pails with covers are the simplest containers and are often used to contain kerosene, mineral spirits, or chlorinated hydrocarbons for hand brush cleaning or wiping.

Soaking tanks of various designs and sizes are used, depending on the nature of the work. Such tanks may be heated by steam coils, but more often they are used at room temperature. Agitation is sometimes provided by mixer impellers or forced air. For in-process cleaning of small parts, such as those encountered on subassembly lines, a variety of specially made safety tanks are available. Some are designed to permit quick opening and closing by means of a foot pedal, minimizing evaporation and fire hazard. Some are equipped to supply fresh solvent quickly to the work zone and dispense contaminated solvent to another reservoir for subsequent discarding or reclamation.

Small bench sprayers, similar to the unit shown in Fig. 1, are used on assembly lines for cleaning delicate components.

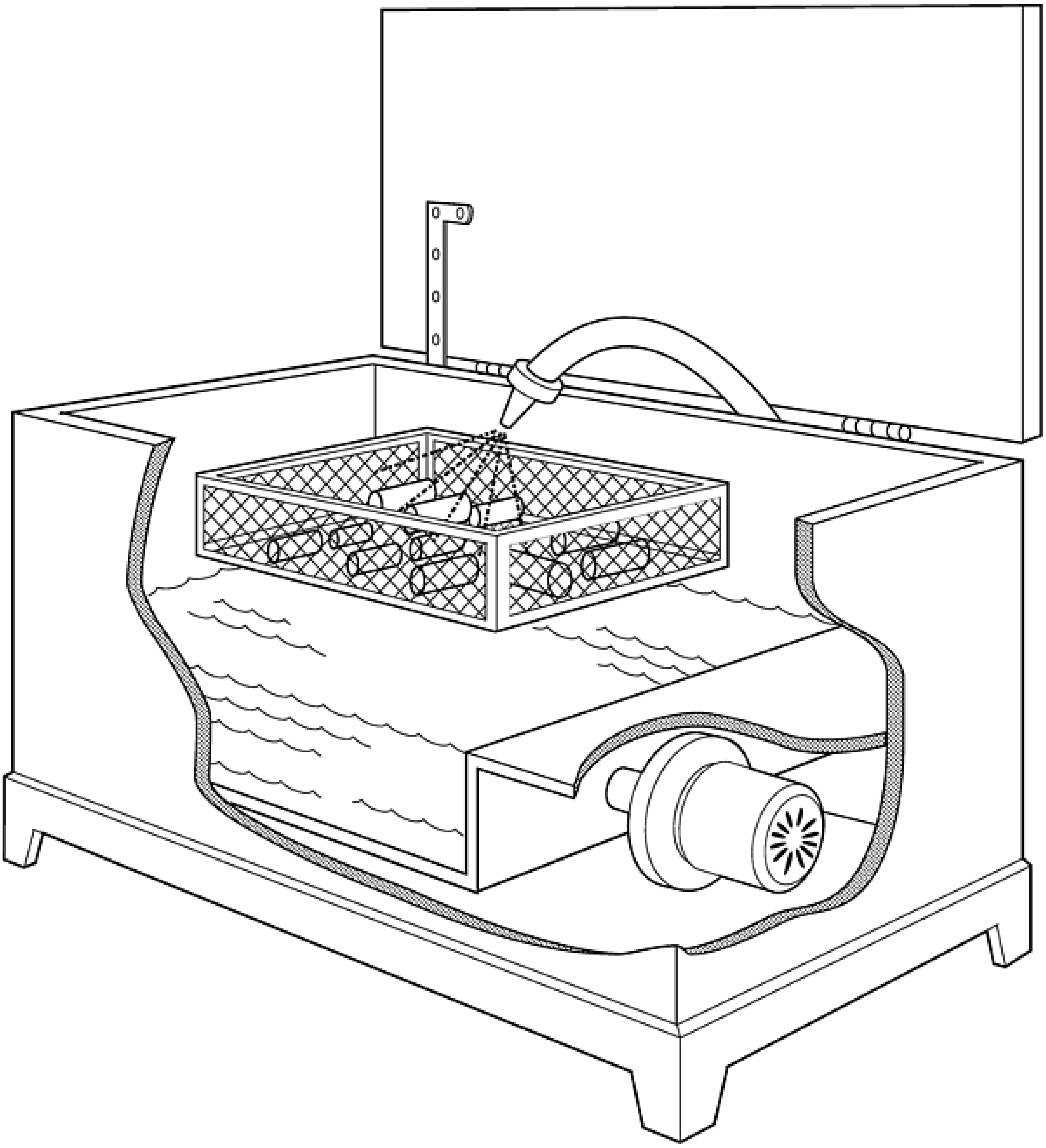

Fig. 1 Spray cleaning equipment

Washing machines also are available for cleaning small precision parts. Some of these machines are similar to home laundry machines in design. Parts are placed on trays, and the agitated solvent provides a constant washing action. In many applications in which the removal of oil and grease is not the main purpose, the equipment is used to remove the residue of polishing or lapping compounds. A filtering system on the machine continuously removes solid particles from the solvent as they are washed from the workpieces.

Equipment requirements for solvent cleaning vary with the size, shape, and quantity of workpieces, as well as the amount of soil to be removed. No matter what equipment is selected, proper covers to minimize solvent loss should be used. Regulations controlling the emissions of smog producing volatile organic compounds require specific designs of cold cleaning equipment and operating procedures in most states. Permits may also be required for construction/installation and operation.

Specific Applications

Solvent cleaning has traditionally been regarded as a method for precleaning or as one reserved for special applications. However, with the rise in the manufacture of electronic components and other assemblies that comprise many small parts, the use of solvents as a final cleaner has increased. At present, most solvent cleaning applications fall within one of the following categories:

- Inexpensive precleaning of parts
- Hand cleaning of parts too large for immersion or spray machine cleaning
- Cleaning heat-sensitive, water-sensitive, or chemical-sensitive parts
- Removal of organic materials such as plating stopoffs, marking crayons, or soldering flux
- Cleaning of precision items in a succession of steps in which the work is first cleaned in nonpolar solvent to remove oil
- Temporary general cleaning where the cost of vapor degreasing equipment is not justified
- Cleaning electrical or electronic assemblies in which the presence of inorganic salt deposits may cause current leakage

Process Limitations

Virtually all common industrial metals can be cleaned in the commonly used cleaning grade solvents without harm to the metal, unless the solvent has become contaminated with acids or alkalis. Cleaning cycles should be adjusted to minimize the immersion time. Certain plastic materials can be affected by cleaning solvents, and tests must be conducted to determine compatibility.

Solvent degreasing is ineffective in removing such insoluble contaminants as metallic salts and oxides; sand; forging, heat treat or welding scale; carbonaceous deposits; and many of the inorganic soldering, brazing, and welding fluxes. Likewise, fingerprints can resist solvent removal.

Size and shape of the workpiece is seldom a limitation. Highly intricate parts have been solvent cleaned by devising techniques of handling that allow the solvent to reach and drain from all areas.

Quantity of Work. Although many high-production applications regularly use cold cleaning, it is more likely to be used for maintenance and intermittent cleaning of small quantities. Because cold cleaning is usually done at or near room temperature, the problem of heating, or otherwise preparing, equipment for a small quantity of work is eliminated. Unless there is some special requirement, other methods of cleaning, such as vapor, alkaline, emulsion, or acid, are usually cheaper and more satisfactory for cleaning large quantities in continuous production.

Lack of uniformity is often a severe limitation of cold cleaning. The process is basically one of dissolving a contaminant in a solvent; therefore, immersion cleaning causes resoiling as the solvent is reused. The work parts do not receive a final rinse in pure solvent as they do in vapor degreasing. The parts are seldom, if ever, perfectly clean. Therefore, except in special applications where spray techniques are used, solvent cleaning is more likely to be used as a preliminary, rather than as a final, cleaning method. The amount of soil that remains on the part depends on how much was there initially and on the quality of the solvent (how often the solvent was reclaimed). In some applications, the use of two or more consecutive solvent baths serves to provide more uniform cleaning results.

Applicability to Soils. The range of soils on which solvents are highly effective is greater than for vapor degreasing because: (a) lower temperatures permit a wider choice of solvents; and (b) lower drying temperatures usually used in solvent cleaning do not bake on insolubles, such as polishing or buffing compounds. Mechanical agitation, ultrasonics, and sometimes hand scrubbing are used in solvent cleaning to help loosen and float away insolubles.

Safety and Health Hazards

Fire and excessive exposure are the greatest hazards entailed in the use of solvents for cleaning. The flash points and permissible vapor concentrations of the solvents adopted for specific operations must be known (Table 1). All flammable solvents should be stored and used in metal containers, such as groundable safety cans.

Adequate ventilation should be provided to prevent accumulation of vapor or fumes. No solvents should be used close to an open flame or heaters with open coils.

Operators should be cautioned against repeated exposure of the skin to solvents. The use of basket, hangers, and other devices that prevent skin exposure is common practice and is recommended. Protective gloves or protective hand coatings should be used to prevent extraction of natural oils from the skin, which can cause cracking of the skin and dermatitis.

Common solvents vary in relative toxicity, and the vapors of these solvents are capable of exerting a potentially lethal anesthetic action when excesses are inhaled. Common solvents have a relatively slight toxic effect, but maintenance workers have lost their lives after working inside tanks containing very high concentrations of vapor, as a result of its strongly narcotic effect. When working in an enclosed space, such as tanks or pits, workers should follow confined space entry procedures.

- Drain and vent thoroughly.
- Check air for adequate oxygen and the absence of flammable or toxic vapor concentrations.
- Always use an air-supplying respirator and life belt.

Any person working with a solvent should be familiar with its material safety data sheet, which can be obtained from the supplier.

Vapor Degreasing

Vapor degreasing is a generic term applied to a cleaning process that uses the hot vapors of a chlorinated or fluorinated solvent to remove soils, particularly oils, greases, and waxes. A vapor degreasing unit consists of an open steel tank with a heated solvent reservoir, or sump, at the bottom and a cooling zone near the top. Sufficient heat is introduced into the sump to boil the solvent and generate hot solvent vapor. Because the hot vapor is heavier than air, it displaces the air and fills the tank up to the cooling zone. The hot vapor is condensed when it reaches the cooling zone, thus maintaining a fixed vapor level and creating a thermal balance. The temperature differential between the hot vapor and the cool workpiece causes the vapor to condense on the workpiece and dissolve the soil.

The soils removed from the workpieces usually boil at much higher temperatures than the solvent, which results in the formation of essentially pure solvent vapors, even though the boiling solvent may be quite contaminated with soil from previous work parts. Vapor degreasing is an improvement over cold solvent cleaning, because the parts are always washed with pure solvent. By contrast, in cold cleaning, the solvent bath becomes more and more contaminated as repeated work loads are processed and redeposition of soil increases. In vapor degreasing, the parts are heated by condensation of the solvent vapors to the boiling temperature of the degreasing solvent, and they dry instantly as they are withdrawn from the vapor zone. Cold-cleaned parts dry more slowly.

To supplement vapor cleaning, some degreasing units are equipped with facilities for immersing work in warm or boiling solvent and for spraying workpiece surfaces with clean solvent. The efficiency of the liquid phase of the cleaning cycle can be augmented by the application of ultrasonic energy.

Solvents

Only halogenated solvents are used in vapor degreasing, and they have the following characteristics in varying degrees:

- Nonflammability and nonexplosiveness under proper vapor degreasing operating conditions. This critical requirement makes solvents with flash points unacceptable.
- High solvency for oil, grease, and other contaminants to be removed
- Low heat of vaporization and low specific heat, to maximize the amount of solvent that condenses on a given weight of metal and to minimize heat requirements
- Boiling point high enough so that sufficient solvent vapor is condensed on the work to ensure adequate final rinsing in clean vapor
- Boiling point low enough to permit the solvent to be separated easily from oil, grease, or other contaminants by simple distillation
- Toxic properties low enough to permit control of worker exposures to Occupational Safety and Health Administration (OSHA) permissible exposure levels
- High vapor density, in comparison with air, and low rate of diffusion into air, to minimize loss of

solvent to the atmosphere

- Chemical stability in the process, which requires the solvents be inhibited or stabilized with chemical additives, if required
- Noncorrosiveness to metals used in workpieces and in construction of equipment for the process, and to plastic parts

Table 2 lists pertinent properties of halogenated solvents used for vapor degreasing. Table 3 is a comparative evaluation of these solvents for vapor degreasing applications.

Table 2 Vapor degreasing solvent properties

Property	**Methylene chloride**	**Perchloroethylene**	**1,1,1-trichloroethane**	**Trichloroethylene**	**Trichloro-trifluoroethane**
Flammability					
Flash point	None	None	None	None	None
Flammable limits at 25 °C[a]	14.5-22	None	7.5-15	8.0-10.5	None
Boiling point, °F(°C)	104 (40)	250 (121)	165 (74)	189 (87)	118 (63)
Specific gravity	1.32	1.62	1.32	1.46	1.57
Density					
Liquid, lb/gal at 25 °C	11.0	13.5	11.0	12.1	13.2
Relative vapor: Air	2.93	5.72	4.6	4.53	6.46
Specific heat (liquid), BTU/lb °F (kj/kg °C)	0.28 (1.2)	0.21 (0.88)	0.25 (1.0)	0.23 (0.96)	0.21 (0.88)
Latent heat, BTU/lb (kj/kg)	142 (330)	90 (209)	102 (237)	103 (240)	63 (147)
Azeotrope with water					
Boiling point, °F (°C)	100.6 (38)	190 (88)	149 (65)	164 (73)	. . .
wt% water	1.5	15.8	4.3	5.4	. . .
Molecular weight	84.9	165.8	133.4	131.4	187.4

Vapor pressure at 25 °C, mm Hg	436	18	124	70	334

(a) vol% in mixtures with air

Table 3 Comparative evaluation for vapor degreasing applications

Property	**Trichloroethylene**	**Perchloroethylene**	**1,1,1-trichloroethane**	**Methylene chloride**
General stability	Good	Excellent	Selective	Good
Solvency	Aggressive	Selective	Selective	Aggressive
Recoverability (steam stripping and carbon adsorption)	Good	Good	Unsuitable	Limited
Parts handling (based on temperature after vapor rinse)	Little delay	Delay	Little delay	Immediate
Removal of high melting waxes	Good	Excellent	Good	Fair
Removal of water (spot free dryer)	Fair	Excellent	Poor	Poor
Cooling water availability and cost	Good	Good	Good	Poor
Cost to vaporize (heat of vaporization)	Moderate	Good	Moderate	High
Cleaning of light-gage parts	Good	Excellent	Good	Poor
Use with water-soluble oils	Good	Excellent	Poor	Poor
Stability towards white metals	Good	Good	Fair	Good
Stability towards caustics	Hazardous	Good	Hazardous	Good
Nonflammability	Good	Excellent	Good	Good
Steam pressures needed	Moderate	High	Fair	Low
Temperature effect on work area	Good	Fair	Good	Excellent
Use history	Very extensive	Extensive	Very extensive	Very limited

Air pollution classification	Nonexempt some areas	Nonexempt	Exempt	Exempt
Cost per pound	Medium	Lower	Higher	Higher

Trichloroethylene (C_2HCl_3) historically has been the major solvent used in industrial vapor degreasing and cleaning applications. Beginning in 1966, air pollution control regulations led to its partial replacement by 1,1,1-trichloroethane. The classification of trichlorotrifluoroethane and 1,1,1-trichloroethane as stratospheric-ozone-depleting chemicals has stimulated interest in returning to trichloroethylene, which is still frequently an excellent solvent choice. It has a very aggressive solvent action on oils, greases, waxes, tars, gums, and rosins and on certain resins and polymers. Its fast, efficient action leaves no residue or film to interfere with subsequent metal treatment such as welding, heat treating, electroplating, or painting.

Trichloroethylene can be safely used with iron, steel, aluminum, magnesium, copper, brass, and various plating metals without harm to the parts or to the degreasing equipment. The listed vapor degreasing solvents should be used with some caution with titanium and its alloys. Residual solvent or chlorides could cause hot salt stress-corrosion cracking if the workpieces are subsequently welded or experience service temperatures of 280 °C (550 °F) or higher. Care must be taken to remove any residuals. Dipping in nitric or nitric-hydrofluoric acid is recommended.

Always avoid the use of strong caustic (sodium hydroxide) around the degreasing operation, because trichloroethylene can react vigorously with this chemical to produce spontaneously flammable dichloroacetylene. Because of the moderate boiling temperature of trichloroethylene, the degreased parts can be handled soon after the vapor rinse is complete. Normal operation uses steam at 69 to 105 kPa (10 to 15 psig).

Perchloroethylene (C_2Cl_4) has been used for many years as an important specialized solvent for difficult industrial cleaning applications. For vapor degreasing, it effectively resists chemical decomposition under heavy work loads and adverse operating conditions. Steam at 345 to 415 kPa (50 to 60 psig) is required for heating. Because of its high boiling point, it has found particular use for removal of high melting waxes, because these are melted for easy solubilization. Perchloroethylene has also been of particular value for spot-free drying of metal parts having a bright finish or an intricate design. Frequently, in such cases, water that is brought into the degreaser is trapped in recessed parts and blind holes even under normal operating conditions. Because the boiling solvent is at a higher temperature than the boiling point of solvent and water, water quickly forms an azeotrope and is swept away. The rather high operating temperature of perchloroethylene also aids in the degreasing of light-gage metals by permitting a longer and more thorough rinsing action with minimum staining. It can be used effectively with iron, steel, aluminum, magnesium, copper, brass, zinc, and various plating metals, without harm to the metal parts or to the degreasing equipment.

Because of the high boiling point of perchloroethylene, vapor degreasing produces work that is too hot for immediate hand processing. This can be dealt with if the work cycle is adjusted to allow for a cooling period after degreasing. Another related problem is that the degreaser itself, operating at the boiling point of perchloroethylene, is a source of extra heat in the work area. This may cause considerable discomfort (and even danger of burns) to the operating personnel. Often the best solution is to insulate the degreaser. At other times, a little extra local ventilation, coupled with the installation of a guard rail, is all that is needed.

1,1,1-trichloroethane ($C_2H_3Cl_3$) was once the most widely used degreasing solvent because it was exempted in most states from regulations controlling chemicals that cause smog (ozone). The current trend is away from this solvent because it has been categorized as a stratospheric-ozone-depleting chemical. Production of 1,1,1-trichloroethane will be progressively limited until it is phased out by 31 Dec 1995 (Table 4).

Table 4 Applicability of key regulations to selected cleaning solvents

Solvent	CAS No.[(a)]	OSHA PEL, ppm[(b)]	ACGIH TWA, ppm[(c)]	Regulated as		Drinking water Standard MCL, µg/L[(f)]	NFPA Code[(g)]	Hazardous waste[(h)]	SARA 313[(i)]	Spill reportable quantity, lb[(j)]
				VOC[(d)]	ODS[(e)]					

Methylene chloride	75-09-2	500 (25)	50	No	No	(5)	2-1-0	Yes	Yes	1000
Methyl chloroform	71-55-6	350	350	No	Yes	200	2-1-0	Yes	Yes	1000
Perchloroethylene	127-18-4	100	25	(No)	No	5	2-0-0	Yes	Yes	100
Trichlorotrifluoroethane	354-58-5	1000	1000	No	Yes	. . .	. . .	Yes	Yes	1000
Trichloroethylene	79-01-6	100	50	Yes	No	5	2-1-0	Yes	Yes	100

Note: Parentheses indicate proposed standards.

(a) Chemical Abstract Service numbers.

(b) Occupational Safety and Health Administration permissible exposure limits.

(c) American Conference of Governmental Industrial Hygienists time-weighted averages.

(d) Volatile organic compounds, chemicals that react to form smog (ozone) in the lower atmosphere. *No* means *not regulated.*

(e) Ozone-depleting substance. *No* means *not regulated.*

(f) Drinking water standards of the Environmental Protection Agency (EPA). Clean Water Act 40 CFR 100-149, 400-690 MCL, maximum contaminant level.

(g) National Fire Protection Association code for health, flammability, and reactivity under fire conditions.

(h) According to EPA Resource Conservation and Recovery Act, 40 CFR 190-299.

(i) EPA Superfund Amendments and Reauthorization Act (SARA), 40 CFR 300-399. Yes indicates that the substance is subject to the SARA toxic chemical release reporting requirements and community right-to-know regulations.

(j) According to SARA

This solvent has properties similar to those of trichloroethylene. It is an excellent solvent for many oils, greases, waxes, and tars, while at the same time it has a unique specificity toward individual plastics, polymers, and resins. Steam pressure usually ranges from 20 to 40 kPa (3 to 6 psig) because it has a lower boiling point than trichloroethylene.

1,1,1-trichloroethane hydrolyzes slowly with free water to produce acidic byproducts. Thus, in a vapor degreasing application, water being introduced on the workpieces should be limited by an efficiently operating water separator. Such a separator, with provisions for cooling the solvent condensate as it leaves the trough or by a coil within the water separator, is recommended for all degreasers. 1,1,1-trichloroethane suitably stabilized for vapor degreasing has been widely used with all types of metal parts. However, stabilizer additives are essential for this solvent in vapor degreasing due to its susceptibility to react with aluminum.

Methylene chloride (CH_2Cl_2) is a versatile solvent, aggressive toward many oils, fats, greases, waxes, tars, plastics, resins, polymers, lacquers, and both synthetic and natural rubber. Use of methylene chloride should be considered particularly where the work parts might be damaged by the higher boiling temperatures of the other chlorinated degreasing solvents or where its aggressive solvency powers are specifically required. In this latter connection, some plastics and elastomers normally used in chlorinated solvents service for hose, gaskets, and containers undergo degradation when continuously in contact with methylene chloride.

For general utility, methylene chloride has the inherent limitations associated with its low boiling point. For economy of use, refrigeration rather than plant water may be needed for efficient condensing of the solvent in the machine. Care should also be exercised that the parts are allowed to dry fully before leaving the freeboard area of the vapor degreaser. Recently, the use of methylene chloride has been boosted by the need for solvents to replace trichloroethane that do not contribute to smog in the lower atmosphere and do not significantly deplete stratospheric ozone.

Trichlorotrifluoroethane ($C_2Cl_3F_3$) is a highly stable solvent requiring little or no additives to maintain its stability in use. It is often referred to as fluorocarbon 113 (FC 113). Fluorocarbon 113 boils only slightly above methylene chloride, and, as with methylene chloride, refrigeration is normally required for vapor condensation and control. While methylene chloride is the strongest solvent, fluorocarbon 113 is the gentlest. This property permits its use in cleaning some assemblies containing sensitive plastic components; however, the gentle solvency is not sufficient for some soils. To compensate and to provide special solvent properties, fluorocarbon 113 is available in azeotropic composition with methylene chloride and acetone. Other admixtures are also available.

Stabilization of the azeotropes is needed for vapor degreasing, particularly for zinc. Fluorocarbon 113 and its blends are more costly, so they are chosen for special applications where other solvents are not suitable. Fluorocarbon 113 is among the select group of solvents identified as not causing smog in the lower atmosphere. Unfortunately, it is a stratospheric-ozone-depleting chemical, and its production will be phased out by 31 Dec 1995.

Solvent stability is usually controlled by the addition of stabilizers when the solvent is manufactured. Trichloroethylene, methylene chloride, 1,1,1-trichloroethane, and perchloroethylene all require stabilizers to perform successfully in vapor degreasing. Quality control of vapor degreasing operations can be conducted by analyzing the stabilizer levels by gas chromatography. The boiling point and/or specific gravity of used solvent can be used to estimate the level of contamination.

Severe degradation problems may result from permitting cross-contamination of solvents during transportation, storage, or use. Particular care should be taken to prevent 1,1,1-trichloroethane contamination of the other solvents, even at levels of 1% or less.

Degreasing Systems and Procedures

Procedures used for cleaning various classes of work and soils by degreasing systems are indicated schematically in Fig. 2. Regardless of the system used, the distinctive features of vapor degreasing are the final rinse in pure vapors and a dry final product.

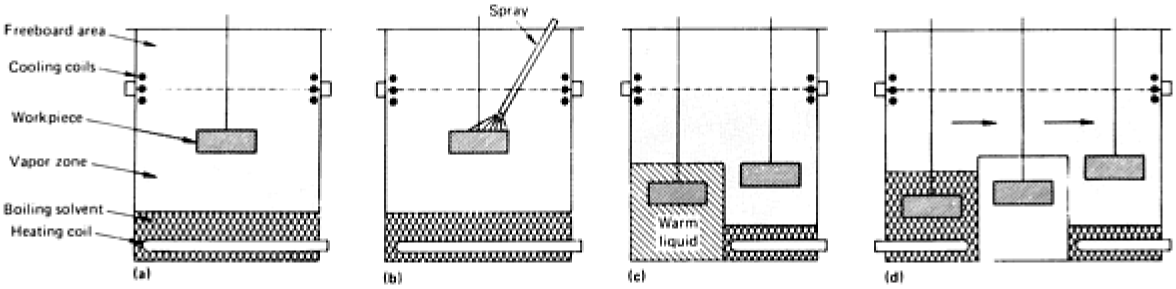

Fig. 2 Principal systems of vapor degreasing. (a) Vapor phase only. (b) Vapor-spray-vapor. (c) Warm liquid-vapor. (d) Boiling liquid/warm liquid-vapor

Vapor Phase Only. The simplest form of degreasing system uses the condensation of solvent vapor only (Fig. 2a). The work to be cleaned is lowered into the vapor zone, where the relative coolness of the work causes the vapor to condense on its surface. The condensate dissolves the soil and removes it from the surface of the work by dripping back into the boiling solvent. When the work reaches the temperature of the hot vapor, condensation and cleaning action cease. Workpieces are dry when removed from the tank.

Vapor-Spray-Vapor. If the workpiece contains blind holes or recesses that are not accessible to the vapor, or if the soil cannot be removed by the vapor, a spray stage may be added. The system then consists of vapor, spray, vapor (Fig. 2b).

Usually, the work to be cleaned is lowered into the vapor zone, where the condensing solvent does the preliminary cleaning; when condensation ceases, the work remains in the vapor zone and is sprayed with warm solvent. The pressure of the spray forces the liquid solvent into blind holes and effects the removal of stubborn soils that cannot be removed by vapor alone. The warm spray also lowers the temperature of the work; after spraying, the work is cool enough to cause further condensation of vapor for a final rinse.

The hot vapor may bake on some soils, such as buffing compounds, and make them difficult to remove. For complete removal of these soils, the work must be sprayed immediately upon entering the vapor and before the heat of the vapor can affect the compounds. The spray nozzle must be below the vapor line, and all spraying takes place within the vapor zone. Normal spray pressure for standard degreasers is 40 kPa (6 psi) and should not exceed 55 kPa (8 psi). Excessive spray pressure disturbs the vapor zone, resulting in a high rate of vapor emission.

Warm Liquid-Vapor. Small parts with thin sections may attain temperature equalization before the work is clean. For these parts, and for other small parts that are packed in baskets, the warm liquid-vapor system is recommended. In the degreasing unit shown in Fig. 2(c), work may be held in the vapor zone until condensation ceases, and then be lowered into the warm liquid, or the work may be lowered directly into the warm liquid. Agitation of the work in the warm liquid mechanically removes some additional soil. From the warm liquid, the work is transferred to the vapor zone for a final rinse.

Boiling Liquid/Warm Liquid-Vapor. For cleaning parts with particularly heavy or adherent soil or small workpieces that are nested or packed closely together in baskets, the boiling liquid/warm liquid-vapor system is recommended. In the unit shown in Fig. 2(d), the work may be held in the vapor zone until condensation ceases and then be lowered into the boiling liquid, or the work may be lowered directly into the boiling liquid. In the boiling liquid, the violent boiling action scrubs off most of the heavy deposit, as well as metal chips and insolubles. Next, the work is transferred to the warm liquid, which removes any remaining dirty solvent and lowers the work temperature. Finally, the work is transferred to the vapor zone, where condensation provides a final rinse.

Ultrasonic Degreasing. Ultrasonic transducers, which convert electrical energy into ultrasonic vibrations, can be used in conjunction with the vapor degreasing process. The transducer materials used are of two basic types, electrostrictive (barium titanate) and magnetostrictive. The latter is capable of handling larger power inputs. Barium titanate transducers generally are operated over a range of 30 to 40 kHz; magnetostrictive transducers usually operate at about 20 kHz, but they may operate at frequencies up to about 50 kHz.

Cleaning efficiency in the liquid phase of a vapor degreasing cycle can be considerably augmented by the application of ultrasonic energy. However, ultrasonic cleaning is expensive and is seldom used in a degreasing cycle unless other modifications have failed to attain the desired degree of cleanness. It is often applied to parts that are too small or too intricate to receive maximum benefit from conventional degreasing cycles.

The inside walls of hypodermic needles can be thoroughly cleaned by ultrasonic degreasing. Other examples of parts cleaned by ultrasonics because they failed to respond to conventional degreasing methods are small ball bearing and shaft assemblies, printed circuit boards (for removal of soldering flux), intricate telephone relays, plug valve inserts (contaminated with lapping compounds), and strands of cable (for removal of oil and other manufacturing contaminants trapped between the strands).

Rustproofing. When a ferrous metal is vapor degreased, organic films are usually removed, and the metal is highly susceptible to atmospheric corrosion. If the surrounding atmosphere is humid or contains products of combustion or other corrosive contaminants, immediate steps must be taken to provide exposed metal surfaces with a protective film. When precision steel parts with a high surface finish (antifriction bearings, for example) are being degreased and complete rust prevention is desired, rustproofing by flushing or immersion should be included as an integral part of the degreasing system.

Control of Solvent Contamination

The cleanness and chemical stability of the degreasing solvent are important influences on the efficiency of vapor degreasing. For example, an excess of contaminant oil raises the boiling point of the solvent and detracts from its effectiveness in cleaning.

Oils. The chlorinated solvents used in degreasers are stabilized or inhibited to resist the harmful effects of many contaminants. However, certain cutting oils with a high content of free fatty acid can overcome the effects of stabilization and may contribute to a sour, acidic condition. Oils with high contents of sulfur or chlorine as additives have the same effect. These oils and greases accumulate in the boiling or vapor chamber and cause foaming and a reduction in solvent evaporation. Baked sludge accumulates on the steam coils and other heated areas, thus reducing the efficiency of the degreaser.

When the oil content of the solvent reaches 25 vol%, the solvent should be replaced and the oily solvent reclaimed. The percentage of mineral oil in trichloroethylene, perchloroethylene, 1,1,1-trichloroethane, and methylene chloride can be determined from the boiling temperatures given in Table 5.

Table 5 Physical properties of mineral oil-in-solvent mixtures

Solvent	Boiling point for vol% oil loading:								Specific gravity at 25/25 °C for vol % oil loading:			
	0		10		20		30					
	°C	°F	°C	°F	°C	°F	°C	°F	0	10	20	30
Perchloroethylene	121	250	122	252	124	255	126	259	1.619	1.542	1.464	1.395
Trichloroethylene	87	189	88	190	89	192	90	194	1.457	1.406	1.345	1.288
1,1,1-trichloroethane	74	165	76	169	77	171	79	174	1.320	1.272	1.227	1.180

Paint Pigments. Pigments from painted surfaces that are washed into the degreaser should be filtered or removed by other mechanical means. The oils in pigment or paint dissolve in the degreasing solvent, but the remaining material is insoluble. This material usually floats on the surface of the degreaser solution and adheres to the work. In addition to reducing cleaning efficiency, these pigments may bake out on the heating coils and the work.

Chips washed from parts into the degreaser should be removed periodically, because they contaminate other parts entering the degreaser. Such contamination is possible even in ultrasonic degreasers when the solution is not filtered continuously. An excessive amount of chips in the vapor or boiling tank reduce heat transfer and evaporation rates. An accumulation of fine aluminum particles may also result in solvent breakdown.

Water can be present in degreasers as a result of the presence of water on parts being degreased or the accumulation of condensate on the cooling coil or jacket of the degreaser. Most chlorinated degreasing solvents are inhibited against the effects of hydrochloric acid formation in the presence of water; nevertheless, to avoid stains, spotting, and rusting of parts, all water must be removed from the degreaser. To accomplish this, degreasers should be equipped with one or more water separators that continuously remove free water from the circulating recondensed solvent (Fig. 3).

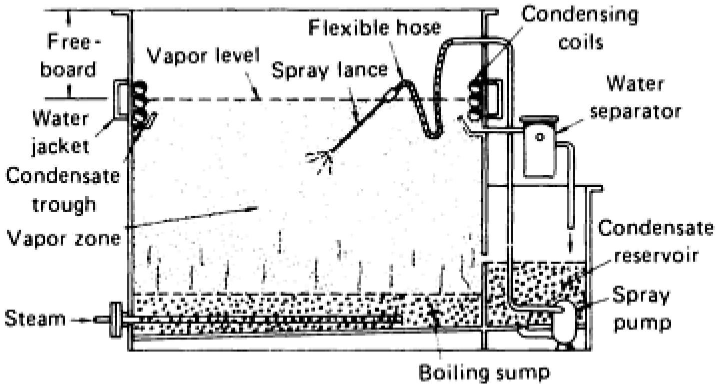

Fig. 3 Vapor degreasing unit designed specifically for a vapor-spray-vapor system

Other contaminants, such as silicones, should not be allowed to enter the degreaser, because they cause foaming at the surface of the liquid solvent. All acids, oxidizing agents, cyanides, or strong alkalis must be prevented from entering the degreasing solvent.

Conservation of Solvent

The maintenance of an adequate volume of solvent in the degreasing tank is important to the efficiency of the degreasing process. Loss of solvent can be minimized by observing the following precautions:

- The vapor degreaser wall (freeboard) should extend above the top of the vapor zone by at least 75% of the width of the degreaser.
- The degreaser should not be located in an area subject to drafts from doors, windows, or fans.
- Dragout loss should be minimized by proper drainage. Specially designed racks or rotating baskets made from wire mesh or round stock are effective.
- Where the work is small and tightly packed into a basket, the basket should be allowed to drain in the vapor area before being removed from the degreaser.
- Spraying, when required, should be held to a minimum and performed well below the vapor level.
- Work should remain in the vapor until all condensation has ceased.
- Work should not be rapidly introduced into or withdrawn from the degreaser. Vertical speed of mechanical handling equipment should not exceed about 3.4 m/min (11 ft/min).
- The degreaser should be covered when not in use. Well-designed manually operated degreasers are provided with suitable covers; conveyorized degreasers are provided with hoods.
- Plumbing, cleanout ports, valves, and pumps should be checked periodically for solvent leakage.

- Introduction of moisture into the degreaser should be avoided. Except in special situations, work that has been wetted in a previous process should not be brought into the degreaser until it is completely dry.
- Work loads should not occupy more than 50% of the open cross-sectional area of the degreasing tank. When work is lowered into the vapors, it absorbs the heat in the vapors, causing the vapor level to drop. Work load should be sized to minimize this fluctuation of the vapor level.
- Porous or absorbent materials should not be degreased.

Recovery of Solvent

Solvent can be recovered from the soils removed in cleaning parts and from solvent vapors in air. Used solvent may be transferred to a still and recovered by distillation with or without steam. Also, the solvent may be recovered by using the degreaser as its own still and drawing off the distillate to storage.

Distillation in the degreasing unit may be accomplished by operating the degreaser with the solvent return line closed. After being passed through the water separator, the distilled solvent may be collected in a clean drum or tank, leaving the sludge behind in the boiling compartment. Some degreasers have built-in tanks for this purpose. As the concentration of high boiling oils in the sludge increases, the amount of solvent recovered decreases sharply until it is no longer profitable to continue distillation.

At no time during distillation should the heating element be exposed. Such exposure may be detected by the copious white fumes generated. The high surface temperature developed by an exposed heater destroys the heater, deteriorates the solvent, and, in extreme cases, may cause a flash fire.

Solvent Still. The use of a special still for solvent recovery is usually justified when large amounts of soil must be removed from the solvent daily, when cleaning requires immersion in a solvent with very little contamination, or when downtime for maintenance must be held to an absolute minimum.

A still may be plumbed directly to a degreaser. A solvent level detector in the still senses when a pump drawing solvent from the degreaser should be turned on and off, in this arrangement. Alternatively, dirty solvent from multiple degreasers may be recovered in a centralized still or by a service company.

Solvent vapors captured in ventilation air streams may be recovered by adsorption on activated carbon. When the carbon becomes saturated with solvent, the solvent can be revaporized with steam, condensed to a liquid, separated from the steam condensate, and collected for reuse.

Vapor Degreasing Equipment

All vapor degreaser designs provide for an inventory of solvent, a heating system to boil the solvent, and a condenser system to prevent loss of solvent vapors and control the upper level of the vapor zone within the equipment. Heating the degreaser is usually accomplished by steam. However, electrical resistance ($\leq$ 3.0 W/cm^2 or $\leq$ 20 W/in.^{2}) heaters, gas combustion tubes, and hot water can be used. Gas combustion heaters with open flames located below the vapor degreaser are not recommended and are prohibited by OSHA regulations. Specialized degreasers are designed to use a heat pump principle for both heating and vapor condensation. In this instance, the compressed gases from the heat pump are used for heating the vapor degreasing solvent, and the expanded refrigeration gases are used for vapor condensation. Such a degreaser offers mobility that permits movement without having to be connected to water, steam, or gas for operation.

Normal vapor control is achieved with plant water circulation through the condensing coils. Refrigeration-cooled water or direct expansion of the refrigeration gases in the condenser coils are effective means of vapor control. Where a sufficient cool water supply is not available, or where plant water is excessively warm, a low boiling vapor degreasing solvent, such as methylene chloride or fluorocarbon 113, is chosen. Refrigerated cooling coils above the normal condenser coils (also called a *cold trap*) can reduce solvent losses.

For safety, economy, and in some cases, to comply with regulations, degreasers are usually equipped with a number of auxiliary devices:

- *Water separator:* a chamber designed to separate and remove water contamination from the degreaser.

Solvent and water condensate collected by the condenser coils are carried by the condensate collection trough and exterior plumbing to the water separator. The water separator is designed to hold 5 to 6 min of solvent and water condensate flow. This provides for nonturbulent flow and flotation of the insoluble water. This water is discharged from the equipment while the solvent condensate is returned to the degreasing equipment.

- *Vapor safety thermostat:* located just above the condensing coils, detects the heat of solvent vapors if they rise above the designed level in the equipment. This could occur with inadequately cool condensing water or condenser water flow interruption. The purpose of this device is to prevent massive solvent vapor escape into the plant atmosphere. When solvent vapors are detected, the heat input to the degreaser is turned off automatically. Manual resetting is preferred and used, because this demands attention and alerts the operator to a malfunction.
- *Boiling sump thermostat:* In the cleaning operation, high boiling oils and greases are removed and collect in the boiling chamber. These contaminants elevate the boiling temperature of the solvent and could cause solvent decomposition if left to accumulate without control. The boiling sump thermostat is located in the boiling chamber solvent and, like the vapor safety thermostat, turns off the heat to the degreaser if it senses temperatures higher than those appropriate for the solvent being used.
- *Condenser water thermostats and/or flow switches:* The water flow switch will not allow heat to be turned on unless condensing water is flowing into degreaser coils, and it will turn off the heat source if flow stops during operation. The condenser water thermostat shuts off the heat source if condensing water leaving the degreaser is too warm, indicating that the water flow through the condenser system is inadequate or that the water temperature is insufficiently cool to control the solvent vapors in the degreaser.
- *Solvent spray thermostat:* a temperature-sensing device, located just below the vapor-air interface in the degreaser and designed to prevent manual or automatic spraying if the vapor zone is not at or above the thermostat level. This device has been required by some regulations. Spraying above the vapor zone can exaggerate solvent losses by causing air and solvent vapor mixing.
- *Liquid level control:* This control shuts the heat off if the liquid level in the boiling chamber drops to within 50 mm (2 in.) of heaters. This control protects the heaters and reduces the possibility of thermal breakdown of solvent.

Modifications in this basic vapor degreaser are designed to permit various cleaning cycles, including spraying of the workpieces or immersion of the workpieces in boiling or cool solvent. Further, vapor degreaser designs are available to provide various conveyor and transport means through the cleaning cycles. Common conveyor systems include the monorail vapor degreaser, the crossrod vapor degreaser, the vibratory conveyorized degreaser, and the elevator degreaser. Open-top degreasers constitute over 80% of the vapor degreasers used in industry. Their sizes range from benchtop models with perhaps 0.2 m^2 (2 ft^2) of open-top area to tanks over 30 m (100 ft) long. The most common sizes range between 1.2 to 2.4 m (4 to 8 ft) long and 0.6 to 1.2 m (2 to 4 ft) wide. The most frequently used cleaning cycle is vapor-solvent spray-vapor. Among the conveyorized vapor degreasers, the monorail is the most prevalent. Generally, open-top degreasers are much lower in cost, permit greater flexibility in cleaning different workloads, occupy much less floor space, and are adaptable to both maintenance and production cleaning. Because of their relatively low cost and minimum space requirements, they are preferred for intermittent operations and for decentralized cleaning where transport of parts to be cleaned to a centralized location adds substantially to the cleaning cost.

Emerging technology combines vacuum autoclave with solvent cleaning. This system cleans in a sealed chamber, using either solvent spray or immersion to clean the parts. The solvent can be perchloroethylene, trichloroethylene, or HFC. After the parts are placed in the chamber to be cleaned, it is dried by evacuating the chamber to 29 mm/Hg. The vacuum reduces the boiling temperature of the residual solvent, flashing it off. The solvent vapors from the chamber are condensed (Fig. 4).

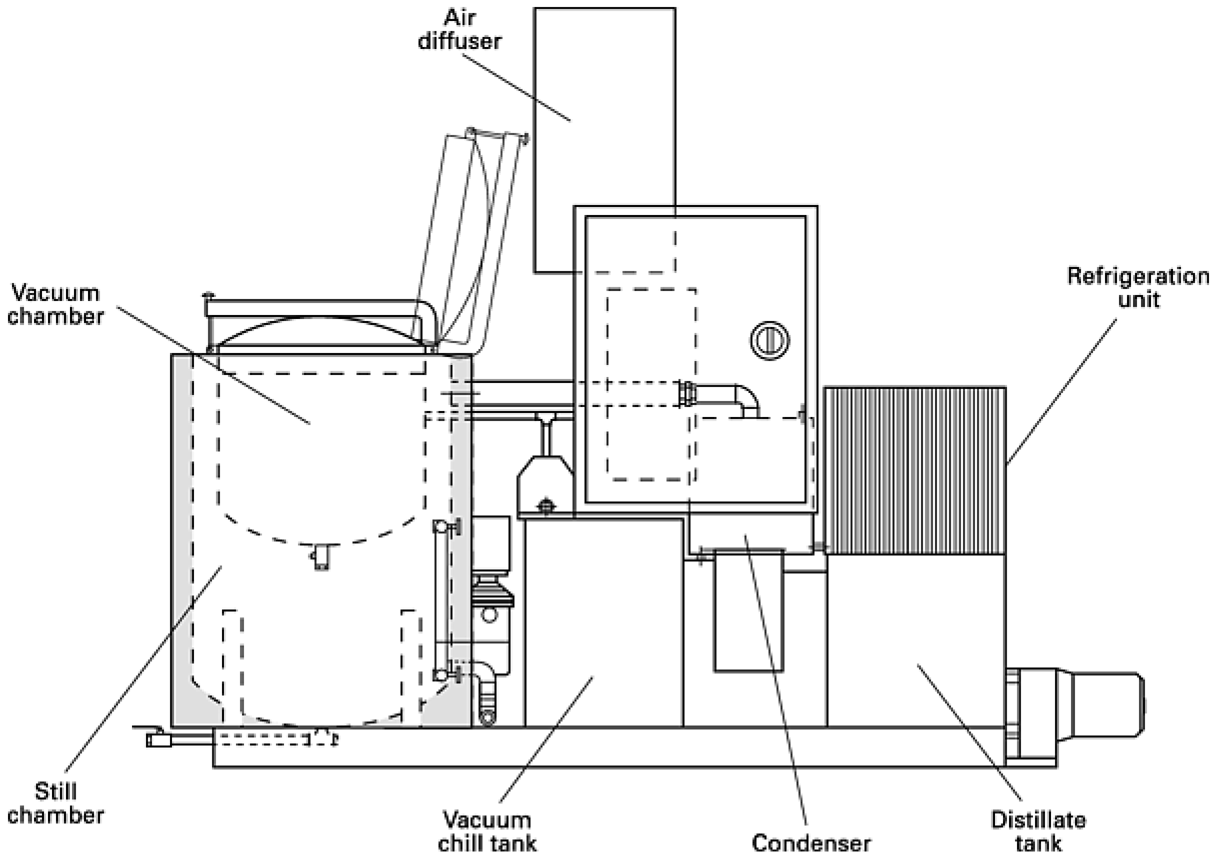

Fig. 4 Vacuum cleaning system. Courtesy of Baron-Blakeslee Company

Installation of degreasing equipment should be supervised by a qualified individual. Some important considerations relating to installation are:

- A degreaser should never be installed in a location that is subjected to drafts from ventilators, unit heaters, fans, doors, or windows. When units cannot be ideally located, such drafts should be reduced by the installation of baffles.
- No degreaser should be installed near open flames unless the combustion products of these flames are exhausted outside the building. Location near welding or other operations using high temperatures must be avoided, because exposure of solvent vapors to high temperatures and high-intensity ultraviolet light results in decomposition to toxic and corrosive substances such as phosgene and hydrogen chloride.
- The flue from the combustion chamber of a gas-fired unit should conform with local laws or ordinances. All exhausts should be discharged outside the building at an adequate distance from air intakes.
- Water outlets from condenser jackets or coils should not be connected directly to sewer lines, but instead should drain freely into a funnel or other open-to-view collecting device that is connected to sewer lines. This prevents back pressure and ensures maximum efficiency of the condensing coils. As water and sewage treatment costs continue to escalate, recirculating condenser water systems such as water chillers and cooling towers are being used. Many degreasers using low-temperature boiling solvents incorporate direct refrigeration. Several manufacturers offer heat recovery of heat recycling systems for use with low-boiling-temperature solvents.
- All degreaser containers should have a legible, highly durable sign attached to them that bears solvent label information (see ASTM D 3698) and operating procedures, as required by most state environmental protection agencies.

Baskets and racks should be constructed of open-mesh, nonporous material. When baskets are completely filled with closely packed small items, basket size should not exceed more than 50% of the work area of the degreaser. For baskets

handling large parts with generous open spaces, however, the 50% maximum may be exceeded slightly. Baskets that are too large may act as pistons as they enter the tank and displace the vapor level, thus forcing the vapor from the unit into the atmosphere.

The placement of work in the basket is critical, particularly when the parts have blind holes, which may entrap solvent. Precautions must be taken to ensure that entrapped air does not prevent liquid solvent or vapor from reaching all surfaces. After cleaning, the solvent must be completely drained from the parts to reduce dragout. To satisfy these requirements, specially designed racks or rotating baskets may be necessary.

Operating and Maintaining the Degreaser

An effective operator training program and a routine maintenance program are important to safe and efficient vapor degreasing. Proper education and maintenance practices can greatly extend working life with assurance of smooth production. Following the checklist provided below should aid in beginning an efficient degreasing operation.

Startup

- Be sure the degreaser operator is adequately trained and equipped with the appropriate safety equipment and clothing. For emergency situations, such as power failures, condenser coolant stoppages, and ventilation interruptions, have organic vapor respirators or air-line masks available for immediate use. Also, be sure the operator knows how to use personal protective equipment, understands first aid procedures, and is familiar with the hazards of the operation.
- Check proper operation of the vent system and leave it on.
- Turn on the condensing water. Observe the rate of flow and check for leaks. Leave the condenser water on. If the cooling water supply of the degreaser is equipped with an outlet water temperature control or a flow control safety shutoff, check these for proper operation. It is easier to do this with the degreaser heat on.
- Adjust the high temperature cutoff control for the boiling sump and the vapor safety thermostat control to the temperatures recommended for the particular degreasing solvent to be used. The high temperature cutoff control setting should be about the boiling point of a 25% mineral oil-in-solvent mixture (Table 6). The vapor safety control setting should be at least 6 °C (10 °F) lower than the boiling point of the solvent-water azeotrope (Table 6). Do not turn on a gas or electrically heated degreaser unless the heaters are covered by solvent. If the machine is steam heated, turn steam on and check for leaks and for proper settings and functioning of pressure gages, reducer valves, and traps. Turn off and cool before adding solvent.
- Add some solvent to the degreaser and check the operation of the liquid level control, if the machine is so equipped. Finish filling the degreaser by adding enough solvent to cover the heating elements by 75 to 150 mm (3 to 6 in.), or up to the bottom of the work rest if the machine is so equipped.
- Turn on the heat and, as the temperature rises, ensure proper operation of the various heat controls that may be in use.
- As condensation begins, observe the flow of condensate from the coil and jacket, through the trough and water separator, and the returning stream to the degreaser. Interrupt the flow of condensing water and observe for proper operation of the vapor safety control.
- Adjust the heat input and/or the condenser water flow so that the vapor zone rises only halfway up the condenser coils.
- Check the functioning of the degreaser auxiliary equipment, such as the sprayer, conveyor, still feed pump, and the still. Look at the solvent levels in each degreaser compartment and adjust to operating levels.
- Begin supplying work to the unit.
- Check the first parts through for satisfactory cleanness and for any signs of machine malfunction.
- Adjust the condenser discharge water temperature to about 8 to 11 °C (15 to 20 °F) above the dew point of the surrounding atmosphere, that is, about 32 to 46 °C (90 to 115 °F), for all the chlorinated solvents except methylene chloride. For methylene chloride or fluorocarbon 113, do not allow the discharge water temperature to go above about 29 °C (85 °F). Degreasers for these two solvents often employ

refrigeration for vapor control.

Operation

- Check the upper level of the vapor zone. The vapor zone should not rise above the midpoint of the condenser.
- While the degreaser is operating, maintain a routine surveillance to see that the work is being cleaned properly and the various systems continue to function satisfactorily.
- Any time work is not being processed in the degreaser, the cover should be closed. Degreaser manufacturers supply covers for their degreasers. The cover should be relatively tight fitting but should allow the degreaser to breathe.
- Give some detailed attention to the arrangement of the work parts being cleaned. It may be necessary to reposition some of the parts to get proper cleaning and free draining. Cup-shape parts, for example, should be positioned as shown in Fig. 5.
- Observe the spraying operation. Be sure that the vapor-air interface is not being unnecessarily disturbed.
- Check to see that the amount of work being fed at one time is not so great that it causes vapor shock. The vapor level should not recede excessively. Be sure the rate of introduction of the work does not exceed 3.4 vertical m/min (11 vertical ft/min). A faster rate of entry increases vapor losses.
- Observe the vapor level as the work is being removed. The vapor level should not rise above the cooling coil or jacket. If the vapor level is rising too much, check the cross section of the work. This generally should not exceed 50% of the open area of the degreaser if the parts are traveling at a rate of about 3.4 vertical m/min (11 vertical ft/min). If the parts are larger than this, the rate of vertical movement should be reduced accordingly.
- Check to see that the parts are within the vapor zone long enough for condensation to cease before the parts are brought up into the freeboard area. Also, see that the parts are remaining in the freeboard area long enough for the solvent to evaporate completely.
- After the degreasing operation has continued for several hours, observe the water separator to see that any water entering the degreaser is being withdrawn efficiently by the separator. A cloudy ghost vapor in the vapor zone of the degreaser is a warning sign that water is not being properly removed. If water is allowed to accumulate in the degreaser, the boiling point of the solvent may drop due to the formation of the solvent-water azeotrope. The direct results are poor cleaning, greater solvent losses, water spotting, and more odor complaints.
- As the solvent level in the degreaser drops due to evaporation and leakage losses, fresh makeup solvent should be added to maintain a solvent level of about 150 mm (6 in.) above the heating elements. Particular care should be exercised that the solvent level in the boil chamber never drops lower than 25 mm (1 in.) above the heating elements. Makeup solvent should be added to the degreaser before startup, that is, while cold.
- On a periodic basis, perhaps every few days during initial operation, the acid acceptance inhibitor level of the solvent should be checked. The acid acceptance value should stabilize at no less than 40% of the original value. Should the inhibitor level show an unexpected drop, the trouble should be traced and eliminated. The problem might be excessive water in the degreaser, introduction of acid soils, soil buildup on, or exposure of, the heating surfaces, or accumulation of excessive amounts of metal fines or soluble soils.
- Based on the total soil load and type, and taking into account work scheduling, regular periodic degreaser cleanouts should be performed. The frequency of cleanout can sometimes be extended by removal of particulate soils from the degreasing solvent by use of an external filtration system. Nevertheless, at intervals varying from a few days to a few months, it is necessary to shut down the degreaser and clean it out. The oily soil level of the degreaser should not be allowed to go higher than 25 vol%.

Shutdown

- A scheduled shutdown should be planned so that work is not inconveniently backlogged. The degreaser, of course, should be shut down only after the last parts in process have cleared the machine.

- Turn off the heat supply to the degreaser. Wait for solvent condensation on the cooling surfaces to cease and the vapor zone to collapse.
- Turn off the cooling water and any unneeded pump.
- If the degreaser is being used to partially distill the solvent, the solvent condensate from the water separator should be directed to storage rather than returned to the degreaser. Heating should be stopped when the boiling chamber solvent level approaches 25 mm (1 in.).
- Additional information is available in the *Manual on Vapor Degreasing* published by ASTM.

Maintenance

- Routine cleanout operations can and should be conducted from outside the equipment. Workers entering vapor degreasing equipment or associated pits should follow the confined-space-entry procedures outlined in the next section.
- For a routine cleanout, allow the machine to cool completely and then drain the soil-laden solvent. Ventilate the interior to outside the plant to remove solvent vapors and dry any remaining solvent.
- Remove any auxiliary equipment from the degreaser that may interfere with the cleaning or might be damaged in the process.
- Clean out the trough, water separator, spray pump sump, and associated piping.
- Scrape and brush out the metal fines and other particulate soils. Pay particular attention to corners and recesses where residues tend to collect.
- Clean off excess rust and corrosion, paying particular attention to the heating elements. Consider replacing mild steel piping with stainless steel if heavy rust is noted.
- Inspect and repair any defective auxiliary equipment. Lubricate pumps and conveyor drives.
- Install a new cleanout door gasket, using as a sealant either plain or litharge-thickened glycerol or ethylene glycol. Reinstall all auxiliary equipment items removed during cleanout.
- If the degreaser has experienced an acid condition, the cleaning procedure should be augmented by charging the compartment with water containing 30 g/L (4 oz/gal) sodium carbonate (soda ash), to a depth of about 300 mm (12 in.). The solution should be boiled for about 15 min, and the compartment should be rinsed and thoroughly dried. The degreasing unit is then ready for recharging with clean solvent. If acid conditions persist, contact the solvent supplier or degreaser manufacturer for detailed procedures to cope with the condition and prevent its recurrence.

Table 6 Applications of vapor degreasing by vapor-spray-vapor systems

Note: Degreasing by vapor only is applicable to the cleaning of flat parts with light soils and little contamination. Anything that can be cleaned by vapor degreasing usually can be cleaned better by liquid-vapor systems

Parts	Metal	Production rate		Soil removed	Subsequent, operation	Notes on processing
		kg/h	lb/h			
Spark plugs	Steel	270	600	Machining oil	. . .	Special fixture and conveyor
Kitchen utensils	Aluminum	450	1000	Buffing compound	Inspection	Special fixture and conveyor
Valves (automotive)	Steel	540	1200	Machining oil	Nitriding	Automatic conveyor
Valves (aircraft)	Steel	590	1300	Machining oil	Aluminum coating	Automatic conveyor

Parts	Metal	Production rate		Soil removed	Subsequent, operation	Notes on processing
		kg/h	lb/h			
Small-bore tubing	Aluminum	680	1500	Wax extrusion lubricant	Annealing	Hoist-operated unit
Builders' hardware	Brass	2270	5000	Buffing compound; rouge	Lacquer spray	Racked work on continuous monorail
Acoustic ceiling tile	Steel	2720	6000	Light oil (stamping lubricant)	Painting	Monorail conveyor
Gas meters	Terneplate	4540	10,000	Light oil	Painting	Monorail conveyor
Continuous strip, 0.25-4.1 mm (0.010-0.160 in.)	Cold rolled and stainless steels; titanium	13,600	30,000	Oil emulsion (steels); palm oil (titanium)	Annealing	Continuous processing at up to 0.6 m/s (120 ft/min)
Automatic transmission components	Steel	18,100	40,000	Machining oil; light chips; shop dirt	Assembly	Double monorail conveyor
Degreasing by warm liquid-vapor system						
Aircraft castings	Magnesium	230	500	Polyester resin (from impregnating)	Curing	Solvent: methylene chloride
Speedometer shafts and gears	Steel; brass	340	750	Machining oil; chips	Inspection; assembly	Rotating baskets (drainage and chip-removal)
Screws	Steel; brass	680	1500	Machining oil; chips	Painting; finishing	Flat and rotating baskets; conveyorized
Automotive die castings	Zinc-base	910	2000	Light oils, grease; tapping lubricants; chips	Assembly	Flat and rotating baskets; conveyorized
Electron-tube components	Steel	910	2000	Light oils	Dry hydrogen fire	Conveyorized unit
Tractor gears and shafts	Steel	910	2000	Machining oil; chips; quenching oil	Nitriding	Elevator-type conveyor handling of work in heat treating trays
Flexible hose connectors	Steel; brass	1250	2750	Machining oil; chips	Assembly	Conveyorized unit

Parts	Metal	Production rate		Soil removed	Subsequent, operation	Notes on processing
		kg/h	lb/h			
Wire, 0.8-3.2 mm (0.030-0.125 in.) diam	Aluminum	1810	4000	Drawing lubricants; light oil	Shipment	Processed at 3 m/s (500 ft/min)
Hand power-tool components	Cast iron; aluminum	2270	5000	Machining oil; chips; polishing; buffing compounds	Painting or plating; assembly	Rotating and flat baskets on conveyorized machine
Tubing, 6-76 mm ($\frac{1}{4}$ -3 in.) diam; 762-1270 mm (30-50 in.) long	Aluminum	5670	12,500	Drawing lubricants	Annealing	Hoist-operated 1134 kg (2500 lb) loads
Degreasing by boiling liquid-warm liquid-vapor system						
Transistors	Gold and tin plated	25	50	Silicone oil; light oil	Painting; branding	Manual; mesh basket
Electron-tube components	Stainless steel	90	200	Light oil	Dry hydrogen oil	Manual; mesh basket
Calculating-machine components	Steel	450	1000	Stamping oil	Painting	Manual operation
Valves (automotive, aircraft)	Steel	450	1000	Machining oil	Welding	Manual operation
Knife blades	Steel	820	1800	Oil; emery	Buffing	Manual operation
Carbide-tip tool holders	Steel	910	2000	Lubricant; chips	Recess milling	Conveyorized unit
Tubing, 60 cm (2 ft) long	Aluminum	910	2000	Drawing lubricants; quench oil	Satin finishing	Conveyorized; tube handled vertically
Calculating-machine components	Steel	1360	3000	Stamping oil	Plating	Conveyorized unit
Hand-tool housings, die-cast	Zinc-base	1360	3000	Tapping oil; chips	Assembly	Automatic conveyor; racks
Screw machine products	Steel; brass	1360	3000	Cutting lubricants; chips	Assembly	Flat and rotating basket; conveyor

Parts	Metal	Production rate		Soil removed	Subsequent, operation	Notes on processing
		kg/h	lb/h			
Cable fittings	Steel	1810	4000	Light oils	Inspection	Conveyorized
Stampings (miscellaneous)	Steel	2270	5000	Light oil; chips	Furnace brazing	Small stampings nested in baskets
Wafers	Silicon	. . .	. . .	Sealing wax; paraffin	Acid etch; diffusing	Manual, in beakers; fixtured

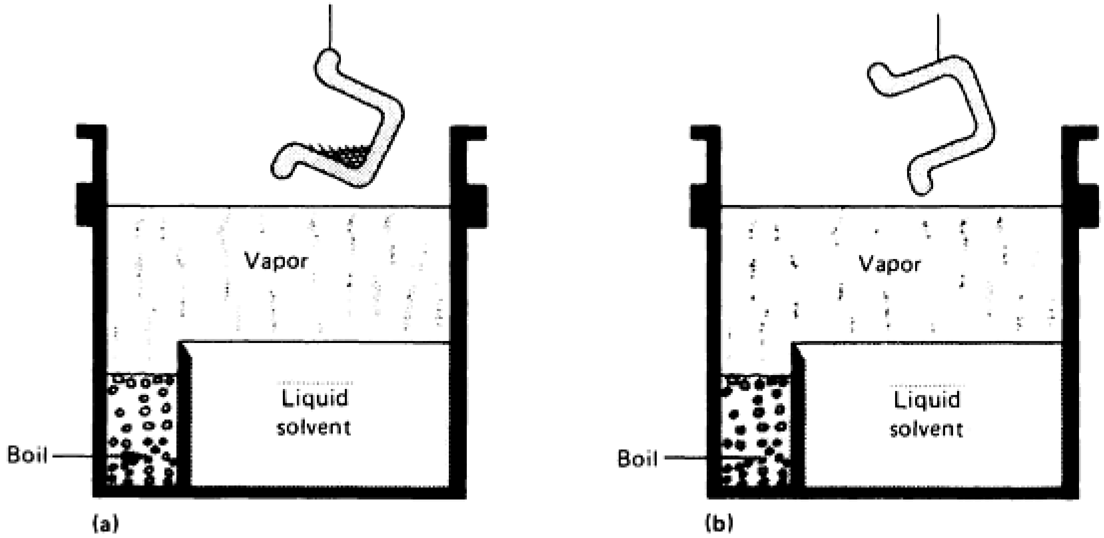

Fig. 5 Positioning of cup-shape parts to drain solvent. (a) Incorrect positioning. (b) Correct positioning

Confined Space Entry

Entering a confined space such as a vapor degreaser is potentially life threatening and requires adherence to OSHA regulations (Section 1910.146 of Title 29 of the *Code of Federal Regulations*). Another resource for information on confined space entry is ASTM D 4276-84. Some of the questions to consider are:

- Is entry required?
- Has management approval been obtained?
- Has the entire solvent volume been drained from all portions of the degreaser, and has all solvent vapor been vented? (Note: Ventilation should continue during tank entry.)
- Has the electric power to conveyors, pumps, and motors been turned off and locked?
- Have all liquid transfer lines been opened and capped?
- Has the atmosphere in the enclosed area been tested for flammable and toxic vapor concentrations and the presence of adequate (19.5%) oxygen in the air?
- Has a properly trained and equipped observer been assigned?

- Have nearby employees been alerted to the tank entry operation, and have enclosed area entry placards been posted?
- Have the person(s) entering the tank and the observer(s) been equipped with a rescue harness and lifeline, a self-contained breathing apparatus, and proper protective clothing (e.g., gloves)?
- Is a hoist or pulley system available in case rescue would require a vertical lift?

Process Applications

The wide range of applications in which vapor degreasing is used are indicated in Table 6, which lists parts and metals cleaned by the degreasing systems, as well as soils removed, production rates, and subsequent operations. The data in this table represent the experience of numerous manufacturing plants.

Process Limitations

The principal limitations of the vapor degreasing process are related to the materials it can clean without damaging effects and the soils it can remove effectively. Size and shape of workpieces, quantity of work, and degree of cleanness obtainable may also limit the applicability of vapor degreasing, but to a lesser extent. Normally, these variables merely determine the degreaser design selected.

Materials. All common industrial metals can safely be degreased with a minimum of difficulty, provided the chlorinated solvent is properly stabilized for vapor degreasing and the degreaser is properly operated. Iron parts are more susceptible to rusting after degreasing, especially in humid atmospheres.

Compatibility with Nonmetals. Some chlorinated solvents attack rubber, plastics, and organic dyes; this must be considered when degreasing assemblies with both metallic and nonmetallic components. Trichlorotrifluoroethane and 1,1,1-trichloroethane are less aggressive to many nonmetallic parts and have been the preferred solvents for these assemblies.

Solvent Stability. Vapor degreasing solvents can be decomposed, resulting in hydrogen chloride gas. This gas is very irritating, toxic, and corrosive to metals. Sources of solvent decomposition include:

- Exposure to surfaces hotter than about 175 °C (350 °F)
- Prolonged exposure to metal fines (particularly aluminum)
- Excessive soil accumulation in the boiling chamber
- Excessive and prolonged exposure to water
- Contamination with aluminum or iron chloride salts
- Exposure of the liquid or vapor to ultraviolet light

The vapor degreasing solvents have variable resistance to decomposition under the various conditions above. Trichlorotrifluoroethane is the most inherently stable of the group. Stabilizers or inhibitors are added to these solvents especially for this use. Solvent products made for other uses are likely to be insufficiently stabilized for the rigors of vapor degreasing. With proper stabilization of the degreasing solvent and good operating and maintenance practices, solvent stability is essentially secured.

Quantity of work to be processed is not a significant factor when considering the use of vapor degreasing, so long as the equipment was designed to mechanically handle the workload and has sufficient heat input. Available units range from those that are suitable for occasional cleaning of a few parts to completely automated installations geared to high-production operations.

Degree of Cleanness Obtainable. Under normal operating conditions, vapor degreasing provides a degree of cleanness that is suitable for subsequent polishing, passivating, assembly, phosphating, or painting. However, when parts are to be electroplated or subjected to other electrochemical treatments, vapor degreasing is seldom adequate and must be followed by another cleaning operation, such as electrolytic alkaline cleaning. Vapor degreasing is used immediately preceding the alkaline cleaners to remove most of the soil, thus prolonging the life of the final cleaners.

Radioactive and water-break testing techniques have indicated that a degree of cleanness between 0.1 and 1.0 monomolecular layers of soil is attainable in vapor degreasing. Under normal operating conditions, the degree of cleanness is usually near the upper level. Surface condition and section thickness may affect the degree of cleanness obtainable by vapor degreasing. For example, a polished surface is easier to clean than a grit-blasted surface. Thin sections receive less cleaning action than heavy sections, because the former equalize in temperature with the vapor zone in less time.

Removal of Difficult Soils

Virtually all ordinary oils and greases are soluble in chlorinated hydrocarbons and can be completely removed by one or more of the methods illustrated in Fig. 2. Other types of soils vary in responsiveness to vapor degreasing, from mild to almost total resistance to solvent cleaning.

Frequently, vapor degreasing is used to remove soils that do not dissolve in the solvents. Among these difficult soils are pigmented drawing compounds, water-based cutting fluids, chips, polishing and buffing compounds, and soldering fluxes. In some instances, it may be possible to substitute more easily cleaned materials. When insoluble soils are encountered, the solvent cleaning may need to be supplemented by mechanical cleaning. Impingement with a spray will remove some insolubles. Brushing may be practical in some situations. Finally, ultrasonic cavitation in the warm dip chamber can often remove the most tenacious soils.

Safety and Health Hazards

The chlorinated hydrocarbons used in vapor degreasing are modestly toxic when inhaled; gross overexposures result in anesthetic effects and may cause death. Prolonged or repeated exposure of the skin to these solvents should be avoided because they extract oils from the skin, causing cracking and dermatitis.

OSHA requires users to obtain Material Safety Data Sheets and to keep them on file and available to employees. They are useful information sources for operator training. Personnel operating degreasers or using chlorinated solvents should be warned of attendant potential hazards and observe proper operating instructions. They should be familiarized with the symptoms of excessive inhalation: headaches, fatigue, loss of appetite, nausea, coughing, and loss of the sense of balance. Maintenance workers have lost their lives climbing inside tanks containing extremely high concentrations of solvent vapors. Death was attributed to the strong anesthetic power or asphyxiation.

Every effort should be made to clean or maintain a degreaser without entering the tank. However, if tank entry is necessary, workers should follow the guidelines given in the section "Confined Space Entry" in this article.

OSHA has the primary responsibility for protecting worker health. Numerous general regulations apply to open tanks or heated equipment. For example, management must provide a cover, guardrails for platforms or walkways, an open-top edge or guardrail 1050 mm (42 in.) high, and enclosed combustion heaters with corrosion-resistant exhaust ducts. Where flammable solvents are used, special devices such as explosion-resistant equipment and fusible link cover supports are required. Solvent spraying in general must be conducted in an enclosure, to prevent spray discharge into the working area. Spraying in a vapor degreaser should be done only below the solvent vapor zone, to prevent forcing air into the vapor zone. Welding and chlorinated solvent cleaning operations must be located separately so that the solvent vapors are not drawn into welding areas. Exposure of the chlorinated solvent vapors to the high-intensity ultraviolet light radiated by welding can cause solvent decomposition to corrosive and toxic products.

The primary health hazard associated with solvent cleaning is the inhalation of excessive vapor concentrations. Acceptable time-weighted average vapor exposure standards have been adopted by OSHA, and it requires that worker exposures be maintained at or below these concentration limits. Mechanical ventilation may be required to control exposures below these concentrations. The measurement of actual exposures to vapor concentrations can be accomplished by industrial hygiene surveys using activated carbon collection tubes and calibrated air pumps, continuous reading vapor detectors, and detector tubes. Additional information can be found in the 29 May 1971 *Federal Register*, p 10466, and in the 27 June 1974 issue, p 23540.

Disposal of Solvent Wastes

The Resource Conservation and Recovery Act, also known as the Solid Waste Disposal Act, promotes the protection of health and the environment and the conservation of valuable material and energy resources. Virtually all chemical wastes

have the potential to be defined as hazardous, because the EPA defines *solid waste* as any solid, liquid, semisolid, or contained gaseous material resulting from industrial, commercial, mining, or agricultural operations, or from community activities. There are exceptions, and a good background document appears in the *Code of Federal Regulations*, Title 40, sections 261-281 (especially section 261.31).

Most electroplating wastes, including solvent residues, require disposal according to these regulations. Quantity exemptions, such as less than 1000 kg (2200 lb) per month, exist in some states for some wastes, providing relief from paperwork; however, proper waste disposal is still required. Solvent distillation can reduce the quantity of waste to a minimum, particularly with the nonflammable vapor degreasing solvents. Under some circumstances, still bottoms (residues) can be used as a fuel in industrial boilers. Nonhazardous waste such as paper should be segregated from hazardous wastes to minimize disposal costs. Incineration is the best known ultimate disposal method for wastes from solvent cleaning operations. However, wastes containing reasonable quantities of solvent may be saleable to local reclaimers.

Introduction

EMULSION CLEANING is an industrial cleaning process that uses an organic solvent as the main active agent. The solvent is usually a hydrocarbon of distilled petroleum dispersed in water. The emulsion, which alone is potentially volatile, is suspended in a nonvolatile aqueous vehicle. Most emulsion cleaners include emulsifying agents, and some are aided by surfactants. Emulsion cleaners are generally used in situations where alkaline or acid cleaners are not applicable.

Emulsion means tiny droplets dispersed in large droplets. An emulsion is simply a colloidal suspension of one liquid into another immiscible liquid. (*Immiscible* means the liquids will not mix.) The oil-in-water emulsion has tiny droplets of an organic (hydrocarbon) solvent dispersed throughout a water solution. This is generally the type used in emulsion cleaning. The other is water-in-oil (natural petroleum), which has tiny droplets of a water solution dispersed throughout an oil. The oil-in-water type can easily be washed off with water and light detergent. The water-in-oil type leaves a greasy film that is much more difficult to remove.

The hydrocarbon can be distilled from any of any of different petroleum products, such as naphtha, kerosine, benzene, carbon tetrachloride, or other chlorinated solvents, including 1,1,1-trichloroethane. Most of these are no longer used because they are flammable and potentially carcinogenic and have been identified as causes of ozone depletion. Most emulsions are now based on a "mineral spirits" derivative, a hydrocarbon mixture with a relatively high boiling point (93 to 150 °C, or 200 to 300 °F). Compositions, operating temperatures, and production applications for emulsion cleaners are summarized in Tables 1 and 2.

Table 1 Compositions and operating temperatures for emulsion concentrates

Maximum safe temperature depends on the flash point of the hydrocarbon (petroleum) solvent used as the major component

Component	Composition, parts by volume		
	Stable[(a)]	Unstable[(b)]	Diphase[(c)]
Petroleum solvent[(d)]	250-300	350-400	250-300
Soaps[(e)]	10-15	15-25	None
Petroleum (or mahogany) sulfonates[(f)]	10-15	None	1-5
Nonionic surface-active agents[(g)]	5-10	None	1-5
Glycols, glycol ethers[(h)]	1-5	1-5	1-5

Aromatics[i]	5-10	25-50	5-10
Water[j]	5-10	None	None

(a) Operating temperature range: 4 to 66 °C (40 to 150 °F).

(b) Operating temperature range: 4 to 66 °C (40 to 150 °F).

(c) Operating temperature range: 10 to 82 °C (50 to 180 °F).

(d) Two frequently used solvents are deodorized kerosine and mineral seal oil.

(e) Most soaps are based on rosin or other short-chain fatty acids, saponified with organic amines or potassium hydroxide.

(f) Low molecular weight petroleum sulfonates (mahogany sulfonates) are used for good emulsification plus some rust protection. High molecular weight sulfonates, with or without alkaline-earth sulfonates, offer good rust inhibition and fair emulsification.

(g) Increased content improves stability in hard water, but increases cost.

(h) Glycols and glycol ethers are used in amounts necessary to act as couplers in stable and unstable emulsions. These agents are frequently used with diphase and detergent cleaners to provide special cosolvency of unique or unusual soils.

(i) Aromatic solvents are used to provide cosolvency for special or unique soils. They also serve to inhibit odor-causing or rancidifying bacteria.

(j) Water or fatty acids, or both, are used to adjust the clarity and the stability of emulsion concentrate, particularly those which are stable or unstable.

Table 2 Production applications of emulsion cleaning

Data represent practices reported by a number of plants

Part	**Soils removed**	**Cleaning cycles**	**Cleaning, time, min**	**Subsequent operations**
Stable emulsion, dip cleaning				
Cast iron parts and machined parts	Machining oil, chips	Alkaline clean, emulsion clean	1	Storage
Stable emulsion, spray cleaning				
Aluminum and brass carburetor parts	Machining oil, shop dirt	Clean, blow off[a]	1	Assembly, storage

Aluminum and brass	Dirt, machining oil	Clean, blow off	2	Assembly, storage
Aluminum cabinets	Machining oil, chips	Clean[(b)]	1	Assembly, storage
Aluminum housing (automatic transmission)	Alkali	Alkaline clean, emulsion clean[(c)]	1	Assembly, storage
Automobile wheel assembly, 0.103 m^2 (160 $in.^2$)	Drawing compound, chips	Clean, no rinse	1	Assembly, storage
Brass valves	Machining oil	Clean, blow off	2	Assembly, storage
Cast iron motor blocks	Machining oil, chips	Clean, no rinse	2	Assembly, storage
Cast iron motor heads	Machining oil, chips	Clean, no rinse	1	Assembly, storage
Retainer plate, 0.01 m^2 (16 $in.^2$)	Shop dirt, drawing compound	Clean	1	Assembly, storage
Steel rings, 100 mm (4 in.) diam	Machining oil	Clean, no rinse	1	Assembly, storage
Steel sinks	Drawing compound, oil	Clean	4	Alkaline soak, then enamel
Tractor parts	Machining oil, dirt	Clean, blow off	1	Wash, then paint
Valves (steel and brass)	Machining oil	Clean, blow off	1	Assembly, storage
Washing machine tubs	Drawing compound	Clean, no rinse	3	Alkaline soak, then paint
Unstable emulsion, spray cleaning				
Brake assembly, 0.01 m^2 (20 $in.^2$)	Shop dirt, chips	Clean, no rinse	1	Assembly, storage
Brake plates, 200 mm (8 in.) diam	Machining oil, chips	Clean, no rinse	1	Assembly, storage
Brake cases, 100 by 100 mm (4 by 4 in.)	Drawing compound	Clean, blow off	2	Assembly, storage
Diphase emulsion, dip cleaning				
Brass or zinc die castings	Buffing dirt	Soak, spray, electroclean,	4	Wash, then plate

		acid pickle		

(a) Emulsion does not plug holes of the needle valves and does not interfere with subsequent gaging operations.

(b) Emulsion does not spot or dull aluminum.

(c) Emulsion furnishes lubricity for interlocking gear parts.

Cleaning Action

In basic terms, cleaning is accomplished when the organic phase dissolves the oil contamination, breaking it up into tiny droplets. The hydrocarbon molecule has two ends. One end tends to bond with oils; the other bonds readily with water molecules. In effect, the hydrocarbon molecule bonds to the oil molecule, which breaks off and floats in the high-volume water phase. Once all of the oil bonds are broken and dispersed throughout the emulsion, the water-oriented end of the molecule remains free. When the rinse is applied it attaches to the "free" water-oriented ends of the surface active agents. As the molecules are rinsed away, the soil that is firmly held by the oil-oriented ends comes loose, too.

Emulsifiable solvent detergents are particularly well suited to the removal of such heavy soils as carbonized grease and oil deposits, and buffing and lapping compound residues. Where parts are very heavily soiled, solvent detergents are frequently used as precleaners before the work is put through the regular alkaline solution. The advantage of solvent precleaning is that heavy surface soil is removed from the alkaline tank, thus prolonging solution life. Precleaning of emulsifiable solvents shortens total cleaning time, and because it allows less frequent dumping of the alkaline tank, it also reduces total cleaning costs.

Applications

Emulsion systems are best used when rapid superficial cleaning is required and when some protection by light residual oil film is desired. Because the solvent phase of the emulsion is a petroleum derivative, a thin film is left behind when the rest of the emulsion dries. This film protects ferrous parts from rust and can aid lubrication in applications such as gears or bearings.

Emulsions are also used to remove heavy oils, because the solvent can clean with soil loading up to 50%. It is often considered more for gross cleaning than for producing a clean, water-break-free surface. (A *water-break-free surface* is clean enough that water runs freely off of it. If impurities such as oil or detergent residue are present, water will tend to bead up and stay on the surface.) The solvent phase of the emulsion is very effective in dissolving oils and grease without attacking the base metal. Thus, an emulsion system should be considered when evaluating the most appropriate cleaning method for:

- *Delicate parts with tenacious contaminants,* such as buffing and polishing compounds that cannot tolerate any mechanical agitation or impingement. The solvent will dissolve the binding agent, allowing the soils to flush away in a basic immersion bath (followed by an alkaline wash to clean off the emulsion).
- *Buffed soft metals:* Buffed or polished parts typically can be cleaned with an alkaline detergent but may require pH > 12. Brass and bronze tend to tarnish in solutions with pH > 10. Thus, emulsions have been widely used for buffed soft metals. (Detergents have recently been developed that clean buffed soft metals without tarnishing.)
- *Intricate internal cavities contaminated only with oils* could be cleaned with an immersion emulsion. Care must be taken to ensure that the emulsion can be thoroughly rinsed unless it is compatible with the subsequent process. For example, in one application, an emulsion was chosen for cleaning of aluminum and brass carburetor parts because it did not plug the needle valve holes or interfere with subsequent gaging.
- *Parts that cannot be heated* may be suitable for cold emulsion if they have light soils. Emulsions work most effectively when heated to 60 to 80 °C (140 to 180 °F), but they will accomplish some cleaning at

lower temperatures. This may be needed, for example, in a totally automated machining cell of tight tolerance parts followed by a coordinate measuring machine, where heat from a detergent washing operation may affect part dimensions.

- *Delicate parts in small volumes* may be suitable for hand wipe. A cold emulsion may be a strong enough cleaning agent.
- *Pigmented drawing lubricants*
- *Residues resulting from magnetic particle inspection*
- *Adhesives that may need an organic solvent to dissolve the gum binder*
- *Multiple-soil and multiple-part applications:* Emulsions can clean many different soils on ferrous and nonferrous parts that must go through one cleaning stage. The petroleum residue tends to protect ferrous metals from short-term rust, and it protects nonferrous parts from oxidation. Compromises will still be required in deciding what solution to use to clean off the emulsion residue.
- *Longevity:* Emulsions can be reclaimed and reused for many cleaning charges. Oils separate and can be decanted off, whereas other contaminants would require separate filtration. Emulsions contain other agents that may be removed in a reclamation process. (Emulsion suppliers can provide information about how to ensure proper regeneration.)

The hydrocarbon solvents in emulsion cleaners are generally safe for use on all metals and plastics. However, some rubbers and synthetic materials may absorb the hydrocarbon and become swollen, which can cause problems if they are being used as seals. Also, the solvent may attack and break down some types of rubber.

Emulsion Cleaning Process

Emulsion cleaners leave an oil-like residue on parts, and very often this is unacceptable to the next process, or the appearance is unacceptable if cleaning is the final process. The emulsion is usually followed with an alkaline detergent wash to remove the last traces of contaminants. Then a plain or deionized water rinse may be required to remove the alkaline. If parts must come out of the system dry, then an ambient or heated air drier must be included. Thus, many emulsion cleaning systems have four stages, which will be discussed below.

Concerns and Limitations

Oil-like Residue. If the oil-like residue is not desired for protection or is not compatible with the next process, it usually can be washed off with an alkaline detergent. Parts that cannot be thoroughly rinsed, such as sintered powdered metal and parts with blind holes, should not be cleaned with emulsion cleaning. On parts that will be plated or painted, it must be ensured that all of the emulsion has been removed, because emulsion can contaminate a plating line or prevent paint adhesion.

Safety. Heat aids the cleaning and drying process, but because emulsions are distilled from petroleum, they have a flash point and are potentially volatile. Depending on the emulsion, these flash points range from 40 to 99 °C (100 to 210 °F). Operating temperatures should be kept 15 °C (30 °F) below the flash point. (Some manufacturers indicate that it is safe to operate within 8 to 10 °C, or 15 to 20 °F, of the flash point.) The margin of safety may be determined by the process control capability of the equipment.

Volatile organic compounds (VOC) are emitted from the emulsion, particularly when it is heated, so adequate ventilation is vital. Depending on the type and volume of solvent discharge, the vent may need carbon absorption or scrubbers. In either case, the process may require a permit from the local air quality management authority.

Spray. Most emulsions should not be sprayed because spraying tends to atomize the solvent phase, which is highly susceptible to "flash." However, emulsions with flash points around 95 °C (200 °F) and used with higher water content can be sprayed in equipment with proper safety controls. These include close temperature control and possibly a backup temperature sensor, extra ventilation, and explosion-proof wiring.

Heat Source. Open fire gas burners should not be used. Steam heat is safest. Electric immersion heaters can be used safely with the proper solution level and electric spark controls.

Drying. Emulsions are generally slow-drying solutions because of the petroleum base. Heating the solution will aid drying, but temperature often needs to be held down due to safety concerns. Ambient air blowoffs are effective only if the air nozzle is very close to the part and is directed into any cavity. This can work with a manual air gun or proper setup on a conveyor belt. It generally does not work for batch processing. Heated air blowoff dryers will work, but caution must be taken to keep the system temperature 15 °C (30 °F) below the flash point.

Superfund Amendments and Reauthorization Act (SARA). Depending on the solvent base and concentration, the emulsion process may need to be reported to the Environmental Protection Agency under the terms of SARA, Title III.

Process Parameters

Process Selection. Determining the most appropriate cleaning method for a given application requires a thorough analysis of the manufacturing process, including:

- Part conformation
- Dirt to be cleaned
- Volume of parts
- Batch size
- Materials handling
- Process before cleaning
- Process following cleaning
- Cleanliness specifications
- Current method
- Budget
- Process limitations (e.g., time or chemistry constraints)

This information will guide the user to the balance of chemistry, method, and process parameters that will provide the proper cleanliness most economically.

Immersion Cleaning

Immersion is the cleaning method most widely used with emulsions, because of the solvent content required and because it provides full exposure of the part to the cleaning agent. Obviously, this method requires a tank large enough to contain the part or batch of parts and enough emulsion for complete immersion. It may be economical to clean small parts with this method, but for even small volumes of very large parts, the cost of thousands of gallons of emulsion may be prohibitive.

Processing Variables

Temperature. Although significant, bath temperature is less important in emulsion cleaning than in alkaline detergent washing. The dispersed oil (solvent) phase can accomplish much of its cleaning at ambient temperature. Higher temperatures are required for high-melting greases, buffing compounds, and waxes. The maximum safe operating temperature must be kept 8 to 15 °C (15 to 30 °F) below the flash point.

Agitation. Some of the oil-based soils can be cleaned in stagnant immersion. However, to ensure full coverage and increase effectiveness, the bath should be mechanically agitated. This can be accomplished with a recirculating "turbulating" pump, mechanical stirring, or air injection. Agitation helps to flush contaminants away from the part surface, allowing the cleaner to attack the next layer.

Ultrasonic energy is another form of agitation that can significantly improve immersion cleaning efficiency and effectiveness. Energy waves go through the solution at frequencies up to 50 kHz, creating millions of tiny bubbles on the part surface that then implode, creating a scrubbing action. Ultrasonics are particularly helpful in cleaning small-diameter or blind holes.

Concentration. In immersion, emulsions are usually used in concentrations of 20 to 30%. However, concentration is not a critical factor, as shown in Table 3. The capacity for dissolving soil increases proportionally with the concentration (volume) of the emulsion, but the solubilizing rates are not similarly affected by an increase in concentration. Some soils do react to varied concentrations, as shown in Fig. 1.

Table 3 Operating conditions for emulsion cleaners

Classification of cleaner	Concentration, %	Operating temperature		Time, min
		°C	°F	
Immersion systems				
General-purpose	5-15	10-71	50-160	2-8
Unstable single-phase[(a)]	10	21	70	1-10
Kerosine-based[(b)]	15-25[(b)]	21	70	2-10
Diphase, heavy-duty	15-25	21-54	70-130	2-10
Emulsifiable solvent	100	21-60	70-140	-2
Spray systems				
General-purpose	1-5	10-71	50-160	-3
General-purpose	2-5	10-77	50-170	-3
Light cleaning	1-2	10-71	50-160	1-3

(a) Requires vigorous agitation.

(b) Water-in-solvent emulsion, 15 to 25% water in kerosine

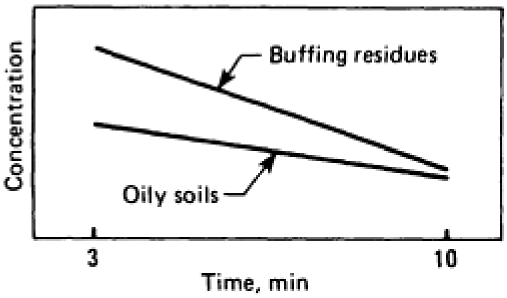

Fig. 1 Approximate relationship of time and concentration for emulsion cleaners used to remove two different soils

Emulsion cleanliness may affect cleaning effectiveness, which would relate to the concentration of the cleaning agent. If smut is seen on parts, then the emulsion is saturated with dirt and can absorb no more soils. To some extent, more emulsion can be added. Then the bath must be regenerated or replaced.

Time/Exposure. Generally an emulsion can accomplish its cleaning in 30 sec to 5 min. If cleaning requires much more time, then it is likely that the wrong emulsion was used or that immersion emulsion is not the proper cleaning method for the application. The length of time can be significantly altered by increasing the heat or changing or increasing the agitation. (Some typical process cycles are shown in Table 4.) Difficult applications may be accomplished with a combination of soak and spray rather than extended soaking time.

Table 4 Cycles for immersion and spray emulsion cleaning

Process sequence	Cycle time, min			
	Easy cleaning[a]		Difficult cleaning[b]	
	Immersion[c]	Spray[d]	Immersion[e]	Spray[f]
Clean[g]	2-4	-1	4-10	1-2
Rinse[h]	$\frac{1}{4}$ -	$\frac{1}{4}$ -	-	-
Rinse[i]	-1	-1	-1	-1

(a) Removing cutting oils and chips from machined surfaces, shop dirt and oil from sheet metals, and drawing compounds from automotive trim.

(b) Removing embedded buffing compounds, impregnated carbonized oils from cast iron motor blocks, and quenching oil from heat treated forgings.

(c) Concentration of cleaner, 1.5 to 6 vol%.

(d) Concentration, 0.6 to 1.5 vol%.

(e) Concentration, 3 to 9 vol%.

(f) Concentration, 0.75 to 1.5 vol%.

(g) 10 to 82 °C (50 to 180 °F).

(h) Unheated rinse.

(i) 54 to 71 °C (130 to 160 °F).

(j) 10 to 71 °C (50 to 160 °F)

Secondary Cleaning

Very often, emulsion cleaning is followed with an alkaline detergent wash, a secondary emulsion cleaning (usually at a lower concentration), or a water rinse. This step cleans off the emulsion residue and any particle contaminants not flushed away in the primary cleaning stage.

A detergent wash is used for secondary cleaning when all emulsion must be removed. This is generally run hot at 50 to 80 °C (120 to 180 °F), with mechanical action. Steel parts still need some rust inhibiting.

A final rinse is almost always used to flush off dirt that remains or has been redeposited since the primary or secondary cleaning. Some emulsions can be flushed off with plain water. In either case, the rinse water should be hot. Heat speeds the process and keeps the parts hot to aid drying. For applications in which absolutely no surface residue can be tolerated, deionized water must be used. Plain tap water contains salts that may adversely affect subsequent processes such as anodizing.

Spray Cleaning

Spray cleaning provides the advantages of power impingement, continuous flushing, and no redeposition of contaminants. The mechanical action of the spray tends to cut into soils to help break them away. The continuous flushing exposes the next dirt layer, allowing the emulsion to work through even heavy buildup quickly. The spray solution can be filtered in series with the wash pump prior to recirculating over parts. The rest of the contaminants are contained in the solution tank below the wash cabinet. Thus, it is possible to get an acceptably clean part in a single-stage spray machine, whereas this is unlikely in a single-stage immersion system.

The main drawback to spraying an emulsion is the increased exposure to VOC. Spraying releases more of the solvent to air and requires significantly more ventilation than an immersion application. In addition, like immersion, spray emulsion leaves an oil-like residue. If this is unacceptable, then subsequent alkaline wash and rinse stages are required, as discussed in the section "Immersion Cleaning" in this article.

Spraying can be done via two methods:

- *Manual spray/flush* over large parts in a vented tank at low pressure (only enough to deliver the

emulsion to the work, approximately 35 kPa, or 5 psi). With the operator at the point of contact, there is still potential exposure, depending on the particular emulsion and the temperature. Fewer vapors are emitted at lower temperatures.

- *By machine,* either in-line or cabinet, usually at 100 to 700 kPa (15 to 100 psi). These pressures atomize the emulsion, which increases the flash potential, particularly at normal operating temperatures of 60 to 70 °C (140 to 160 °F). Explosion-proof cabinets and electrical controls should be critically analyzed before spray emulsion is attempted.

For very large parts, an emulsion can be flushed on manually at high concentrations, then rinsed off with a power spray.

Processing Variables

Temperature. Some cleaning is accomplished at ambient temperature, but spray emulsion is more efficient and effective at elevated temperatures. Temperatures should be kept 15 to 20 °C (25 to 40 °F) below the flash point.

Agitation. The mechanical power of spray significantly reduces cleaning time and increases the ability to flush out cavities. Spray pressure should be kept to the minimum required. If pressures greater than 515 kPa (75 psi) are required to accomplish cleaning, a different process may be more appropriate.

Concentration. For spray emulsion, emulsion cleaners are typically used in concentrations of 1 to 5% (Table 3) because the spray adds power and exposure speed. These concentrations, 85% less than those used for immersion, make spray emulsion a very economical process. Also, a low volume of emulsion (diluted in 95 to 99% water) does reduce the risk of VOC exposure and flash, and it results in less residue on the parts. This is a second reason that spray emulsion can sometimes be used without secondary cleaning.

Time. Power spray in-line or cabinet equipment reduces cleaning time up to 75% compared to the time required for immersion, even at lower concentrations (Table 4).

Emulsion Cleaners

Emulsion cleaners are broadly classified into four groups on the basis of stability:

- *A stable single phase, or permanent, emulsion* is one in which the discontinuous phase is dispersed throughout the continuous phase. This requires no more agitation to maintain a uniform dispersion than that provided by thermal gradients and the motion of the work being cleaned.
- *An unstable single phase emulsion* has a uniformly dispersed phase that tends to separate and form a solvent layer. Solvents with specific gravity of less than 1.0 form a top layer, and those with a specific gravity greater than 1.0 form a bottom layer. These cleaners require moderate to considerable agitation to maintain complete dispersion.
- *A diphase, multiphase, or floating layer emulsion* forms two layers in the cleaning tank and is used in this separated condition. Work is immersed through the solvent-rich surface layer into the water-rich lower layer, permitting both cleaning phases to come in contact with the surfaces to be cleaned. When used in a spray system, a diphase cleaner resembles an unstable single phase cleaner, because the solvent and water phases are mixed in the pumping action.
- *An emulsifiable-solvent system* is one in which the as-received, undiluted solvent is applied to the surface to be cleaned by hand or by use of a dip tank. It is followed by a water rinse that emulsifies and removes the solvent and soil.

Because *stability* is a relative term, the definitions of these four types of cleaners can overlap. The advantages and disadvantages of the first three types are as follows.

Stable emulsion cleaners are the most economical. They are practical for removing light shop soils, especially in applications where in-plant rust protection is required. These cleaners contain hydrocarbon solvents such as kerosine, which can dissolve and clean light soils. Two to three weeks of rust protection can be expected for ferrous metal parts cleaned by a properly constituted stable cleaner. Such a cleaner maintains an emulsion with water for many hours, requiring a minimum amount of agitation.

A 2% stable emulsion spray rinse often follows alkaline cleaning. This procedure has provided rust protection for as long as three to four weeks in storage areas where humidity is not excessive and unusual changes in temperature are not encountered.

Although 75 °C (170 °F) is the recommended maximum operating temperature, stable emulsions can be operated safely at temperatures up to 80 °C (180 °F). The higher temperatures, sometimes advantageous when rapid drying of the work is desired, increase evaporation rates and may cause polymerization of emulsion and the formation of a varnish-like film that is difficult to remove from work. When large quantities of parts are cleaned in a continuous production flow in automatic spray washers, stable emulsion cleaners are preferred because of their lower initial cost and ease of maintenance.

Stable emulsion cleaners do have disadvantages. Their efficiency is low in removing hydrocarbon soils if more than 10% of the soil has a solidification temperature within 10 °F of the temperature of the emulsion. In hard water, stable emulsions form insoluble precipitates that may plug drains and increase maintenance.

Unstable emulsion cleaners, although higher in cost than stable emulsion cleaners, perform more efficiently in removing heavy shop soils, such as oil-based rust preventatives and lubricants used in stamping and extruding. The hydrocarbon fraction of unstable emulsion cleaners makes more intimate contact with the work surface, permitting greater action of the solvent on soil. Unstable emulsions are also successful in hard waters that cause stable emulsions to break down.

Unstable emulsions, as well as the equipment required for using them, are less costly than diphase emulsions. However, their cleaning power approaches that of diphase systems, and they are widely used for the removal of heavy hydrocarbon soils. Phosphates may be added to hard waters to increase the efficiency of unstable emulsions.

The concentration of an unstable emulsion can generally be determined by gravimetric separation. Operation above or below the preferred concentration range lowers cleaning efficiency or causes excessive cleaner consumption. The operating temperature of an unstable emulsion is critical and must not exceed 70 °C (160 °F). The usual range is 63 to 68 °C (145 to 155 °F).

Diphase emulsion cleaners are used for removing the most difficult hydrocarbon soils, such as lapping compounds, buffing compounds, and oxidized oils. They provide a higher degree of cleanliness than can be obtained with stable or unstable emulsions. The flash points of diphase emulsion cleaners cover a wide range, permitting operating temperatures up to 80 °C (180 °F). The monomolecular layer of oil that remains after diphase cleaning provides good rust protection.

In diphase cleaning, the solvent in the bottom phase is very powerful and a 100% concentrated product. It is not an emulsion with water. Hence, these cleaners provide better cleaning than regular emulsion cleaners.

Diphase cleaners are most frequently used in dip tanks. However, with specially designed equipment or the addition of emulsifiers to retard separation into solvent and water layers, these cleaners can be used in recirculating spray washers. Diphase cleaners also have disadvantages:

- They are adversely affected by hard water, and preconditioning the water with phosphates is unsuccessful.
- They cost more than stable or unstable cleaners.
- Vaporization of hydrocarbon layers requires more ventilation than is needed for stable and unstable cleaners to avoid fire and health hazards.
- No easy test is available for determining diphase cleaner concentration.

Selecting an Emulsion System

Factors that influence the choice of a stable, unstable, or diphase emulsion system include:

- Type of soil to be removed
- Size and quantity of work
- Need for rust protection
- Water condition
- Cleaning sequence (especially if emulsion cleaning is preceded by alkaline cleaning)
- Cost

Production applications for the principal emulsion cleaners and pertinent operating data are given in Table 2.

Analysis

Analysis of the more stable emulsion cleaners can be made at the tank. However, distillation techniques are used for the unstable and diphase cleaners, requiring analysis in a laboratory. To obtain a good representative sampling, samples should be taken from various locations. In an immersion installation, samples should be taken from tanks with a glass tube. In a spray installation, samples should be taken from the jets after the washer has been in operation for some time, because soluble oils become more emulsified as spraying continues. One simple and rapid method of analysis is:

1. Place approximately 90 to 95 mL of emulsion in a 100 mL glass-stoppered graduated cylinder.
2. Measure and record the actual amount of sample.
3. Cautiously add 5 mL of sulfuric acid.
4. Place a stopper on the cylinder and shake until the emulsion begins to break.
5. Allow the emulsion to cool to 20 °C (70 °F) and separate completely.
6. Measure and record the amount of separated emulsifiable material or oil. The volume percentage of oil in the emulsion is the volume of soluble oil divided by the volume of original sample, multiplied by 100.

Composition

Stable, unstable, diphase, and other emulsion cleaners cover a wide range of solvent and emulsifier compositions. The solvent is generally of petroleum origin and may be heterocyclic (Mpyrol), naphthenic, aromatic, or of hydrocarbon nature (kerosine).

Solvents are available with boiling points of 60 to 260 °C (140 to 500 °F) and flash points ranging from room temperature to above 95 °C (200 °F). Because the solubility factor increases as the molecular weight of the solvent approaches that of water, low-to-medium molecular weight solvents are usually more effective in removing soils. However, fire hazards and evaporation losses increase as boiling and flash points decrease.

Emulsifiers include:

- Nonionic polyethers and high-molecular-weight sodium or amine soaps of fatty acids
- Amine salts of alkyl aryl sulfonates (anionic)
- Fatty acid esters of polyglycerides
- Glycerols
- Polyalcohols

Cationic ethoxylated long-chain amines and their salts are also used in emulsions.

Emulsifiers must have some solubility in the solvent phase. When solubility is low, it can be increased by adding a coupling agent (hydrotrope), such as a higher-molecular-weight alcohol, ester, or ether. These additives are soluble in oil and water.

Emulsion Types and Stability. The stability of emulsion cleaners depends on the properties of emulsifying agents that are capable of causing oil and water to mix uniformly. Because oil and water do not mix naturally, an oil-in-water mixture that does not contain an emulsifying agent or dispersant requires constant mechanical agitation to prevent the oil and water from separating into two layers. Emulsifying agents can be placed in two categories:

- Those that promote the formation of solvent-in-water emulsions, in which water constitutes the continuous phase and solvent constitutes the discontinuous phase
- Those that promote the formation of water-in-solvent emulsions, in which water is the dispersed discontinuous phase

Equipment for Immersion Systems

Tanks for cleaning solution should be constructed of hot-rolled steel. Depending on tank capacity , steel gage requirements are as follows:

- Up to 380 L (100 gal), 12 gage
- 380 to 1890 L (100 to 500 gal), 10 gage
- Over 1890 L (500 gal), 7 gage

All seams should be penetration welded and dye checked for leaks. Channel or angle iron reinforcements should be welded wherever they are required for strength or rigidity. All tanks should be built up on a frame so they can be insulated underneath and so they can be picked up. Tanks should have a minimum of 25 mm (1 in.) of insulation with light-gage, cold-rolled steel cover panels for energy efficiency.

Tanks can be heated with steam or immersion electric elements. Gas burners are not recommended because of potential flash. Where steam is used, coils are preferred to an open line. Condensate from an open line will dilute the solution. Coils must, of course, be fabricated of a substance compatible with the solution to be heated. Iron or steel tubing is recommended for alkaline solutions, while acid-resistant metals, graphite, and impervious carbon are recommended for acidic solutions. The steam coil length depends on the type of tank, the coil diameter (not less than 1 in.), the steam pressure available, and the speed with which the solution is expected to heat to optimum temperature. Commercially available plate coils are most efficient.

Electricity as a tank heating method is most efficiently applied by means of electrical resistance elements, encased in protective jackets and immersed within the solution. Where possible, the heat-transmitting medium should be readily removable from the tank. It should not be located on the tank bottom where scale or sludge can reduce its efficiency or where it could be damaged when sludge is shoveled out.

Emulsion solutions with $pH > 8$ will provide rust protection so the wash tanks can be carbon steel. Alkaline wash tanks can also be carbon steel. Rinse tanks should be stainless steel.

Provision of agitation is important. Agitation keeps bringing fresh solution into contact with the work and introduces a degree of physical force to supplement chemical activity. The result is faster cleaning.

Draining is an important consideration. An overflow surface drain permits surface grease and oil to be skimmed off, preventing rapid solution contamination. A bottom drain is also necessary, to discard solution.

Equipment for Spray Systems

Spray Washing Machines.

Where metal is washed in volume on an assembly line, spray application of the detergent solution in an automatic or semiautomatic spray washing machine is the faster possible cleaning method. It combines the mechanical force of spray jets with the chemical and physical action of the cleaning solution.

Spray washing machines are usually engineered to a particular installation. Part, size, volume, time necessary to clean and rinse, and subsequent operations are factors that influence individual machine design. Many machines provide for more than one washing stage, as well as for rinsing and forced air drying. They can be batch cabinet style or in-line conveyor. The proper type is the one that matches the materials handling and product flow of the rest of the manufacturing process.

Work is transported through the various spray washer stages on a flat conveyor belt, in a screwlike drum that keeps work moving forward, or suspended from an overhead monorail. Spray machines deliver a solution through fixed nozzles, to impinge on work from all angles as it passes through. Soiled work is typically exposed to a detergent spray solution for about one minute, sometimes less.

For batch washers, the sprays can be either fixed or moving. Most operations have fixed sprays with a rotary table turning relatively slowly (usually 2 to 10 rpm) through the sprays to ensure overall cleaning. The use of programmable logic controllers in batch cabinet spray washers can allow multistage processing in a single cabinet. The key is to keep solutions separate and develop a system to prevent cross-contamination. This includes using separate spray headers or having a way to evacuate one solution before second-stage processing. If a dry stage is required, the cabinet must be designed so that the solution tanks can be closed off from the spray cabinet; otherwise, moisture will continue to flow into the cabinet. Parts will not dry in a wet cabinet.

Solution tanks should be sized to hold a volume of two to three times the pump flow rate. The tank bottom should be sloped for easier cleanout, and the entire tank should be insulated for efficiency and operator safety. The pump intake should be above the bottom of the tank and should be equipped with a screen to prevent the intake of sediment and chips. In handling unstable emulsions, pump intakes should be located at the interfaces of oil and water. In some applications, more than one intake is necessary. The reservoir tank is usually constructed of low-carbon steel. The thickness of the steel depends on the size of the equipment, but it should not be less than 10 gage.

Piping System.

For effective spray cleaning, nozzle pressure should be at least 105 kPa (15 psi) to provide adequate mechanical action at the surface of the workpiece. Higher pressures can be used, but they tend to atomize more of the emulsion, which increases the risk of flash. The nozzles should be readily accessible and removable for cleaning. To prevent overspraying, end nozzles in the cleaning and rinsing chambers should be deflected inward approximately 30°. All nozzles should be staggered to ensure complete coverage of the workpiece.

Conveyor.

The use of a variable speed conveyor should be considered in the initial installation to permit some latitude in the retention time of parts in the cleaning cycle.

Heating.

Steam is widely used as a source of heat in spray cleaning units. Gas immersion burners are not recommended, because they prevent a fire hazard. The capacity of the steam coils or plates should be sufficient to heat the solution to operating temperature within 30 min to 1 h.

Air Drying.

Forced air is used to dry parts after cleaning and rinsing. It may be heated or kept at room temperature. Heated air has three advantages:

- Drying is hastened.
- Floor space is conserved.
- Less air is required for the same number of parts.

Safety

The potential exposure and flash of solvent emulsions has been mentioned several times in this article. This is not to say that these solutions are unsafe, only that they are safe when used properly, particularly those recently developed

formulations with flash points above 95 °C (200 °F). Keeping the heat 8 to 20 °C (15 to 40 °F) below the flash point and using steam or electric heat are the main factors in reducing flash potential. Wiring used in the vicinity of emulsion cleaning operations should be explosion-resistant for immersion systems, explosion-proof for spray systems.

Emulsions are not highly toxic or carcinogenic. (Those currently sold in the market do not use a chlorinated solvent base.) Generally, manufacturers recommend that operators wear a minimum of rubber gloves and apron. Normal eye protection is suggested, but most emulsions do not require full face shields.

The type of proper ventilation varies with different emulsions. Some require special permits or exhaust stack controls.

Waste Disposal

One of the advantages in using emulsion cleaners is that they can be reused many times. However, when it is time to change solutions, disposal of spent emulsions is a problem. Most emulsions have an organic/oil base, and most local water authorities have reduced the acceptable concentration of oil permitted for sewer discharge well below 100 ppm.

Concentrated emulsions should be removed by an authorized hazardous waste hauler and incinerated in a fuels blending program. Most emulsified solutions separate when cooled, given enough settling time. The oils can be skimmed off, and the emulsion concentrate will float on the water so that it can be separated. The water portion may be neutralized and the particles filtered out. This may be able to be discharged into the sewer after checking with local authorities. If that is not permitted, it could perhaps be processed with an ultrafilter, depending on the particular emulsion and contaminants. In some areas, the water may be evaporated off to concentrate the volume for proper disposal.

Information on emulsion cleaning of specific metals and alloys can be found in the Sections "Surface Engineering of Irons and Steels" and "Surface Engineering of Nonferrous Metals" in this Volume.

Molten Salt Bath Cleaning

James C. Malloy, Kolene Corporation

Introduction

MOLTEN SALT BATHS are anhydrous, fused chemical baths used at elevated temperatures for a variety of industrial cleaning applications. Among the more common uses of these baths include:

- Removal of organic polymers and coatings
- Dissolution of sand, ceramic, and glassy materials
- Stripping of plasma carbide coatings

In addition, molten salt baths may be used to pretreat cast iron surfaces before brazing and bonding operations.

Molten salt baths for cleaning applications are chemically active or reactive fluids with unique process capabilities. They are quite distinct from other molten salt compositions that are used for simple heat transfer or heat treatment applications. Equipment requirements for successful use of these processes also differ from molten salt heat transfer or heat treatment equipment. Larger volumes of insoluble cleaning byproducts are usually formed that must be effectively and safely collected and removed from the baths.

Cleaning salt baths are formulated from a variety of inorganic chemical compounds. Among the more common ingredients are alkali hydroxides, alkali nitrates and nitrites, alkali chlorides, and alkali fluorides. By adjusting the ratios of the various ingredients, a wide range of melting points, operating temperature ranges, chemical reactivity, and other parameters can be obtained. As a whole, they offer combinations of reactivity, solvency, and speed unavailable in any other cleaning medium. The chemistry involved during various cleaning applications ranges from simple dissolution of contaminants to more complex reactions involving the thermochemical oxidation of organics and the electrolysis of molten salts.

Applications

As with any cleaning process, molten salt baths are used to remove some type of unwanted surface soil, contamination, coating, or other substance from a substrate to allow further processing or reclamation of the substrate. Due to the relatively high temperatures involved with molten salt processing (205 to 650 °C, or 400 to 1200 °F), substrates to be cleaned are restricted to those materials that are compatible with the operating temperatures of the various processes. Because these baths are also chemically active, the substrate must also be chemically compatible with the various molten salt systems. While most metals that are temperature compatible will also be chemically compatible, there are notable exceptions to this general statement. For example, magnesium and its alloys must not be processed in oxidizing salt baths because of the potent oxidation-reduction reaction that may occur at elevated temperatures. This would result in ignition of the metal and destruction of the component.

Paint stripping in molten salts is a simple immersion process and is applicable to a wide variety of organic coatings, including solvent-based, water-borne, cured powders and high-performance coatings such as fluorinated polymers. Depending on the type and thickness of the paint coating to be removed, the stripping reaction time can vary from several seconds to a few minutes. The operating temperature depends on the specific process used, but it normally falls in the range of 290 to 480 °C (550 to 900 °F). The lower-temperature processes are generally used to reclaim reject-coated products and on temperature-sensitive materials and components. The higher-temperature processes are used for stripping more robust components.

The higher temperatures are also used for "maintenance" paint stripping of hooks, racks, carriers, and similar fixtures that serve as extensions or add-ons to the conveyor system that carries components to be painted through the paint line. Hooks and racks generally hang down from an overhead conveyor system, while carriers generally "ride" on a floor track or floor conveyor. The components to be coated are affixed to the hooks, racks, and so on and are transported through the various coating operations such as surface pretreatment, coating area, and curing ovens. At the end of the line, the finished parts are removed and "raw" unpainted parts are placed on the fixtures. Because the hooks and racks may pass through the coating line numerous times between stripping operations, they may receive numerous layers of coatings.

Stripping is accomplished by a thermochemical reaction between the oxidizing molten salt and the organic portion of the paint. Alkali nitrate, usually present in an oxidizing salt bath, donates the oxygen required to allow the organic material to be completely oxidized to carbon dioxide while immersed in the bath:

$$C + 2NO_3^- \rightarrow CO_2 + 2NO_2^- \qquad \textbf{(Eq 1)}$$

During the course of the reaction, nitrate is chemically reduced to nitrite. Contact with atmospheric oxygen then reoxidizes the nitrite back to nitrate, helping to regenerate the bath:

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^- \qquad \textbf{(Eq 2)}$$

Alkali carbonates are formed as a result of the stripping from the reaction between carbon dioxide and caustic alkalis present in the bath:

$$CO_2 + OH^- \rightarrow CO_3^{2-} + H_2O\uparrow \qquad \textbf{(Eq 3)}$$

The alkali carbonates continue to increase in the bath until the bath becomes saturated with them. After saturation has been reached, the bath continues to react with any additional organics introduced. The additional carbonates, however, begin to precipitate out of solution in the form of sludge. Molten salt stripping equipment typically is designed with collection devices into which the sludge, which is denser than the host salt, settles for subsequent removal from the bath. Along with the alkali carbonates, the sludges may also contain insoluble inorganic pigments, fillers and so on, that were present in the original paints that were stripped.

Upon removal from the molten salt, the components are rinsed in water to cool them and to remove the thin film of salt residue present on the components. Additional post-treatments, such as acid brightening, neutralizing, and so on, are also commonly used to prepare the components for recoating.

Polymer Removal. The removal of solidified synthetic polymer residues is another common use for oxidizing molten salts. Synthetic fiber production involves the use of intricate dies or spinnerets and associated components such as filter packs and distributor plates. The molten polymer (for example, nylon, polyester, or polypropylene) is extruded through the spinneret under pressure to form the fiber strand. It becomes necessary to disassemble and clean the packs and spinnerets when blockages are present or when production schedules dictate a "changeout" of the packs. The chemistry involved is the same as described above for paint stripping.

Great care must be taken when cleaning spinnerets because of their delicate hole geometries, low root-mean-square (rms) surface finishes, and high intrinsic value. To clean spinnerets and screens of polymeric material, the initial salt composition should be essentially neutral. Buildup of alkaline reaction products ultimately leads to some attack (pitting) of the workpieces and can cause an accumulation of undesirable ions (for example, chromate) in the salt. The spinneret with its solidified polymer residues is immersed in the cleaning bath and a polymer is quickly and completely removed via thermochemical oxidation, without harming the spinneret's properties.

Casting Cleaning. The cleaning of castings with molten salt processes is applicable to both investment castings (lost wax) and sand castings. Investment castings are processed in molten salt baths to remove residual external shell and to leach out preformed ceramic internal coring. Sand castings are processed to remove binder residues and burned-in core sand. Salt bath cleaning is usually used after preliminary cleaning operations such as shakeout and mechanical blasting.

Investment Castings. In the case of investment castings, a small amount of external shell is usually still present after mechanical cleaning operations. Salt bath processing is then used as a scavenger to remove these residues. Relying on the reaction between silica present in the shell and caustic alkalis in the salt bath, the silica is converted into an alkali silicate that is soluble in the bath:

$$SiO_2 + 2OH^- \rightarrow SiO_3^{2-} + H_2O \uparrow \quad \textbf{(Eq 4)}$$

Within the bath's normal operating temperature range of 480 to 650 °C (895 to 1200 °F), the water formed during the reaction is released from the bath as vapor and is visible as a mild effervescence on the bath surface. Inert shell and core constituents such as zircon or aluminosilicates simply slough off the casting as the silica is removed from the shell or core.

Sand castings are cleaned using a method similar to that used to clean investment castings. Again, the principal reaction is between silica (sand) and the alkalis present in the molten salt. When cleaning cast iron, however, the process is usually performed electrolytically.

Incorporating direct current into the molten salt cast iron cleaning process allows simultaneous removal of sand, surface graphite, and scale. The casting to be cleaned is normally subjected to an initial reducing (cathodic) cycle to dissolve sand and produce an oxide-free casting. This procedure not only produces a casting that is free from any sand contamination, but also greatly improves the machinability (and machine tool life) of the casting by removing the tough, hard surface scale. The scale reduction also helps to expose any sand particles that may have been masked by scale at the metal surface; the now-exposed sand is then dissolved by the bath (Fig. 1a and b). To prepare cast iron surfaces (either as-cast or machined) for subsequent brazing, babbitting, or other metal coating operations, the electrolytic process becomes somewhat more involved.

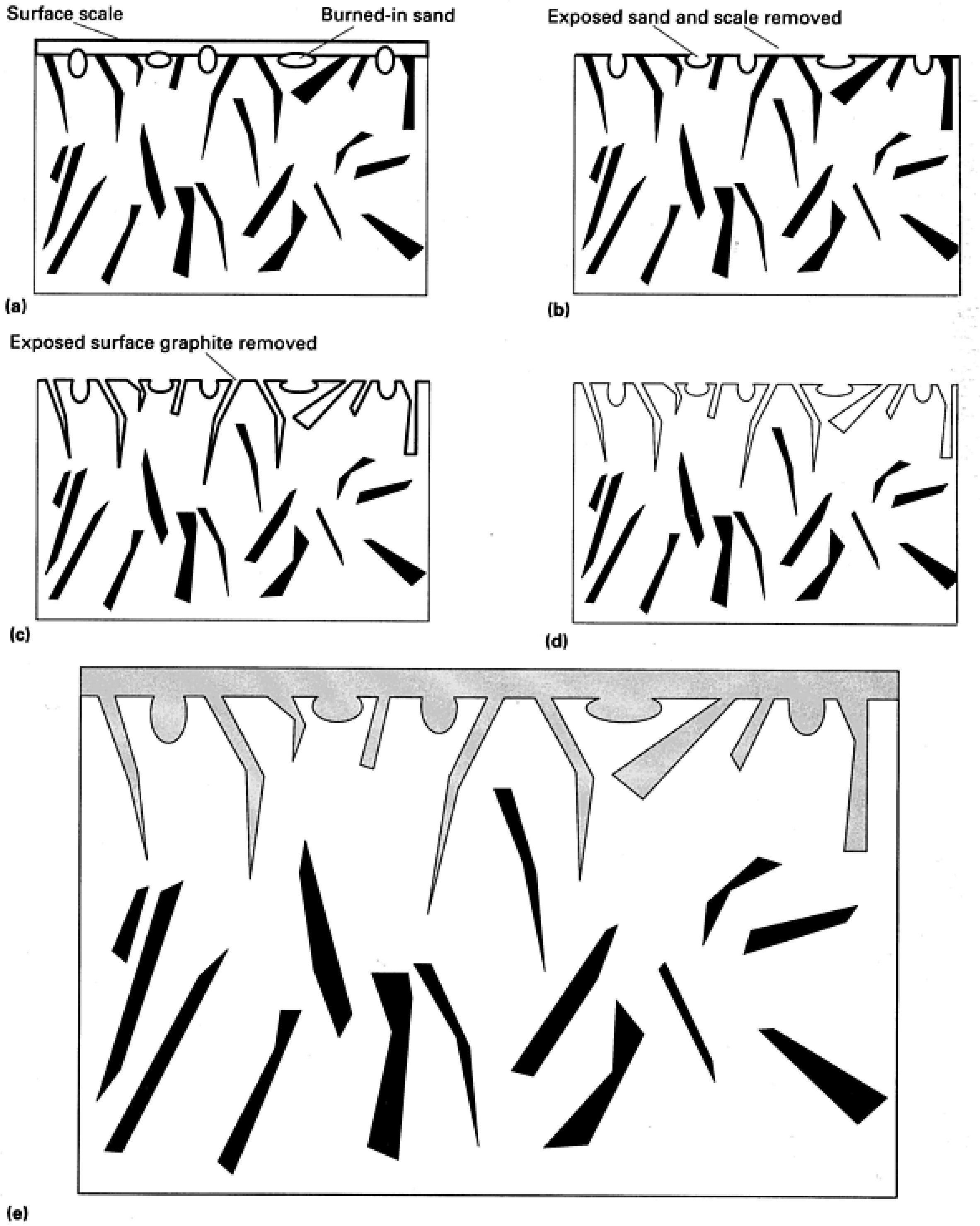

Fig. 1 Schematic cross section of the surface of a cast iron component as it is modified by cleaning in a molten salt bath. (a) As-cast. Note surface scale, burned-in core/mold sand particles, and flake graphite extending to surface. (b) After first reduction cycle. Exposed sand particles have been chemically dissolved, while the original casting oxide has been electrochemically reduced. The original flake graphite is unaffected and intact at this stage of processing. (c) After oxidation cycle. The original flake graphite has been electrochemically oxidized to carbon dioxide. The entire exposed cast surface is now covered with a very thin, uniform layer of iron oxide. (d) After second reduction cycle. The cast surface is now free of all original cast scale, sand inclusions, and exposed graphite flakes. The final reduction cycle also removes the thin layer of iron oxide that was formed during the oxidation cycle. (e) After brazing. The braze metal uniformly "wets" the surface of the metal and freely flows into the surface voids previously occupied by graphite flakes.

The initial cleaning cycle usually incorporates a reducing cycle to remove sand and surface scale as described above. The polarity of the direct current is then reversed, effectively electrolytically oxidizing the casting. This converts any exposed surface graphite to carbon dioxide (Fig. 1c). To remove the thin, uniform layer of iron oxide from the casting formed by the oxidizing treatment, the current is once again reversed to produce a final reducing cycle. This results in a scale-free, sand-free, graphite-free surface ready for coating or joining operations (Fig. 1d). When joined, the brazing alloy uniformly "wets" the metal surface and penetrates the voids previously occupied by the graphite flakes (Fig. 1e).

The amount of foreign material removed from a given casting will vary widely from application to application. In the case of investment castings, it will depend on the size of the casting, how much preliminary mechanical cleaning (e.g., shot blast) the casting receives prior to salt bath cleaning, and the geometry of the casting itself. It may range from as low as a fraction of an ounce to several pounds. Likewise, the amount of material removed from a sand casting will depend on the amount of burned-in mold and core sand that is present after mechanical shakeout. These amounts are somewhat more predictable and usually fall in the range of fractional ounces to a few ounces for a typical cast iron engine head or hydraulic valve body.

Glass Removal. Molten salts are an effective medium for removing both solidified glasses and glassy coatings from metals. They are commonly used for cleaning glass fiber production equipment, such as spinnerets and spinner disks, and removing the glassy lubricants commonly used in high-temperature forging operations. Reactions involved are analogous to those for sand removal (see the section "Sand Castings" in this article).

Plasma/Flame Spray Removal. Oxidizing molten salt baths are effective in removing a variety of flame spray or plasma coatings. It is necessary to strip these wear-resistant and protective coatings when jet-engine components are repaired or rebuilt, when tooling and jigs are cleaned during plasma coating, or whenever these tough coatings are not wanted.

The stripping reaction usually involves both the metallic and carbide portions of the coating. Soluble alkali salts are formed by the metallic constituent, while the carbide portion is oxidized to from carbon dioxide. In the case of chromium carbide, the net reaction products are alkali chromates and alkali carbonates. The simplified reaction is as follows:

$$\mathrm{CrC} + 5\mathrm{N}O_3^- + 4\mathrm{OH}^- \rightarrow \mathrm{Cr}O_4^{2-} + \mathrm{C}O_3^{2-} + 2\mathrm{H_2O} + 5\mathrm{N}O_2^- \quad \textbf{(Eq 5)}$$

Analogous reactions take place with tungsten carbide. Stripping rates are quite rapid, with typical stripping times of 15 to 30 min being common to remove a "full-thick" plasma coating. The actual coating thickness depends on the coating process but generally ranges from a few to several mils (0.001 to 0.015 in.). Removal of worn coatings during rework or overhaul requires correspondingly less time.

Salt Bath Equipment

Design Considerations. Basic design considerations for salt bath cleaning systems (see the article "Salt Bath Equipment" in *Heat Treating,* Volume 4 of the *ASM Handbook*) are similar to those of heat treatment salt bath furnaces. However, the actual process equipment is unique. Two main distinctions between heat treatment/heat transfer salts and cleaning salts are that the cleaning salts are chemically active and the byproduct generation in cleaning baths is potentially much greater. Both of these factors must be taken into account when designing and engineering appropriate salt bath equipment.

Basic design considerations such as throughput, heat capacity, and part geometries are similar to those for heat treating baths. Because the baths are chemically active, the materials of construction must be carefully selected. Materials commonly used for fabricating heat treatment transfer/heat salt bath equipment are generally not suitable as cleaning salt baths because of chemical interactions with the cleaning salts.

Heating systems for molten salt baths may be either electric or gas fired. Due to the generation and settling of reaction byproducts and their insulating effects, most heating designs use internal or immersion heating devices, as opposed to external heaters. (Certain higher-temperature cleaning processes, however, may require external heating systems to achieve good heating system longevity. Care must be taken when using outside heating, to prevent localized "hot spots" where reaction byproducts may accumulate and retard heat transfer in the salt bath furnace.)

Electric immersion heaters may be either resistance elements, enclosed in a tube or bayonet, or electrode configurations that rely on the conductivity and resistance of the molten salt itself to convert electrical energy to heat. Due to their higher energy efficiencies and simplified electrical circuits, resistance immersion elements are more commonly employed with cleaning salt bath equipment than are electrode-type heating systems. Resistance heaters also offer easier and safer start-up than electrode systems. Electrode systems require a molten pool of salt for electrical conduction. In a cold, solidified bath, this is formed by a "starting torch" or auxiliary resistance heater. Once an ample amount of salt has been melted, the auxiliary heater may be turned off and the main electrode system energized. Electrode systems also pose a potential safety hazard if a bath should partially "freeze over," forming an impermeable solid salt crust. The volume of a molten salt increases with increasing temperature, so if the electrode heating system is activated while the bath is crusted, the fluid or molten salt beneath the crust will attempt to expand against the crust. As the salt expands, its pressure increases until the crust ruptures. This sudden release of pressure may result in an eruption of the salt through the crust and possible injury of personnel and equipment.

Gas-fired immersion heating systems are very reliable and economical to use. Consisting of either an open-head or closed-head burner system, the ignited fuel mixture is drawn or forced through a burner tube immersed in the salt (Fig. 2).

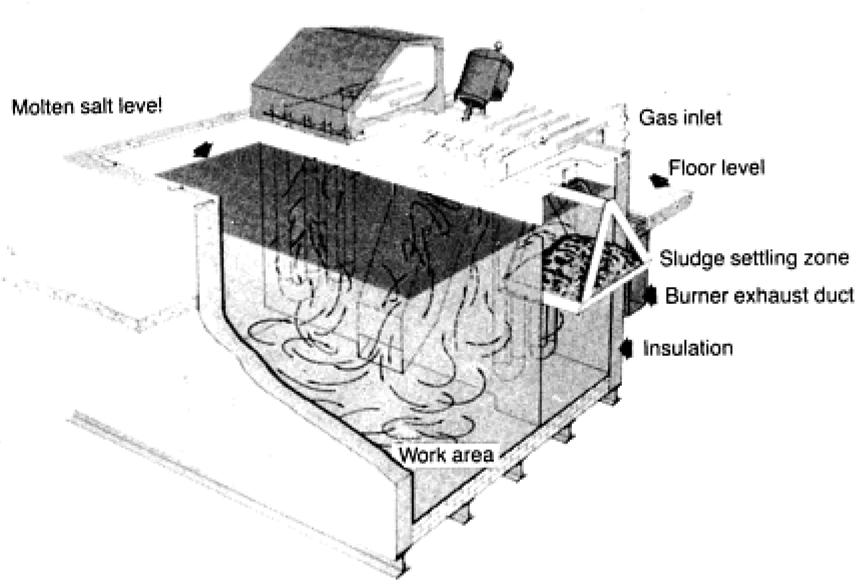

Fig. 2 Cutaway view of a salt bath furnace incorporating an agitated molten salt bath and a sludge settling zone

Byproduct Collection and Removal. Provisions must also be made for the effective collection of reaction byproducts formed during cleaning operations. In addition, subsequent removal of these byproducts from the bath must be accomplished in a convenient, safe, and efficient manner. Most cleaning baths do not require routine chemical monitoring, but rather rely on the removal of reaction byproducts and additions of fresh process chemicals to maintain proper chemical balance and performance. If the byproduct collection system is ineffective, or the removal of the collected byproducts is inconvenient or unsafe, this necessary routine maintenance function will not be performed. This will result in overall process degradation and will eventually necessitate the complete disposal of the spent molten salt and recharge with fresh product.

Molten salt bath processes require properly designed and engineered equipment for their safe operation. In most installations, it is highly desirable to have the salt bath furnace and its associated process tanks (quench water, rinse water, sludge, or byproduct discharge zone) situated under a common hood system (Fig. 3, 4). The ventilated hood, outfitted with observation windows, internal lighting, exhaust system, and so on, protects the operator from accidental contact with the molten salt. It also captures and exhausts the steam generated during the quenching and/or rinsing of hot workloads.

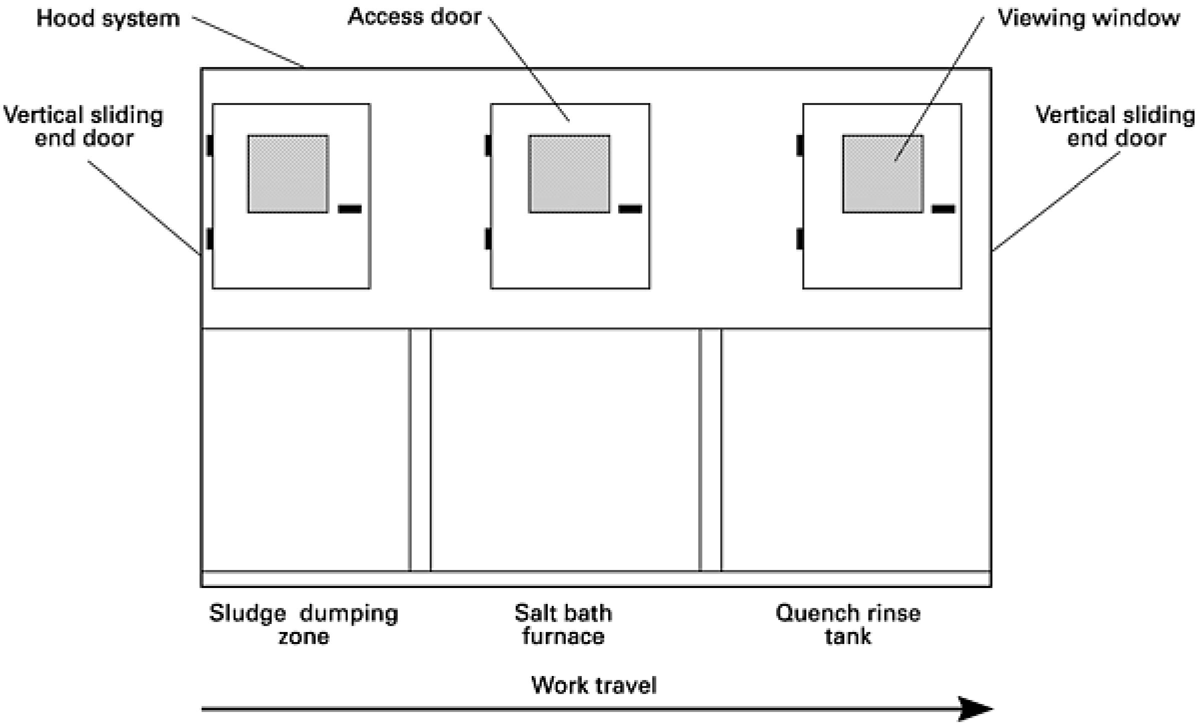

Fig. 3 Schematic of an enclosed molten salt bath cleaning line

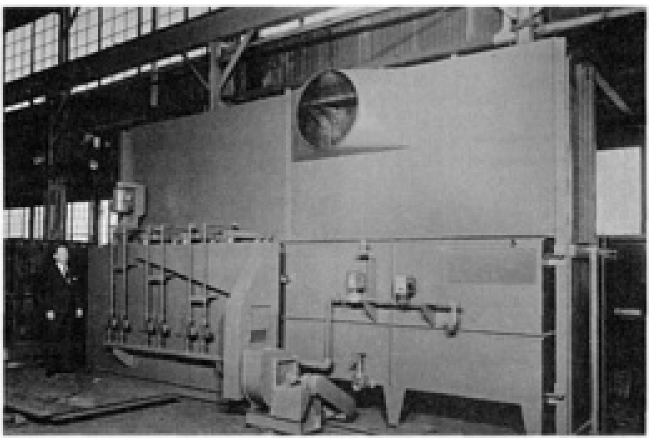

Fig. 4 Fused salt cleaning system that is completely enclosed by a hood to comply with Occupational Safety and Health Administration guidelines

Personnel Safety

One of the most important safety considerations with cleaning-type molten salts is properly designed equipment. As discussed in the section "Salt Bath Equipment" of this article, a common hood structure over the salt bath, quench and rinse tanks, and sludge removal zone forms an effective barrier between the operator and the process (Fig. 3, 4). Operators must have a thorough understanding of the process, receive adequate training, and comply with standard operating procedures and process user's guides.

The molten salt is both a thermal and a chemical hazard to the worker. As with any high-temperature molten process, the salt will burn human tissue. Because many of the compounds used in formulating these salts rely on caustic alkalis, contact with molten or dry salt also poses a risk of chemical burns. All operating personnel, along with plant safety and hygiene monitors, should be familiar with the proper handling procedures for these compounds and the appropriate

response procedures. This information is generally contained in the supplier's Material Safety Data Sheet for the specific process chemical being used.

Environmental Impact

Most cleaning salts are formulated from alkali metal salts, as previously described. Some of these ingredients may be highly alkaline and corrosive. Process chemicals formulated for salt bath cleaning applications do not contain restricted or heavy metals in their "fresh" condition.

The byproducts or sludge that must be removed from an operating bath will contain the materials that were processed in it. For example, byproducts formed from paint stripping applications will contain heavy metals if the paints stripped in them contained heavy metals. Likewise, byproducts formed during the stripping of chromium carbide will contain significant amounts of hexavalent chromium (Cr^{6+}) due to the reaction between an oxidizing molten salt and the chromium content in the original coating being removed.

Once byproducts are removed from a bath, they solidify upon cooling into a dense solid. Most sludges are freely soluble in water, allowing subsequent treatment operations to be readily performed. In the absence of heavy or restricted metals, the pH level is often the only adjustment that is necessary. This is usually accomplished by the controlled addition of a mineral acid such as sulfuric acid. In facilities where other metal finishing operations are performed, the alkaline values of the sludge solution are often used to adjust the pH level of acidic streams from other processes. When heavy metals are present in the sludge, more involved waste treatment procedures are necessary. These commonly include reduction of oxidized metal species (for example, the reduction of hexavalent chromium to trivalent chromium, with subsequent pH adjustment, metals precipitation, and filtration/separation of solids). Numerous proprietary and nonproprietary approaches may be used for in-plant treatment of sludge. Sludges may also be disposed of off-site in an approved disposal facility. Representative samples would require testing for corrosivity, restricted metals, and so on, as dictated by applicable regulations, to determine their ultimate disposal classification.

Ultrasonic Cleaning

Jeff Hancock, Blue Wave Ultrasonics

Introduction

ULTRASONIC CLEANING involves the use of high-frequency sound waves (above the upper range of human hearing, or about 18 kHz) to remove a variety of contaminants from parts immersed in aqueous media. The contaminants can be dirt, oil, grease, buffing/polishing compounds, and mold release agents, just to name a few. Materials that can be cleaned include metals, glass, ceramics, and so on. Ultrasonic agitation can be used with a variety of cleaning agents; detailed information about these agents is available in the other articles on surface cleaning in this Section of the Handbook.

Typical applications found in the metals industry are removing chips and cutting oils from cutting and machining operations, removing buffing and polishing compounds prior to plating operations, and cleaning greases and sludge from rebuilt components for automotive and aircraft applications.

Ultrasonic cleaning is powerful enough to remove tough contaminants, yet gentle enough not to damage the substrate. It provides excellent penetration and cleaning in the smallest crevices and between tightly spaced parts in a cleaning tank.

The use of ultrasonics in cleaning has become increasingly popular due to the restrictions on the use of chlorofluorocarbons such as 1, 1, 1-trichloroethane. Because of these restrictions, many manufacturers and surface treaters are now using immersion cleaning technologies rather than solvent-based vapor degreasing. The use of ultrasonics enables the cleaning of intricately shaped parts with an effectiveness that corresponds to that achieved by vapor degreasing. Additional information about the regulation of surface cleaning chemicals is contained in the article "Environmental Regulation of Surface Engineering" in this Volume. The article "Vapor Degreasing Alternatives" in this Volume includes descriptions of cleaning systems (some using ultrasonics) that have been designed to meet regulatory requirements while at the same time providing effective surface cleaning.

Process Description

In a process termed *cavitation*, micron-size bubbles form and grow due to alternating positive and negative pressure waves in a solution. The bubbles subjected to these alternating pressure waves continue to grow until they reach resonant size. Just prior to the bubble implosion (Fig. 1), there is a tremendous amount of energy stored inside the bubble itself.

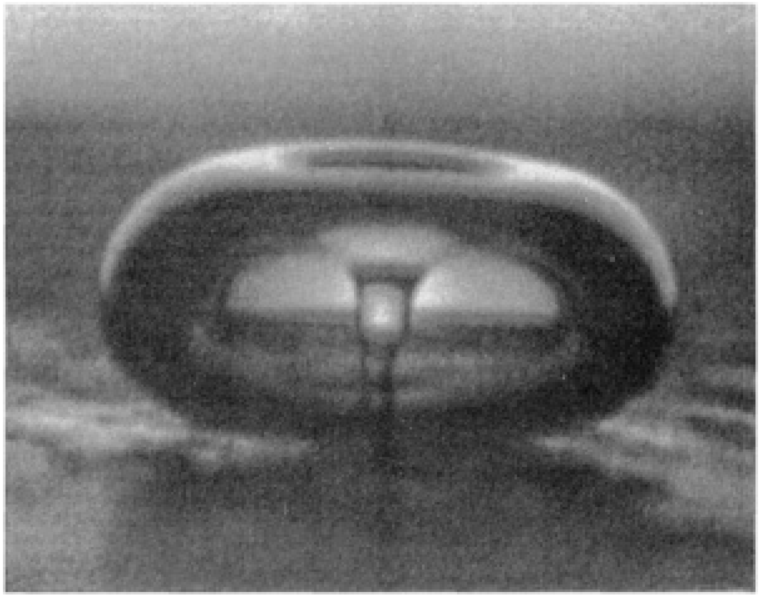

Fig. 1 Imploding cavity in a liquid irradiated with ultrasound captured in a high-speed flash photomicrograph. Courtesy of National Center for Physical Acoustics, University of Mississippi

Temperatures inside a caviting bubble can be extremely high, with pressures up to 500 atm. The implosion event, when it occurs near a hard surface, changes the bubble into a jet about one-tenth the bubble size, which travels at speeds up to 400 km/hr toward the hard surface. With the combination of pressure, temperature, and velocity, the jet frees contaminants from their bonds with the substrate. Because of the inherently small size of the jet and the relatively large energy, ultrasonic cleaning has the ability to reach into small crevices and remove entrapped soils very effectively.

An excellent demonstration of this phenomenon is to take two flat glass microscope slides, put lipstick on a side of one, place the other slide over top, and wrap the slides with a rubber band. When the slides are placed into an ultrasonic bath with nothing more than a mild detergent and hot water, within a few minutes the process of cavitation will work the lipstick out from between the slide assembly. It is the powerful scrubbing action and the extremely small size of the jet action that enable this to happen.

Ultrasound Generation In order to produce the positive and negative pressure waves in the aqueous medium, a mechanical vibrating device is required. Ultrasonic manufacturers make use of a diaphragm attached to high-frequency transducers. The transducers, which vibrate at their resonant frequency due to a high-frequency electronic generator source, induce amplified vibration of the diaphragm. This amplified vibration is the source of positive and negative pressure waves that propagate through the solution in the tank. The operation is similar to the operation of a loudspeaker except that it occurs at higher frequencies. When transmitted through water, these pressure waves create the cavitation process.

The resonant frequency of the transducer determines the size and magnitude of the resonant bubbles. Typically, ultrasonic transducers used in the cleaning industry range in frequency from 20 to 80 kHz. The lower frequencies create larger bubbles with more energy, as can be seen by dipping a piece of heavy-duty aluminum foil in a tank. The lower-frequency cleaners will tend to form larger dents, whereas higher-frequency cleaners form much smaller dents.

Equipment

The basic components of an ultrasonic cleaning system include a bank of ultrasonic transducers mounted to a radiating diaphragm, an electrical generator, and a tank filled with aqueous solution. A key component is the transducer that generates the high-frequency mechanical energy. There are two types of ultrasonic transducers used in the industry,

piezoelectric and magnetostrictive. Both have the same functional objective, but the two types have dramatically different performance characteristics.

Piezoelectric transducers are made up of several components. The ceramic (usually lead zirconate) crystal is sandwiched between two strips of tin. When voltage is applied across the strips it creates a displacement in the crystal, known as the *piezoelectric effect.* When these transducers are mounted to a diaphragm (wall or bottom of the tank), the displacement in the crystal causes a movement of the diaphragm, which in turn causes a pressure wave to be transmitted through the aqueous solution in the tank. Because the mass of the crystal is not well matched to the mass of the stainless steel diaphragm, an intermediate aluminum block is used to improve impedance matching for more efficient transmission of vibratory energy to the diaphragm. The assembly is inexpensive to manufacture due to low material and labor costs. This low cost makes piezoelectric technology desirable for ultrasonic cleaning. For industrial cleaning, however, piezoelectric transducers have several shortcomings.

The most common problem is that the performance of a piezoelectric unit deteriorates over time. This can occur for several reasons. The crystal tends to depolarize itself over time and with use, which causes a substantial reduction in the strain characteristics of the crystal. As the crystal itself expands less, it cannot displace the diaphragm as much. Less vibratory energy is produced, and a decrease in cavitation is noticed in the tank. Additionally, piezoelectric transducers are often mounted to the tank with an epoxy adhesive, which is subject to fatigue at the high frequencies and high heat generated by the transducer and solution. The epoxy bond eventually loosens, rendering the transducer useless. The capacitance of the crystal also changes over time and with use, affecting the resonant frequency and causing the generator to be out of tune with the crystal resonant circuit.

Energy transfer of a piezoelectric transducer is another factor. Because the energy is absorbed by the parts that are immersed in an ultrasonic bath, there must be a substantial amount of energy in the tank to support cavitation. If this is not the case, the tank will be "load-sensitive" and cavitation will be limited, degrading cleaning performance. Although the piezoelectric transducers utilize an aluminum insert to improve impedance matching (and therefore energy transfer into the radiating diaphragm), they still have relatively low mass. This low mass limits the amount of energy transfer into the tank (as can be seen from the basic equation for kinetic energy, $\frac{1}{2}\ mv^2$). Due to the low mass of the piezoelectric transducers, manufacturers must use thin diaphragms in their tanks. A thick plate simply will not flex (and therefore cause a pressure wave) given the relatively low energy output of the piezoelectric transducer. However, there are several problems with using a thin diaphragm. A thin diaphragm driven at a certain frequency tends to oscillate at the upper harmonic frequencies as well, which creates smaller implosions. Another problem is that cavitation erosion, a common occurrence in ultrasonic cleaners, can wear through a thin-wall diaphragm. Once the diaphragm is penetrated, the solution will damage the transducers and wiring, leaving the unit useless and requiring major repair expense.

Magnetostrictive transducers are known for their ruggedness and durability in industrial applications. Zero-space magnetostrictive transducers consist of nickel laminations attached tightly together with an electrical coil placed over the nickel stack. When current flows through the coil it creates a magnetic field, and nickel has a unique property of expanding or contracting when it is exposed to the magnetic field. This is analogous to deformation of a piezoelectric crystal when it is subjected to voltage. When an alternating current is sent through the magnetostrictive coil, the stack vibrates at the frequency of the current.

The nickel stack of the magnetostrictive transducer is silver brazed directly to the resonating stainless steel diaphragm. This has several advantages over an epoxy bond. The silver braze creates a solid metallic joint between the transducer and the diaphragm that will never loosen. The silver braze also efficiently couples the transducer and the diaphragm together, eliminating the damping effect that an epoxy bond creates. The use of nickel in the transducers means there will be no degradation of the transducers over time; nickel maintains its magnetostrictive properties on a constant level throughout the lifetime of the unit. Magnetostrictive transducers also provide more mass, which is a major factor in the transmission of energy into the solution in the ultrasonic tank. Zero-space magnetostrictive transducers have more mass than piezoelectric transducers, so they drive more power into the tank, and this makes them less load-sensitive than piezoelectric systems.

A radiating diaphragm that uses zero-space magnetostrictive transducers is usually 5 mm ($\frac{3}{16}$ in.) or greater in thickness, eliminating any chance for cavitation erosion wearthrough. Heavy nickel stacks can drive a plate of this thickness and still get excellent pressure wave transmission into the aqueous solution.

In summary, the advantages of zero-space magnetostrictive transducers are:

- They are silver brazed for permanent bonding with no damping effect
- They provide consistent performance throughout the life of the unit with no degradation of transducers
- Their high mass results in high energy in the tank and less load sensitivity
- Their thick diaphragm prevents erosion wearthrough

The magnetostrictive transducer is not as efficient as a piezoelectric transducer. That is, for a given voltage or current displacement, the piezoelectric transducer will exhibit more deflection than the magnetostrictive transducer. This is a valid observation; however, it has offsetting disadvantages. The efficiency of concern should be that of the entire transducing system, including not only the transducer but also the elements that make up the transducer, as well as the diaphragm and the effectiveness of the bond to the diaphragm. It is the interior mounting and impedance matching of a piezoelectric-driven diaphragm that reduces its overall transducing efficiency relative to that of a magnetostrictive transducer.

The ultrasonic generator converts a standard electrical frequency of 60 Hz into the high frequencies required in ultrasonic transmission, generally in the range of 20 to 80 kHz. Many of the better generators today use advanced technologies such as sweep frequency and autofollow circuitry. Frequency sweep circuitry drives the transducers between a bandwidth slightly greater and slightly less than the center frequency. For example, a transducer designed to run at 30 kHz will be driven by a generator that sweeps between 29 and 31 kHz. This technology eliminates the standing waves and hot spots in the tank that are characteristic of older, fixed-frequency generators. Autofollow circuitry is designed to maintain the center frequency when the ultrasonic tank is subject to varying load conditions. When parts are placed in the tank or when the water level changes, the load on the generator changes. With autofollow circuitry, the generator matches electrically with the mechanical load, providing optimum output at all times to the ultrasonic tank.

Ultrasonic tanks are generally rectangular and can be manufactured in just about any size. Transducers are usually placed in the bottom or on the sides, or sometimes both when watt density (watts per gallon) is a concern. The transducers can be welded directly into the tank, or watertight immersible units can be placed directly into the aqueous solution. In some instances the immersibles may be mounted at the top of the tank, facing down. For applications such as strip cleaning, one immersible is placed on top and one on the bottom, with minimal distance between them. The strip is then run through the very high energy field. A tank should be sturdy in construction, ranging from 11 to 14 gauge in thickness. Larger, heavy-duty industrial tanks should be 11 to 12 gauge and should contain the proper stiffeners for support due to the weight of the solution.

Solution

The solution used in ultrasonic cleaning is a very important consideration. Solvents such as 1,1,1-trichloroethane and freon have been used effectively for many years, with and without ultrasonics. However, with the advent of the Montreal protocol, which calls for elimination of key ozone-depleting substances by 1996, companies are searching for more environmentally friendly methods to clean their parts. Chemical formulators are developing products that meet the demands of cleaning operations, yet are compatible with the health and well-being of society.

Whenever possible, it is best to use a water-based detergent in the ultrasonic cleaning process. Water is an excellent solvent, nontoxic, nonflammable, and environmentally friendly. However, it can be difficult and expensive to dispose of soiled water. Rinsing and drying can also be difficult without detergents. High surface tension exists in solutions without detergents, thus making rinsing difficult in hard-to-reach areas. Detergents can therefore be added to lower the surface tension and provide the necessary wetting action to loosen the bond of a contaminant to a substrate. As an added bonus, the cavitation energy in a water-based solution is more intense than in an organic solvent.

Table 1 is a guide for selection of appropriate cleaning agents for use with ultrasonic cleaning. Additional information about many of these agents is available in the other articles in this Section of the Handbook.

Table 1 Solutions used with ultrasonic cleaning of various parts

Material of construction	**Types of parts**	**Contaminants**	**Suitable Cleaning agent**
Iron, steel, stainless steel	Castings, Stampings, machined parts, drawn wire, diesel fuel injectors	Chips, lubricants, light oxides	High caustic with chelating agents
	Oil-quenched, used automotive parts; fine-mesh and sinterd filters	Carbonized oil and grease, carbon smut, heavy grime deposits	High caustic, silicated
	Bearing rings, pump parts, knife blades, drill taps, valves	Chips; grinding, lapping, and honing compounds; oils; waxes and abrasives	Moderately alkaline
	Roller bearings, electronic components that are affected by water or pose drying problems, knife blades, sintered filters	Buffing and polishing compounds; miscellaneous machining, shop, and other soils	Chlorinated-solvent degreaser (inhibited trichloroethylene, for example)
Aluminum and zinc	Castings, open-mesh air filters, used automotive carburetor parts, valves, switch components, drawn wire	Chips, lubricants, and general grime	Moderately alkaline, specially inhibited to prevent etching of metal, or neutral synthetic (usually in liquid form)
Copper and brass (also silver, gold, tin, lead, and solder)	Printed circuit boards, waveguides, switch components, instrument connector pins, jewelry (before and after plating), ring bearings	Chips, shop dirt, lubricants, light oxides, fingerprints, flux residues, buffing and lapping compounds	Moderately alkaline, silicated, or neutral synthetic (possibly with ammonium hydroxide for copper oxide removal)
Magnesium	Castings, machined parts	Chips, lubricants, shop dirt	High caustic with chelating agents
Various metals	Heat-treated tools, used automotive parts, copper-clad printed circuit boards, used fine-mesh filters	Oxide coatings	Moderately to strongly inhibited proprietary acid mixtures specific for the oxide and base metal of the part to be cleaned (except magnesium)
Glass and ceramics	Television tubes, electronic tubes, laboratory apparatus, coated and uncoated photographic and optical lenses	Chips, fingerprints, lint, shop dirt	Moderately alkaline or neutral synthetic
Plastics	Lenses, tubing, plates, switch components	Chips, fingerprints, lint, lubricants, shop dirt	Moderately alkaline or neutral synthetic
Various metals, plastics (nylon,Teflon, epoxy, etc.), and organic coatings when	Precision gears, bearings, switches, painted housings, printed circuit boards,	Lint, other particulate matter, and light oils	Trichlorotrifluoroethane (fluorocarbon solvent), sonic-vapor degreaser

water solutions cannot be tolerated	miniature servomotors, computer components		

Source: Ref 1

Solution temperature has a profound effect on ultrasonic cleaning effectiveness. In general, higher temperatures will result in higher cavitation intensity and better cleaning. However, if the temperature too closely approaches the boiling point of the solution, the liquid will boil in the negative pressure areas of the sound waves, reducing or eliminating cavitation. Water cavitates most effectively at about 70 °C (160 °F); a caustic/water solution, on the other hand, cleans most effectively at about 82 °C (180 °F) because of the increased effectiveness of the chemicals at the higher temperature. Solvents should be used at temperatures at least 6 °C (10 °F) below their boiling points (Ref 2).

References cited in this section

1. Ultrasonic Cleaning, *Tool and Manufacturing Engineers Handbook,* Vol 3, *Materials, Finishing, and Coating,* C. Wick and R.E Veilleux, Ed., Society of Manufacturing Engineers, 1985, p 18-20 to 18-24
2. EJ. Fuchs, Ultrasonic Cleaning, *Metal Finishing Guidebook and Directory,* Elsevier Science, 1992, p 134-139

System Design

Considerations in the design of any cleaning system include the contaminants on the part(s), the required cleanliness level, the geometry and material of the part(s), the quantity to be processed, and the previous system design and layout (if applicable). The part geometry, production rate, and cleaning time required will determine the size of the cleaning system, once the overall process has been decided. Typical tanks range from 20 to 4000 L (5 to 1000 gal), and some are even larger.

Industrial, heavy-duty applications require industrial, heavy-duty ultrasonic equipment. Other factors that need to be considered are cleaning solutions and temperatures, rinsing (with or without ultrasonics), drying, automation, and load requirements. Most manufacturers of ultrasonic cleaning systems will assist in these decisions and will offer laboratory services and technical expertise. A typical system is shown in Fig. 2.

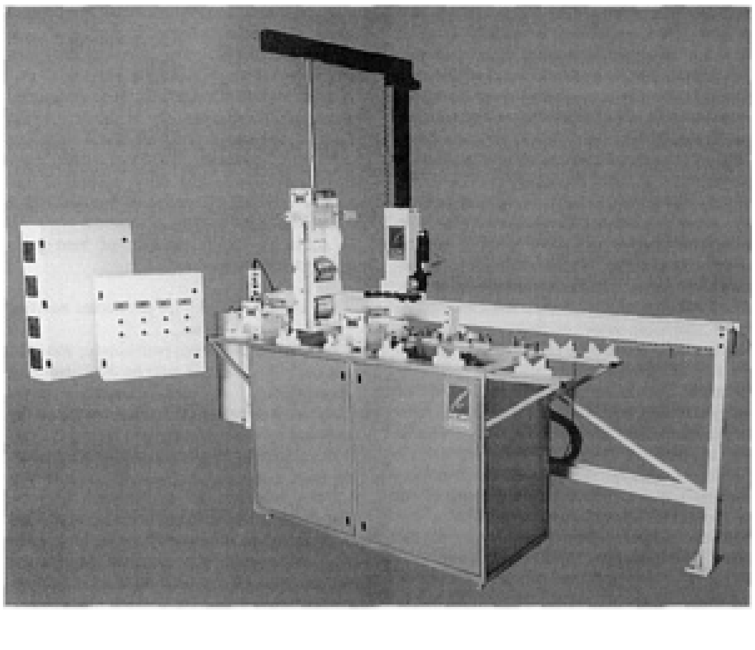

Fig. 2 Automated ultrasonic cleaning system. This system is designed to clean intricate metal hearing-aid components using a neutral-pH solution at 60 °C (140 °F) and three rinse stages at 70 °C (160 °F). Basket rotation (1 to 3 rpm) is used during each stage to ensure adequate cleaning and rinsing. The system computer

controls all functions, including the hoist, and allows for storage of different process parameters for different types of parts. Courtesy of Blue Wave Ultrasonics

Cleanliness Considerations. In a typical aqueous ultrasonic cleaning system, it is the cleaning stage(s) that will remove or loosen the contaminants. The following rinse stage(s) remove any remaining loosened soils and residual detergent, and a dryer removes any remaining rinse water. The overall process of the system is usually determined experimentally. Most reputable industrial cleaning equipment manufacturers have an applications lab where, through a process of experience, trial, and error, a properly designed cleaning process can be determined to meet the cleanliness levels specified.

There are a variety of ways to check for cleanliness. Some are as simple as a water break test on the part to see if most oil has been removed. Others are as elaborate as surface quality monitoring that uses optically stimulated electron emission technology to measure thin films of contaminants down to the Angstrom level.

Changing Existing Systems. If a current system exists, such as a vapor degreaser or soak tank, several things need to be considered. It may be practical, and possibly most economical, to retrofit the existing unit from one that uses solvent an organic solvent to one that uses an aqueous cleaner. Ultrasonic transducers can be added to an existing tank by cutting a hole in the tank and welding the transducer(s) in, or by simply dropping a watertight immersible unit into the tank. The latter method will take up some room in the tank, but it requires less labor. Additional work may have to be done to the tank, such as removing the cooling coils from the vapor degreaser, adding additional fittings for a filtration system, and so on.

In some existing systems, there is a large inventory of stainless steel baskets for handling the parts throughout the cleaning system. If possible, it is best to use these baskets due to the relatively high cost of replacement. In ultrasonic cleaning, the mesh size or hole configuration of the basket is very important. Some mesh sizes will inhibit the cavitation process inside the basket, thereby affecting the overall cleaning capability. Mesh sizes greater than 200 mesh or less than 10 mesh work best. An interesting note is that ultrasonic activity will pass through a variety of media. For example, solution A placed in a Pyrex beaker will cavitate if placed in solution B, which is cavitating in an ultrasonic tank.

Additional information on adapting vapor degreasing systems for ultrasonic immersion cleaning is provided in the article "Vapor Degreasing Alternatives" in this Volume.

Part Handling. The geometry of the parts must be carefully analyzed to determine how they will be placed in the cleaning tank. Large parts, such as engine blocks, can be suspended directly from a hoist, whereas smaller parts will usually be placed in a basket. The most important factor in parts placement is to be sure that air is not trapped anywhere inside the part. If an air pocket is allowed to form, such as in a blind hole that would be facing downward toward the bottom of the tank, the cleaning solution and effects of cavitation will not be able to reach this particular area. The part will have to be rotated somehow in the tank during the cleaning process to allow the cleaning solution to reach the area where air was previously trapped. This can be accomplished either manually, by the attending operator, or by a rotating arm on an automated lift mechanism.

It is best if small parts can be physically separated when placed in a basket. An example would be to place machined valve bodies in a basket with some type of divider or locator for each one. Many times, however, in high output lines it is not possible to separate parts physically, such as in the manufacture of electrical connector pins where thousands of parts may need to be cleaned at one time because of the high production output and the small size. Ultrasonic agitation will be able to reach between these parts and allow the solution's scrubbing power to remove the contaminants, even if the parts are stacked on top of one another. On the other hand, rinse water may not remove all of the residual detergent, and a dryer has a very hard time removing moisture from embedded parts. The problem is easily solved by having an automated hoist with a constant rotating fixture on the arm that allows the basket to tumble at 1 to 2 rpm. This rotation allows the parts to tumble slowly and exposes the embedded pieces for proper rinsing and drying.

Acid Cleaning

Revised by Kenneth J. Hacias, Parker + Amchem, Henkel Corporation

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Introduction

ACID CLEANING is a process in which a solution of a mineral acid, organic acid, or acid salt, in combination with a wetting agent and detergent, is used to remove oxide, shop soil, oil, grease, and other contaminants from metal surfaces, with or without the application of heat. The distinction between acid cleaning and acid pickling is a matter of degree, and some overlapping in the use of these terms occurs. Acid pickling is a more severe treatment for the removal of scale from semifinished mill products, forgings, or castings, whereas acid cleaning generally refers to the use of acid solutions for final or near-final preparation of metal surfaces before plating, painting, or storage. Acid pickling is discussed in the article "Pickling and Descaling" in this Volume.

The focus of this article is on acid cleaning of iron and steel. Some limited information on acid cleaning of nonferrous metals is included at the end of this article; additional information is available in the Section "Surface Engineering of Non-ferrous Metals" in this Volume.

Mineral Acid Cleaning of Iron and Steel

Cleaner Composition

A variety of mineral acids and solutions of acid salts can be used, either with or without surfactants (wetting agents), inhibitors, and solvents. The large number of compositions that are used may be classified as:

- Inorganic (mineral) acid solutions
- Acid-solvent mixtures
- Solutions of acid salts

Many acid cleaners are available as proprietary compounds, either as a liquid concentrate or a powder to be mixed with water. Compositions of several solutions used for cleaning ferrous metals are given in Table 1. Table 2 contains some possible operating conditions when cleaning ferrous metals.

Table 1 Typical composition of acid cleaners for cleaning ferrous metals

Composition of each constituent is given in percent by weight.

Constituent	Immersion		Spray		Barrel	Wipe	Electrolytic
Phosphoric acid	70	. . .	70	. . .	. . .	15-25	. . .
Sodium acid pyrophosphate	. . .	16.5	. . .	16.5	16.5	. . .	. . .
Sodium bisulfate	. . .	80	. . .	80	80	. . .	. . .
Sulfuric acid	. . .	. . .	. . .	. . .	. . .	. . .	55-70
Nonionic wetting agent[a]	5	. . .	5	. . .	. . .	7-20	. . .
Anionic wetting agent	. . .	3	. . .	3	3	. . .	. . .
Other additives	[b]	[b]	[b][c]	[b][c]	[b][c]	[b][d]	[b]
Water	25[e]	. . .	25[e]	. . .	. . .	bal	bal

(a) Ethylene glycol monobutyl ether is used.

(b) Inhibitors up to 1 % concentration may be used to miminize attack on metal.

(c) An anti-foaming agent is usually required when the cleaner is used in a spray or barrel system.

(d) Small additions of sodium nitrate are often used as an accelerator in cleaning rolled steel; nickel nitrate is used in cleaning galvanized steel.

(e) Before dilution

Table 2 Operating conditions for acid cleaners for ferrous metals

Type of acid cleaner	Concentration		Temperature	
	g/L	oz/gal	°C	°F
Immersion	120 60-120	16 8-16	71 60	160 140
Spray	60 15-30	8 2-4	60 60	140 140
Barrel	15-60	2-8	Room	Room
Wipe	. . .	. . .	Room	Room

(a) Current density, 10 A/dM^2 (100 A/ft^2)

Sulfuric and especially hydrochloric acids are the most commonly used for cleaning operations. They are relatively economical to use and in some cases can be reclaimed by ion exchange or chilling methods whereby the dissolved iron is removed. Reclamation can have a significant positive impact on disposal and operating costs where large quantities of acid are consumed.

Typical operating concentrations are 20 to 60 vol% for hydrochloric acid and 4 to 12 vol% for sulfuric acid. Normally both are highly inhibited to minimize the attack of the base metal and process equipment.

Organic acids such as citric, tartaric, acetic, oxalic, and gluconic, and acid salts such as sodium phosphates, ammonium persulfate, sodium acid sulfate, and bifluoride salts, are used in various combinations. Solvents such as ethylene glycol monobutyl ether and other glycol ethers, wetting agents and detergents such as alkyl aryl, polyether alcohols, antifoam agents, and inhibitors may be included to enhance the removal of soil, oil, and grease.

Strength of the acid solutions varies from as weak as 5.5 pH for acid-salt mixtures to the equivalent of the strong acids used for pickling.

The phosphoric acid and ethylene glycol monobutyl ether mixtures (Table 1) are used for removing grease, oil, drawing compounds, and light rust from iron and steel. In various concentrations, these mixtures are adaptable to immersion, spray, or wiping methods and leave a light phosphate coating (110 to 320 mg/m^2, or 10 to 30 mg/ft^2) that provides a paint base or temporary resistance to rusting if the parts are to be sorted.

Chromic acid solutions are used occasionally to clean cast iron and stainless steel. A chromic acid formula used for cleaning stainless steel is 60 g/L (8 oz/gal) chromium trioxide, 60 g/L (8 oz/gal) sulfuric acid, and 60 g/L (8 oz/gal) hydro-fluoric acid in water, used at room temperature in an immersion system. Another solution used frequently for cleaning stainless steel is a solution of nitric acid (10 to 50 vol%) and hydrofluoric acid (1 to 3 vol%) in water. The steel is immersed in the solution at room temperature for 3 to 30 min.

Chromic acid solutions and mixtures containing chromic acid are often used as final rinses in acid cleaning-phosphating systems. The acid enhances the corrosion resistance of the coated surface. Paint applied following such a treatment gives greater protection against corrosion by salt and humid environments. Chromic acid is used in solutions of low pH when a strong oxidant is required. Nitric acid is also a strong oxidant, and a 10 to 20% nitric acid solution is used to brighten stainless steel.

For electrolytic cleaning applications, very high concentrations of sulfuric acid (Table 1) are recommended although hydrochloric acid may also be used. Phosphoric acid, however, is unsuitable due to its high gassing characteristic.

Various soils, including light rust, are removed by combining acid cleaning with mechanical action. Acid salts such as sodium acid pyrophosphate, sodium bisulfate, and mixtures of the two are sometimes used to clean ferrous metal parts in rotating barrels. (A formula is given in Table 1.) A solution with this formula may also be used for parts that are immersed or sprayed.

Additives such as oxalic acid occasionally are used with the acid salts when ferrous metal parts are being cleaned in rotating barrels. Oxalic acid attacks steel, but seldom to an objectionable degree. Thiourea is a good inhibitor, if inhibited oxalic acid solutions are required. The addition of fluoride salts to acid salts, such as 8 to 15 g/L (1 to 2 oz/gal) sodium fluoride or ammonium bifluoride, improves efficiency in the removal of silica sand from castings when parts are cleaned in a barrel or tank.

A formula used for wipe cleaning is also given in Table 1. Other cleaners used for wiping are 6 to 8 vol% sulfuric acid in water; 70% phosphoric acid, 5% wetting agent, and 25% water; and a paste made of 85 to 95% ammonium dihydrogen phosphate and the remainder wetting agent, used on a wet cloth or sponge.

Inhibitors are often included in cleaners used on ferrous metals to minimize attack on metal and lower acid consumption. Composition of inhibitors varies widely. Numerous byproducts, such as sludge acid from oil refineries, waste animal materials, waste sulfite cellulose liquor, offgrade wheat flour, and sulfonation products of such materials as wood tar, coal tar, and asphaltum, have been successfully used. These materials cost less than synthetic inhibitors but can vary widely in uniformity and effectiveness and may contain toxic or carcinogenic substances. For these reasons, synthetic inhibitors now dominate the market.

Synthetic inhibitors are usually complex organic compounds. One of the most common inhibitors for hydrochloric-acid-based cleaners was propargyl alcohol, which is poisonous and has been removed from most acid cleaners. Most often, a given compound or class of compounds will function most effectively with only one type of acid, so choosing the proper inhibitor should not be a haphazard process. Many proprietary compositions of these chemicals are available for use in various acid systems.

The amount of inhibitor used depends on the workpiece composition, acid cleaner formulation, temperature of operation, and nature of soil being removed. From $\frac{1}{2}$ to 1% inhibitor before dilution with water is used. Higher percentages of inhibitor may be used for higher acid concentrations and operating temperatures. Once the optimum concentration is established for a particular operation, higher concentrations have no positive effect and result in increased cost.

Antifoaming agents may be required in acid spray cleaners to prevent excessive foaming. Sometimes foaming can be reduced by using naturally hard water or by adding small amounts of calcium chloride, up to 30 grains hardness. Addition of a plasticizer such as triethylhexylphosphate or one of the high-molecular-weight polyols (organic alcohols) reduces foaming. Because of variation in water and other conditions in a specific installation, several additives may need to be

tried before foaming is brought under control. Silicones are usually effective as antifoaming agents, but they should not be used if parts are to be painted or plated, because of residual contamination. Paint or plating does not adhere to the silicone contaminated areas, resulting in a fisheye appearance at the contaminated spots.

Foaming agents may be desirable in certain immersion applications, to reduce acid fume evolution to the atmosphere and to provide an insulating blanket on the surface of the tank to decrease heat loss from evaporation. Proprietary inhibitors having controlled foaming properties are available.

Methods of Application

Wipe on/wipe off, spray, immersion, flooding, and rotating barrel methods are all used extensively for acid cleaning. Although heating greatly increases efficiency, cleaning is frequently done at room temperature for superior process control and economy of operation. When heat is used, the temperature range of the cleaner is usually 60 to 82 °C (140 to 180 °F) with temperatures up to 93 °C (200 °F) used occasionally. Time cycles for acid cleaning are short compared to acid pickling, especially when stronger acids are being used. Selection of method depends on the nature of soil being removed, the size and shape of the workpiece, quantity of similar pieces to be cleaned, and type of acid cleaner used.

Wipe on/wipe off is the simplest method of acid cleaning; virtually no equipment is required. Using a formula such as that shown in Table 1, an operator suitably protected by rubber gloves, eye protection, and apron wipes the soiled workpieces with an acid-impregnated cloth or sponge. After the cleaner is allowed to react (2 or 3 min is usually sufficient), work is rinsed with water.

The wiping method is practical only for cleaning a few parts at a time or for large, bulky parts that cannot be immersed conveniently in a cleaning bath. Labor cost becomes excessive if many parts are cleaned. Cleaner concentrations are stronger than in dip and spray solutions, and the cleaner is not usually recovered for further use.

Spray cleaning is more practical than wiping when larger quantities of bulky parts are acid cleaned. Multistage spray washers have been designed to accommodate a variety of work that can be racked or suspended from hooks. Large components, such as truck cabs and furniture, are usually cleaned by this method. Cost of labor is lower than for hand wiping. Also, consumption of cleaner ingredients is considerably less because concentrations are lower, and cleaner is recirculated for reuse. The capital investment for spray cleaning equipment is high, and large production quantities are usually needed to justify the expense. Steady or high production quantities are not always necessary to warrant the installation of spray equipment. It is sometimes feasible to accumulate parts for about 2 days and then operate the washer for part of a day.

In one automotive plant, a spray system replaced a hand wiping system with the following results. A wipe on/wipe off system using phosphoric acid-ethylene glycol monobutyl ether was used to prepare large steel stampings for painting. A total of 46 supervisory and production employees were required. Installation of an automatic spray system decreased cleaner consumption and provided the same productivity with only six employees. In addition, a heavier phosphate coat was obtained, 5400 to 6500 mg/m^2 (500 to 600 mg/ft^2) by spraying, compared to 1100 to 2200 mg/m^2 (100 to 200 mg/ft^2) by wiping in subsequent zinc phosphating stages.

Immersion is the most versatile of the acid cleaning methods, particularly for cleaning irregular shapes, box sections, tube, and cylindrical configurations that cannot be penetrated using spray systems. The operation may vary from hand dipping a single part or agitating a basket containing several parts in an earthenware crock at room temperature to a highly automated installation operating at elevated temperature and using controlled agitation. The types of cleaner used in immersion systems are often chemically similar to spray cleaners but due to lack of impingement are generally run at higher concentrations (Table 1). Efficient cleaning by immersion depends on placing workpieces in baskets or on racks to avoid entrapment of air or nesting of parts.

Barrel cleaning is often used for large quantities of small parts. Perforated barrels containing 225 to 900 kg (500 to 2000 lb) of parts are immersed and rotated in tanks of cleaning solution. Solutions of acid salts (Table 1) are used for this method, although other cleaning solutions may be applicable. In some instances, a medium such as stones is added to the charge, frequently comprising up to two-thirds of the total load. The medium aids in cleaning by providing an abrading action. It also prevents workpieces from damaging each other. Acid cleaning in barrels is usually performed at room temperature. Heated solutions can be used if required by the nature of the soil being removed.

Barrel methods can be used for cleaning in continuous high production. Several barrels can be arranged so that some can be loaded while others are in the cleaning tank. The chief limitation of the barrel method is the size and shape of workpieces. Parts such as bolts are ideal for barrel cleaning, while delicate stampings are not.

Electrolytic cleaning is effective because of the mechanical scrubbing that results from evolution of gas and the chemical reduction of surface oxide films when used anodically. Sulfuric acid baths are most commonly electrolyzed (Table 1) and are usually used as a final cleaner before plating. All grease and oil should be removed before electrolytic cleaning, to reduce contaminating of the electrolytic bath. If alkaline cleaners are used as precleaners, the rinse must be thorough or the acid bath can be neutralized by the alkali. Time cycles in electrolyzed acid solutions must be short, usually less than 2 min, or excessive etching can occur. Current distribution must be uniform, or localized etching may damage the workpiece.

Selection Factors

In any acid cleaning operation, etching usually occurs. In many instances, this light etching is advantageous for final finishing operations. However, if etching is not permissible, some other cleaning process should be used.

Limitations of acid cleaning include:

- Inability to remove heavy deposits of oil or grease without large additions of expensive material such as surfactants and detergents
- Attack on the metal to some degree, even when inhibitors are used
- Requirement of acid-resistant equipment

If parts are soiled with heavy deposits of oil or grease, as well as rust, preliminary alkaline cleaning preceding acid cleaning is most often a necessity. Multiple rinses should be used to prevent carryover of alkali.

Selection of Process

Reasons for selecting acid cleaning and specific acids are illustrated in the following examples. Parts deep drawn from low-carbon sheet steel as received from the supplier were covered with pigmented drawing compound and other shop soil and frequently became rusty during transit. Alkaline cleaning, even with hand scrubbing, did not consistently remove the drawing compound and allowed most of the rust to remain. Acid cleaning in a multistage spray washer completely removed all soil and rust without hand scrubbing. A phosphoric acid and ethylene glycol monobutyl ether mixture (Table 1) was spray applied using a concentration of about 60 g/L (8 oz/gal) at 66 °C (150 °F). In addition to thorough cleaning, the process deposited the light phosphate coating that was desired as a base for subsequent painting.

Finish-machined surfaces on large castings showed a light blushing rust after a weekend in high humidity. Abrasive cleaning could not be used because of possible damage to finished surfaces. The rust was removed without etching by hand wiping with a pastelike compound of about 90% ammonium dihydrogen phosphate and 10% wetting agent, followed by wipe rinsing.

Combinations of alkaline and acid cleaning methods are often used advantageously. Machined parts having heavy deposits of oil, grease, and light blushing rust were being acid cleaned using phosphoric acid and ethylene glycol monobutyl ether in an immersion system at 60 °C (140 °F). Results were satisfactory, but the cleaner became contaminated from the oil and grease so rapidly that the replacement cost of cleaner became excessive. Adding a preliminary alkaline cleaning operation removed most of the soil. Parts were then rinsed, first in unheated water, then in an unheated neutralizing rinse containing 2% chromic acid. Immersion in the phosphoric acid and ethylene glycol monobutyl ether mixture removed the rust and provided a surface ready for painting. This practice prolonged the life of the acid cleaner by a factor of five or more.

In other instances, combining alkaline and acid cleaning does not prove economically feasible. In one plant, small steel Stampings were being prepared for painting by removing light oil and some rust in a five-stage spray washer. The first stage was alkaline, followed by water rinsing, then two stages of phosphoric acid cleaning, followed by water rinsing and a rinse in chromic acid solution. Alkaline contamination of the first acid stage was excessive, necessitating weekly dumping of the acid cleaner. A change to three successive stages of acid cleaning followed by one plain water rinse and

one rinse with chromic acid in water proved more economical and satisfactory. The practice was then to dump the cleaner periodically from the first stage and decant the second stage cleaner to the first stage, recharging the second stage while maintaining the third stage.

For small parts that are not easily bent or otherwise damaged, barrel methods often are the most satisfactory. Small miscellaneous parts having no deep recesses required removal of light oil and minor rust. They were placed in a horizontal barrel and rotated in a solution of acid salt cleaner (similar to the composition shown in Table 1) at room temperature using a concentration of 45 to 60 g/L (6 to 8 oz/gal). After tumbling for 10 to 20 min, the barrel was removed from the cleaner tank, drained, rinsed, drained, and tumbled for 30 to 60 min at room temperature in a tank containing 45 to 60 g/L (6 to 8 oz/gal) of alkaline cleaner. The charge was then rinsed in water, unloaded, and dried. Tumbling in the alkaline solution neutralized residual acid and produced a shine on the workpieces.

If optimum equipment is not readily available, requirements may sometimes be met with available equipment. Box-shape cast iron parts, 200 by 150 by 100 mm (8 by 6 by 4 in.) deep, open on one end and having several drilled holes, were covered with light mineral oil. Parts needed to be cleaned and provided with a phosphate coating suitable for painting. Available equipment was a two-stage alkaline spray washer. Parts were washed in this equipment and then dipped in a phosphating tank. Because the workpieces were heavy and bulky, this procedure was inadequate to meet the production demand of 2500 to 3000 parts in 8 h. The problem was solved by changing the alkaline solution in the spray washer to an acid phosphate cleaner that contained low-foaming surfactants (wetting agents). Parts were sprayed for 1 min with a solution containing 110 g (4 oz) of acid phosphate cleaner per 4 L (1 gal) of solution, operated at 71 °C (160 °F). They were then sprayed with unheated water for 30 s, dipped in water-based inhibitor, air dried, and painted.

For parts that are to be electroplated, electrolytic acid cleaning is often used. After precleaning small parts to remove most of the oil, the following cycle was established for small carbon steel parts before electroplating:

1. Water rinse at 82 °C (180 °F)
2. Immerse for $\frac{3}{4}$ to 2 min in 55 to 70% sulfuric acid at 21 °C (70 °F), using a current density of 10 A/dm^2 (100 A/ft^2)
3. Flowing water rinse for 15 to 30 s at room temperature
4. Repeat step 3 in a second tank
5. Dip in 20% hydrochloric acid for 15 s at room temperature
6. Flowing water rinse for 15 to 30 s at room temperature

Electrolytic cleaning was successfully used in this application. Auto bumpers were cold formed from phosphated and lubricated sheet steel. Alkaline cleaning was used to remove mill dirt and soap-type lubricant. Electrolytic acid cleaning followed the alkaline treatment to ensure removal of the phosphate coating and residual lubricant. Because of scrubbing action by the gas evolved at the work surface, the electrolytic bath assisted in removing adherent solid particles that were the residue of a polishing compound. Slight metal removal occurred that removed metal slivers and produced a microetch suitable for plating. The ability of this bath to remove tenacious oxide coatings permitted the electroplating of nickel with good adhesion. While this cleaning could have been done by other means, the electrolytic acid system proved to be the most satisfactory method for this application.

Equipment

Wipe on/wipe off cleaning requires only the simplest equipment. Acid-resistant pails and protective clothing, and common mops, brushes, and wiping cloths are all that is needed.

Immersion systems require equipment varying from earthen crocks for hand dipping at room temperature to fully automated systems using heat and ultrasonic or electrolytic assistance. The construction for an acid tank is shown in Fig. 1. Tanks for sulfuric acid may be lined with natural rubber and acid-resistant red shale or carbon brick joined with silica-filled hot poured sulfur cement. Liners or freestanding fabricated tanks of polypropylene are also used. Tanks intended to contain nitric or hydrofluoric acids may be lined with polyvinyl chloride and carbon brick joined with carbon-filled hot poured sulfur cement. Carbon brick liners are not needed for nitric acid, but they are usually used to contain hydrofluoric acid.

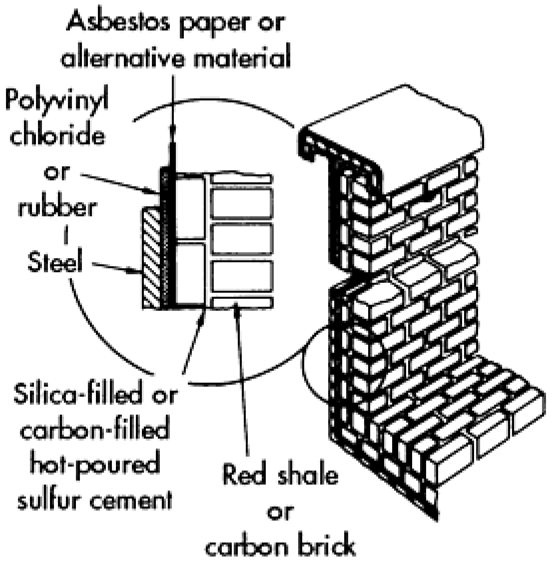


Fig. 1 Section of an acid cleaning tank. Inner lining of brick acts only as a thermal shield and as a protection against mechanical damage to the corrosion-resistant polyvinyl chloride or rubber membrane.

If the cleaning operation uses only acid solutions, an immersion installation would consist of an immersion tank for the acid solution, capable of being heated to 82 °C (180 °F), two rinse tanks for flowing cold water, and drying facilities, either convection or infrared.

Various modifications can be made for specific conditions. If parts are precleaned in alkaline solutions, two water rinse tanks should precede the acid cleaning tank. One of these two rinses may be a still tank containing dilute chromic acid. The final may be a heated still tank containing dilute chromic acid or a hot water tank (up to 82 °C, or 180 °F). One advantage in using heat in the final rinse is that subsequent drying is accelerated.

Various degrees of automation are feasible with immersion systems. Automated cleaning of racked parts can be applied to immersion systems by using an overhead monorail that raises and lowers racks according to a predetermined cycle.

Electrolytic acid cleaning tanks must be constructed to resist acids. Venting is recommended and usually required; otherwise, these tanks are no different from tanks used for electrolytic alkaline cleaning. A typical electrolytic cleaning tank is shown in the article on alkaline cleaning. Various types of auxiliary equipment may be used for removing fumes from an electrolytic tank. Electrodes are preferably made of lead.

Rinse tanks should be as small as is compatible with easy handling of the largest load to be rinsed, yet allow for adequate overflow to minimize contamination. For a given overflow rate, smaller tanks allow better mixing and faster rinsing of impurities. If a series of rinse tanks is used, all should be uniform in size for simple flow rate control.

Polyvinyl chloride is a proven material for rinse tanks. Polypropylene, which can withstand higher temperatures than polyvinyl chloride, has also been used, as well as polyester, rubber, brick, lead, and plain carbon steel coated with protective paint. Stainless steel can be used in rinse tanks where chloride solutions are not used. Chlorides cause pitting of stainless steel, especially if tanks are used intermittently.

Rinse tanks can be equipped with automatic controls that flush tanks when impurities reach an established level, as monitored by continuous measurement of the electrical conductivity.

Spray systems are designed with special features for high-production acid cleaning. The number of stations varies, but a five-stage system is usually used for cleaning and phosphating parts such as large stampings. The first stage is acid cleaning (usually phosphoric and ethylene glycol monobutyl ether) and is followed by a spray rinse followed by a phosphating stage. The process is completed by using either two successive stages of unheated water rinsing or one stage of unheated water and one of unheated or heated mild chromic acid solution. Parts are conveyed from stage to stage singly on a belt or by using an overhead monorail system with parts hanging singly or on racks.

Heating Equipment. Acid cleaners are rarely heated above 82 °C (180 °F). Improved detergent systems in recent years have permitted a much wider range of work to be acid cleaned at room temperature with consequent energy savings, but removal of rust or stubborn soils such as buffing compounds usually benefits from the application of heat. The temperature range most frequently used when acid cleaners are heated is 60 to 71 °C (140 to 160 °F).

Drying is usually accomplished by heated forced air. However, temperatures higher than about 100 °C (212 °F) are generally not used, for economic reasons. Infrared dryers may be used if controlled to proper operating temperature.

Acid Attack and Sludge Formation. In phosphoric acid cleaning and coating systems, acid attack on work is minor, although some metal is dissolved. Iron phosphate sludge is a natural byproduct of cleaning and coating with phosphoric acid-based chemicals. The amount of phosphate compounds in the sludge, as well as the severity of acid attack on the work, depends on the temperature and acid concentration.

Acid attack on the major items of equipment is almost negligible. For example, tanks and pipes used in one high-production installation have not been replaced during the first 16 years of operation and are still in serviceable condition. The tanks and pipes for this installation were made of low-carbon steel; pumps and nozzles were made of stainless steel. Most equipment deterioration is caused by erosion on parts such as pump impellers, riser pipe elbows, tees, and nipples. Some attack occurs initially, but once the steel surface has become coated with phosphate, attack is substantially reduced. Also, deposits of scale serve as inhibitors of acid attack and further protect the metal from the acid. The major cause for replacing parts such as risers and nozzles is clogging by sludge and scale.

In a spray system, sludge is usually removed by filters. In immersion systems, the sludge accumulated at the bottom of the tank is usually shoveled out after most of the still-usable solution has been removed (decanted). A sludge pan is often helpful. Such a pan covers the entire bottom of the tank except for small areas at the edges. This permits easy removal. The pan is usually 75 to 125 mm (3 to 5 in.) deep. Rods with hooks extending above the solution level allow the pan to be lifted to remove sludge. Thus, the solution need not be decanted, downtime is minimized, and labor is saved.

Handling and Conveying. Parts such as nuts and bolts are most commonly cleaned in rotating barrels. However, if barrel equipment is not available, such parts can be cleaned in baskets. Conveyance may be by hand, by lift systems, by belt when a spray is used, or by a combination of these systems. Small parts that cannot be tumbled in barrels may be placed in wire baskets, racked for immersing or spraying, or placed singly on belts in a spray system.

Racks, hooks, and baskets are usually made of a metal that will resist acids. Types 304, 316, 316L, and 347 stainless steel are successful for these components. Where racks or hooks travel through a series of cleaning, phosphating, and painting systems, the racks are continually recoated, making low-carbon steel an acceptable rack material. A rack used for cleaning and phosphating of small Stampings, such as doors for automobile glove compartments, is illustrated in Fig. 2. Large components are usually hung singly on hooks and transported by an overhead monorail. Figure 3 illustrates an arrangement for carrying truck cabs through a five-stage spray cleaning installation.

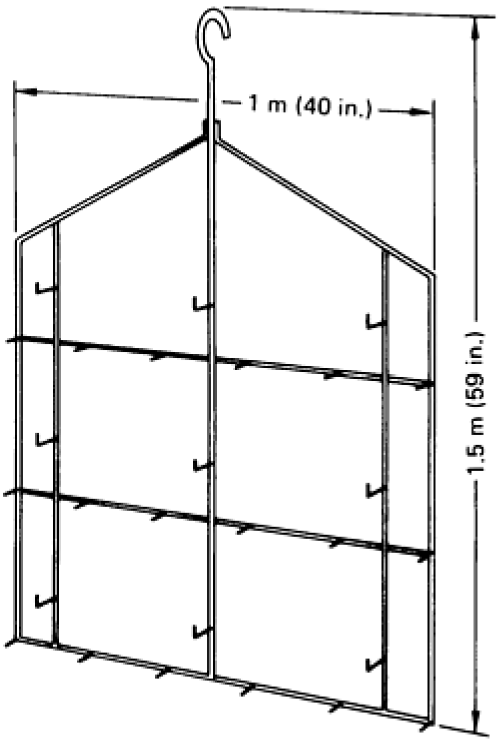


Fig. 2 Rack used for cleaning and phosphate coating small stampings

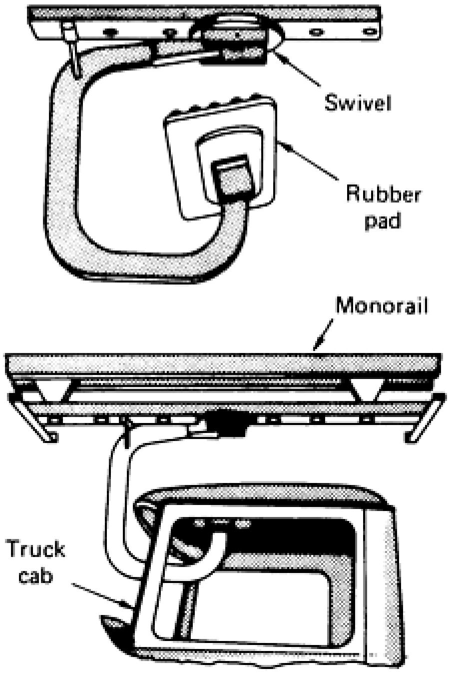


Fig. 3 Arrangement for conveying truck cabs through a five-stage spray cleaning installation

Control of Process Variables

Agitation, operating temperature, acid concentration, solution contamination, and rinsing are the principal variables that affect efficiency and quality in acid cleaning.

Agitation, either of the solution or the work-pieces, is usually necessary in all systems. In wipe on/wipe off methods, agitation is under direct control of an operator. In spray systems, agitation is provided by the impingement of the solution on the workpieces, and the impingement is basically controlled by the pressure. Pressures used in spray systems are commonly 100 to 170 kPa (15 to 25 psi), measured at the pump. Pressures up to 280 kPa (40 psi) are sometimes used for removing tenacious soils. For cleaning complex parts, some experimentation is usually required in adjusting the nozzles to achieve a spray pattern that reaches cavities and crevices.

Immersion systems use a variety of methods for agitation. In smaller production quantities, parts contained in baskets are hand agitated by raising, lowering, and turning. Underwater air jets or mechanical propellers are also effective for agitation in cleaning tanks, and they can decrease the soaking period. In automated immersion systems, the forward motion of parts often provides sufficient agitation. However, this can be enhanced if necessary by simultaneously agitating the solution. In barrel cleaning, agitation of both work and solution is provided by the rotation of the barrel.

Ultrasonic cleaning methods can be applied to acid cleaners in the same manner as is done with other cleaning methods. Because initial cost and maintenance of ultrasonic equipment is high, this form of energy is used only when simpler methods fail to achieve satisfactory cleaning, either because the soil is extremely difficult to remove or because the shape of the workpiece is complex.

Electrolytic cleaning provides agitation from gas evolution, which produces a scrubbing action.

Operating Temperature. Although the efficiency of soil removal increases as temperature increases, a significant amount of acid cleaning is done in unheated solutions, because heated solutions may present the following disadvantages:

- Attack on workpieces increases with temperature Cleaners deteriorate or are used up more rapidly, in part because of dissolved metal
- Surfaces emerging from hot acid solutions are likely to dry and become streaked before they are rinsed
- The life of the tanks and other equipment decreases as operating temperature is increased

As mentioned previously, when acid solutions are heated, temperatures ranging from 60 to 70 °C (140 to 160 °F) are most frequently used. Higher temperatures (up to 80 °C, or 180 °F) are sometimes required to remove soils such as drawing compounds that contain high-melting waxes or greases. In barrel cleaning with solutions of acid salt, temperatures up to 95 °C (200 °F) are sometimes used, but these cleaners are relatively mild so that problems of attack on workpieces and equipment are not great. Maintenance of temperature within ±3 °C (±5 °F) usually provides adequate reproducibility.

Control of cleaner composition is necessary for consistently satisfactory results. Depletion of cleaner by its reaction with workpieces or equipment, dragout, drag-in of alkali or other contaiminants, and decomposition of the cleaner constituents are factors that affect cleaner life.

Chemical analysis using simple titrations for acid and metal content permit control of solution composition. Visual inspection of processed workpieces also indicates condition of the cleaner. In a new installation, when a new solution is being used, or when a different soil is being removed, the solution should be checked every hour until the required frequency of testing is established.

Control of rinsing is necessary for consistently good results. Cold water is adequate for most purposes except when high-melting waxes and greases are being removed. Residues of such soils may set from cold water rinsing. An initial rinse with demineralized water at 70 to 82 °C (160 to 180 °F) is often used when removing these soils. Rinsing qualities of water can be greatly improved by adding a wetting agent at a low concentration. Agitation during rinsing is important and is achieved by the same means used with cleaning solutions.

Rinsing is expensive, but cost can be minimized by using tanks as small as possible, tanks of uniform size if in a series, automatic flush control of contamination limit, and using counterflow rinse tanks.

Sludge buildup is proportional to the amount and type of soils entering the system. Even though sludge buildup does not directly impair the efficiency of an immersion system, a large amount of sludge should not be allowed to accumulate because it may foul heating or control equipment. In spray systems, good filtration and screening are required to prevent fouling of nozzles and related equipment.

Maintenance

For obtaining consistently good results, a regular schedule of maintenance is recommended for any immersion or spray cleaning installation. The required frequency of maintenance varies considerably with the specific operation. Experience with a particular installation soon indicates the items that need close attention to prevent costly shutdowns or inadequate cleaning. The following list suggests a program for maintaining immersion and spray systems:

Daily

- Check temperature
- Check solution concentration
- Check and adjust spray nozzles
- Clean screens in spray systems

Weekly

- Decant or dump solutions and recharge
- Remove sludge from tanks, heating coils, and temperature regulators
- Flush risers in spray systems
- Remove and clean spray nozzles

Monthly

- Inspect exhaust hoods
- Clean tank exteriors
- Check temperature control systems
- Inspect pumps in spray systems
- Inspect spray nozzles, and replace if necessary

Semiannually

- Clean heating coils and exhaust hoods
- Clean and paint exterior components
- Clean riser scale
- Dismantle and repair pumps

Waste Disposal

Disposal of waste acid cleaners is a problem, regardless of whether the location is urban or rural. Several federal, state, and local groups regulate waste disposal. Laws and regulations, such as the Federal Resource Conservation and Recovery Act of 1976, as amended, are subject to change. Therefore, local authorities should be consulted about proposed and current operations.

Safety Precautions

Acids, even in dilute form, can cause serious injuries to the eyes and other portions of the body. Acids are destructive to clothing as well. Therefore operators should be protected with face shields and rubber boots and aprons. Eye fountains and showers adjacent to acid cleaning operations should be provided for use in case of accidents. Nonslip floor coverings in the vicinity of tanks or spray operations are also advised.

Precautions must be taken against cyanides entering the acid cleaning system to avoid formation of deadly hydrogen cyanide (HCN) gas.

Electrolytic cleaning systems are potentially dangerous because of splashing; therefore, rubber shoes and gloves are necessary to protect operators working near these installations. Electric power at 5 to 15 V is not hazardous to operators.

Mist from spray systems or from gassing can be a health hazard. Mist formation increases with the amount of work in process, the temperature, the acidity of the solution, and the current density in electrolytic cleaning. This mist contains all the ingredients of the acid solution. Adequate ventilation is important. Additional information concerning hazards in the use and disposal of acids is given in the article on pickling of iron and steel in this Volume.

Health and safety regulations are made and enforced by several groups within the federal, state, and local governments. Since the regulations vary and are subject to change, the several sets of regulations should be considered when planning an installation or major changes in operations.

Organic Acid Cleaning of Irons and Steels

Organic acids are presently used in a variety of metal cleaning applications. Primary organic acids used in metal cleaning include acetic acid, citric acid, ethylenediamine tetraacetic acid (EDTA), formic acid, gluconic acid, and hydroxyacetic acid. Depending on the application, acids may be used alone, but often are formulated with bases and other additives. Organic acids often replace mineral acids, such as hydrochloric and sulfuric acid, in many metal cleaning applications. Advantages in using organic acids include:

- Efficiency in removing certain metal oxides
- Low corrosivity to base metal
- Safety and ease of handling
- Ease of disposal

Disadvantages of organic acids include longer cleaning times, higher temperature requirements, and higher costs compared to other cleaning operations.

Advantages of Organic Acids

Although organic acids are relatively weak, they remove metal oxides through the following mechanisms. As the organic acid reacts with the metal to produce citrates, acetates and other byproducts, hydrogen gas is released. The hydrogen builds up under the scale and can often lift the remaining oxides off the metal. In addition, organic acids act as sequesterants by tying up the dissolved metal ions and carrying them away from the surface being cleaned. With the use of heated solutions and proper circulation of cleaning solution, organic acids efficiently remove metal oxides.

Low corrosivity to the cleaned metal surface is another important reason for choosing an organic acid over a mineral acid. Mineral acids have high corrosion rates, and repeated cleanings with these solvents can significantly corrode fabricated metal parts. The low corrosion rates of organic acids can be reduced further with the use of corrosion inhibitors. In addition, the sequestering ability of the organic acids allows cleaning at a higher pH, reducing corrosion rates even further. The weak acidic nature of most organic acids and the use of a higher pH than that in mineral acid-based processes provide for safe, easy-to-handle compositions. The cleaning solutions can be used with handheld steam and high-pressure spray equipment. Proper safety equipment should be used when using formic and acetic acids at high concentrations. Most of the organic acids are nonvolatile; therefore, harmful vapors are not released during the cleaning operation.

Spent organic acid cleaning solutions can be disposed of with relative ease. A variety of methods, such as biodegradation, chemical treatment, and incineration, are being used for disposal of organic acid-based cleaning solutions. Spent solutions can be regenerated with techniques such as ion exchange, electrodialysis, and reduction of metal ions with reducing agents.

Applications

Boiler Cleaning

A patented process (Ref 1) removes boiler deposits containing iron oxides, copper oxides, and copper metal with a single filling solution. For iron and copper oxide removal, a 3 to 5% citric acid solution is treated with sufficient ammonia to

achieve a pH of 3.5. The boiler to be cleaned is filled with this solution, heated to 93 °C (200 °F), and the solution is circulated until iron oxide removal is complete. The progress of the iron removal operation is monitored analytically until the iron removal rate levels off. Any copper oxides present are rapidly dissolved in the low-pH citric acid solution; however, dissolved copper ions tend to plate out on the cleansed steel.

This plated copper is removed during the second stage of the cleaning process, which also results in a passive metal surface. The second-stage cleaning solution is prepared by ammoniating the same filling solution to pH 9.5 and allowing the temperature to drop to 49 °C (120 °F). An oxidant, such as sodium nitrite at a level of 0.25 to 0.5% of the solution weight, is added to oxidize ferrous ions to ferric ions, which are responsible for dissolving the plated copper according to the following equation:

$$2Fe^{+3} + Cu^{0} \rightarrow 2Fe^{+2} + Cu^{+2}$$

The dissolved copper is stabilized as the copper-ammonium complex, $Cu(NH_3)_4^{+2}$. The high-pH solution is also responsible for producing a film of hydrated iron oxide, which results in a passivated surface that remains rust-free while the citrate solution is removed and the boiler is rinsed with water. The unit is then ready to be placed back into service. To further protect the boiler components during the cleaning cycle, acid inhibitors designed for use with citric acid are available.

Stainless Steel Cleaning

Some of the uses for organic acids in the cleaning and finishing of stainless steels are presented below.

Acid Cleaning. Organic acid solutions are used to remove rust and mill scale from newly fabricated stainless steel stock. By removing embedded iron and scale from the stainless steel surface, the appearance and corrosion resistance of the alloy are restored. A typical formulation for this application consists of 5% dibasic ammonium citrate containing 0.1% wetting agent at a temperature of 80 °C (180 °F). This solution finds particular use in cleaning equipment for storage and manufacture of foods, beverages, fine chemicals, and pharmaceuticals.

Steam Cleaning. A particularly useful technique for cleaning these types of fabricated stainless steel tanks, as well as stainless steel machinery, trucks, and railroad cars, involves steam cleaning. A concentrated organic acid solution is injected into a high-pressure jet of steam at a rate that yields 1 to 5% concentration by weight in the superheated solutions. A low-foaming nonionic wetting agent added to the acid solution removes oil and grease from the steel surfaces.

Alkaline Cleaning. Caustic gluconate solutions, prepared by dissolving gluconic acid or sodium gluconate in caustic soda, are useful for removing both organic soils and metal oxides with one solution. Also, because the solution is on the alkaline side, the cleaned metal surface has little tendency to rerust (Ref 2).

Nuclear Power Plant Decontamination. Oxidation products of alloys used in nuclear power plant construction must be dissolved and flushed out of the unit. Because these oxidation products often contain radioactive materials, solvent and rinse waters require care in disposal. The following considerations are important for proper disposal of waste material: solvent volumes should be as slow as possible; the solvent should be compatible with different waste disposal methods, and quantitative stabilization of the radioactive materials in solutions should be maintained throughout solvent transfer and sampling. Among the cleaning methods employed, most involve an oxidizing pretreatment with alkaline permanganate (AP) followed by a chelant removal of the deposit. Among the chelant treatments are the following:

- Alkaline permanganate-ammoniated citric acid (APAC) -- citric acid, 5 to 10%, ammoniated to pH 5 to 7
- Alkaline permanganate-ammoniated citric acid-EDTA (APACE) -- citric acid, 2%; dibasic ammonium citrate, 5%; disodium EDTA, 0.5%

Additional benefits of using organic acids in stainless steel cleaning solutions are that they are chloride-free, which eliminates the problem of chloride-stress cracking, and their weakly acidic nature reduces the chances of hydrogen embrittlement (Ref 3). Additional applications include cleaning lube oil systems, heat exchanger surfaces, pendant

superheaters and reheaters, and startup and operational cleaning of once-through boilers (Ref 4). Two new applications for organic acids have been developed.

Removal of Iron- and Copper-Bearing Deposits

A citric acid-based cleaning method is used to derust the steel shells of heat exchangers containing a high ratio of copper to iron, such as is found in marine air conditioning units. When the fluorocarbon refrigerant becomes contaminated with small amounts of water, corrosive hydrochloric and hydrofluoric acids are formed, causing significant corrosion of the steel shells. These corrosion products must be removed to restore the unit to its proper functioning.

Standard organic acid cleaning techniques are inadequate in this application due to the large amounts of copper oxides present, which are more easily dissolved than the iron oxide and tend to consume the organic acid before the iron oxides can be removed. To overcome this problem, a citrate-based cleaning formulation is modified to contain a reducing agent, which reduces the dissolved copper oxides to precipitated copper metal, which is filtered from the solution. This precipitated copper removal restores the citric acid content of the solution, making it available to dissolve the iron oxides. Any copper metal residue remaining in the system from the first solution is removed in a second step, which is also a citric acid-based solution. The second step also passivates the steel surfaces. The specific formulas for step one and step two are:

- **Step 1: Iron and copper oxide removal** 3% citric acid, 3% erythorbic acid, pH adjusted to 3.5 with triethanolamine (replaces ammonia, which is corrosive to copper).
- **Step 2: Copper metal removal and passivation** A second solution is prepared as follows: 3% trisodium citrate, 1.2% triethanolamine, 1% sodium nitrite (Ref 5). It is important that the order of additions be followed precisely to avoid toxic nitrogen oxide gas generation.

Another new application is the use of an EDTA-based solution to dissolve iron- and copper-bearing deposits from pressurized water reactor nuclear power plants. In pressurized water reactor nuclear power plant steam generators, the accumulation of secondary side corrosion deposits and impurities forms sludges that are composed primarily of metal oxides and metallic copper deposits. To remove these deposits, the following solution has been found effective:

Iron solvent

- 10% EDTA
- 1% hydrazine
- Ammonium hydroxide to pH 7
- 0.5% inhibitor CCI-80/1 applied at 90 to 120 °C (195 to 250 °F)

Copper solvent

- 5% EDTA
- Ammonium hydroxide to pH 7
- EDA (ethylenediamine) to pH 9.5 to 10.0
- 2 to 3% hydrogen peroxide applied at 32 to 43 °C (90 to 110 °F) (Ref 6)

References cited in this section

1. S. Alfano, "Process for Removing Copper-Containing Iron Oxide Scale from Metal Surfaces," U.S. Patent 3,072,502
2. W.J. Blume, Role of Organic Acids in Cleaning Stainless Steels, *Cleaning of Stainless Steels,* STP 538, ASTM, 1973, p 43-53

3. "Chemical Cleaning with Citric Acid Solutions," Data Sheet No. 672, Pfizer, Inc., 1981, p 13-14
4. A.H. Roebuck, Safe Chemical Cleaning--The Organic Way,*Chem. Eng.,* 31 July 1978, p 107-110
5. D.R. Uhr, Jr., Citric Acid-Based Cleaning of Mixed Metal Systems, Paper No. 217, *Corrosion 80,* 3-7 March 1980
6. D.J. Stiteler et al., A Chemical Cleaning Process to Remove Deposits from Nuclear Steam Generators, Paper No. 32, *Corrosion 82,* 22-26 March 1982

Acid Cleaning of Nonferrous Alloys

Aluminum Alloys. Acid cleaning of aluminum may be used alone or in conjunction with other acid, alkaline, or solvent cleaning systems. Vapor degreasing and alkaline cleaning may be required for removal of heavy oils and grease from workpieces before they are immersed in an acid bath. One of the main functions of an acid cleaner is the removal of surface oxides prior to resistance welding, painting, conversion coating, bright dipping, etching, or anodizing.

A mixture of chromic and sulfuric acids is commonly used to remove surface oxides, burntin oil,water stains or other films, such as the iridescent or colored films formed during heat treating. This acid mixture cleans and imparts a slightly etched appearance to the surface, preparing it for painting, caustic etching, conversion coating, or anodizing. Nonpolluting, proprietary products free of chromic acid are available for acid cleaning and deoxidizing.

When tungsten and molybdenum are slightly oxidized on the surface or after the heavily oxidized workpiece is cleaned with molten caustic, acid cleaning is used. The acid solution consists of 50 to 70 vol% concentrated nitric acid, 10 to 20% concentrated hydrofluoric acid, remainder water. The cleaning solution is best when maintained at temperatures of 50 to 65 °C (120 to 150 °F).

Tantalum and Niobium. After mechanical grinding, abrasive blasting, or alkaline cleaning, tantalum and niobium are cleaned further with an acid solution. This consists of 40 to 60 vol% concentrated nitric acid, 10 to 30% concentrated hydrofluoric acid, remainder water. This cleaning solution is best when maintained at temperatures of 50 to 65 °C (120 to 150 °F). After acid cleaning, the workpiece should be washed with water or rinsed thoroughly with a jet of water to remove any traces of acids.

Good ventilation and drainage systems should be installed in the acid cleaning or pickling room. A recycling system to remove the residues and to refresh the acid is preferred for both economical and ecological reasons.

Mechanical Cleaning Systems

Revised by Ted Kostilnik, Wheelabrator Corporation

Introduction

MECHANICAL CLEANING SYSTEMS are available for most industrial production applications to remove contaminants and prepare the work surface for subsequent finishing or coating operations. Typical uses include:

- Removing rust, scale, dry solids, mold sand, ceramic shell coatings, or dried paint
- Roughening surfaces in preparation for bonding, painting, enameling, or other coating substances
- Removing large burrs or weld spatter
- Developing a uniform surface finish, even when slightly dissimilar surfaces are present
- Removing flash from rubber or plastic molding operations
- Carving or decorative etching of glass, porcelain, wood, or natural stone such as granite or marble

The types of workpieces that can be mechanically cleaned include:

- Ferrous and nonferrous castings
- Forgings or stampings
- Steel plate, strip, or structural shapes

- Weldments and fabrications of ferrous and nonferrous materials
- Aluminum, magnesium, or zinc permanent mold or diecast items
- Thermoplastic or thermoset plastics
- Steel bar stock and wire rod
- Precision molded rubber parts
- High-alloy dies and molds for rubber, plastic, glass, or metal parts
- Miscellaneous exotic parts

Mechanical cleaning systems use various types of abrasive materials that are energized or propelled against the work surface of the part through one of three principal methods: airless centrifugal blast blade- or vane-type wheels; compressed air, direct-pressure dry blast nozzle systems; or compressed-air, indirect-suction (induction) wet or dry blast nozzle systems. Other available methods, not discussed in this article, include aggressive vibratory systems, media tumbling systems, and part-on-part tumbling systems.

Propelling Abrasive Media

Abrasive blast cleaning began commercially with air or steam directed through a conduit of pipe or hose with a final nozzle to direct the impacting abrasive stream. Both pressure blast and suction blast nozzle systems require high power to generate the compressed air or pressurized steam that is used to accelerate and propel the abrasive. This requirement is due to aerodynamic inefficiencies in accelerating the spherical and angular abrasive particles, especially the higher-density ferrous abrasives.

Wheels. Airless abrasive propelling wheels that use blades or vanes require about 10% of the horsepower required by air blast systems to throw equal volumes of abrasive at the same velocities. The power losses in an airless system are the friction between the abrasive and vanes, the impeller-control cage interference, and the wheel-drive system.

Airless abrasive blast wheels are generally of the blade type, as shown in Fig. 1. These wheels may have one or two side plates, one of which is attached to a hub, shaft bearings, and belt drive, or the side plate may be attached directly to the shaft of a suitable motor. The side plate holds four to twelve throwing blades, depending on the size of the wheel. Blade tip diameters range from 205 to 660 mm (8 to 26 in.) and blade widths range from 40 to 125 mm (1.5 to 5 in.). Rotational speeds range from 500 to 4000 rev/min or more. Usable abrasive velocities range from 15 m/s (50 ft/s) to 122 m/s (400 ft/s), with 75 m/s (245 ft/s) the most widely used velocity. Abrasive flow rates with steel shot range from 23 kg/min (50 lb/min) up to 1040 kg/min (2300 lb/min) with a 100 hp motor.

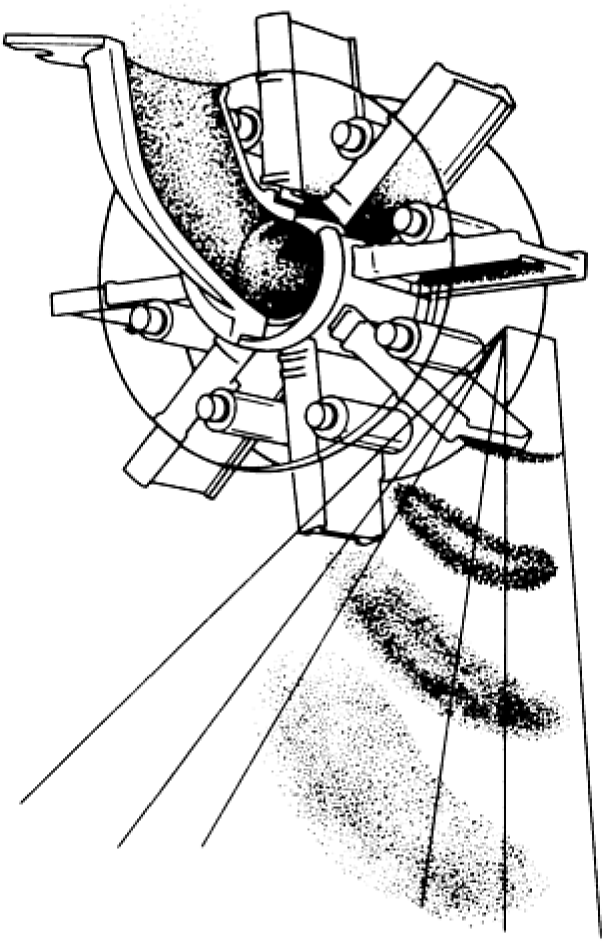


Fig. 1 Blade-type airless centrifugal abrasive blast wheel

Figure 1 also shows the operation of a blade-type wheel. A controlled flow of abrasive (through a valve not shown) is fed by gravity into an abrasive feed spout from which it flows into a rotating vaned impeller. The impeller rotates at the same speed as the bladed wheel, and the number of vanes is equal to the number of wheel blades. The impeller rotates in a stationary cylinder (referred to as a control cage or impeller case) that is equipped with an opening that may be rotated and locked in a preferred position. As the impeller forces the abrasive out of the control cage opening, each of the blades picks up a metered amount of abrasive at the inner end of the blade and accelerates the abrasive to produce a tent blast pattern, as shown.

Centrifugal blast wheel units are enclosed in housings to prevent the discharge of stray abrasive. The principal wearing parts of the blast wheel assembly are the impeller, control cage, wheel blades, and housing liners. These parts are most economically made of high-alloy cast iron, and each can be individually replaced. Unalloyed cast iron parts, although less expensive, have a very short life under normal operating conditions.

The life of these parts is influenced primarily by the type and condition of the abrasive medium and contaminants picked up in the cleaning process. Abrasive materials are discussed in depth later in this section. Clean steel shot provides the longest useful life of wheel and guard housing liners. Much greater wear results from the use of nonmetallic abrasives such as sand, aluminum oxide, and silicon carbide. Table 1 shows the effects of abrasive in various conditions on the life of the components of a centrifugal blast wheel unit. Relatively little wear on wheel parts and housing liners is caused by glass beads, nonferrous shot, or the agricultural abrasives frequently used in deburring and special finishing applications.

Table 1 Effect of abrasives on life of components of a centrifugal blast wheel unit

Abrasive	Life of components[(a)], h

	Blades	Impeller	Control cage/case	Alloy housing liners
100% steel shot (few fines)	600	600	600	3000
Steel shot, 1% sand	100-200	100	100	2000
Steel shot, 3% sand	15-50	50	50	1500
100% steel grit[(b)]	125-150	150	150	1000-1500
100% sand	4-6	4-8	4-8	500

(a) Life based on running time of centrifugal blast wheel 495 mm (19 $\frac{1}{2}$ in.) diam and 65 mm (2 $\frac{1}{2}$ in.) wide, 30 hp drive and flow rate of 375 kg/min (830 lb/min).

(b) G25 grit; hardness, 55 to 60 HRC

Centrifugal wheel-type blast machines may be relatively simple, having a single blast wheel, a simpler work conveyor, an abrasive recycling system, and a dust collection device.

Pressure blast nozzle systems generally rely on a 685 kPa (100 psig) air supply to propel the abrasive through a special nozzle. A typical intermittent pressure tank (Fig. 2) has dimensions of 610 by 610 mm (24 by 24 in.) and an abrasive discharge capacity of 0.12 m^3 (4.2 ft^3). This capacity is adequate to operate one 6 mm ($\frac{1}{4}$ in.) diameter blast nozzle for 30 to 60 min. This type of tank is refilled through the filling valve by gravity when the air supply is shut off. Without air pressure in the tank, the filling valve is pushed down and open by the weight of the abrasive. When the air pressure is turned on again, the valve rises and stops the flow of abrasive into the tank. The abrasive in the now-pressurized tank moves into a mixing chamber. Mixing chambers usually are equipped with an adjustable control to regulate the flow rate of abrasive into the mixing chamber and on through the hose and nozzle assembly. The pressure tank and filling valve may be vertically doubled with a timer and proper valving to provide a continuous automatic pressure tank.

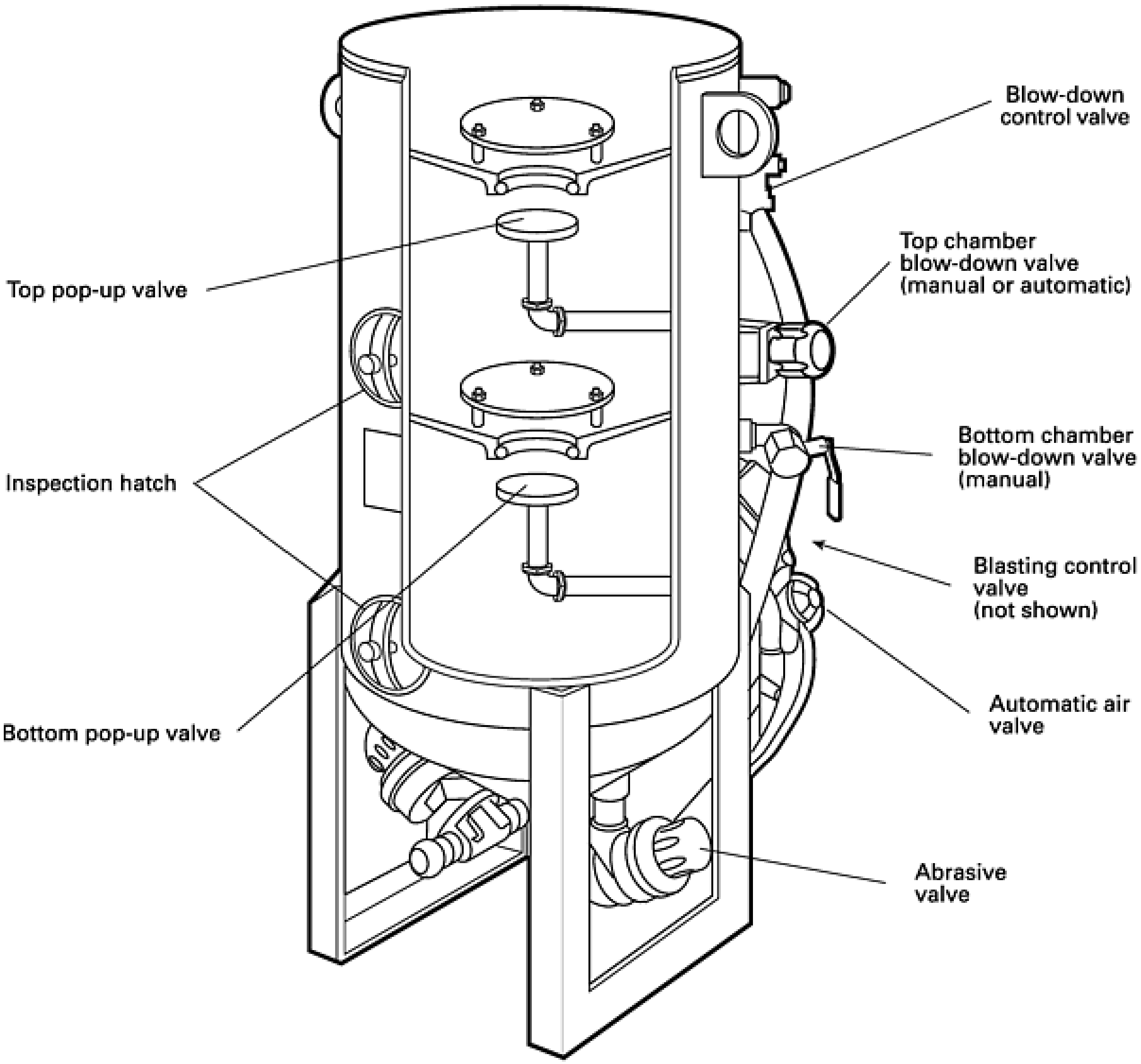


Fig. 2 Double-chamber abrasive blast pressure tank. Courtesy of Bob Thompson, Schmidt Manufacturing Inc.

Airblast nozzles are used in a variety of shapes, some as simple as a piece of pipe. Most systems are replaceable nozzles of metal alloys or nozzles with wear-resistant ceramic inserts. The latter nozzles may be of straight bore or venturi cross section. All types of abrasive may be handled with the pressure blast system in a variety of environments. In exceptional cases, air pressure blasting is performed in an open field with sand as the abrasive. Protective clothing and a helmet with air supply are the only health precautions taken. Quite often the sand is not recovered after use.

Suction blast cabinets are generally considered the simplest form of abrasive blast equipment. They may be used manually or have fixed or oscillating nozzles. Figure 3(a) illustrates a 1220 by 915 by 840 mm (48 by 36 by 33 in.) suction blast cabinet.

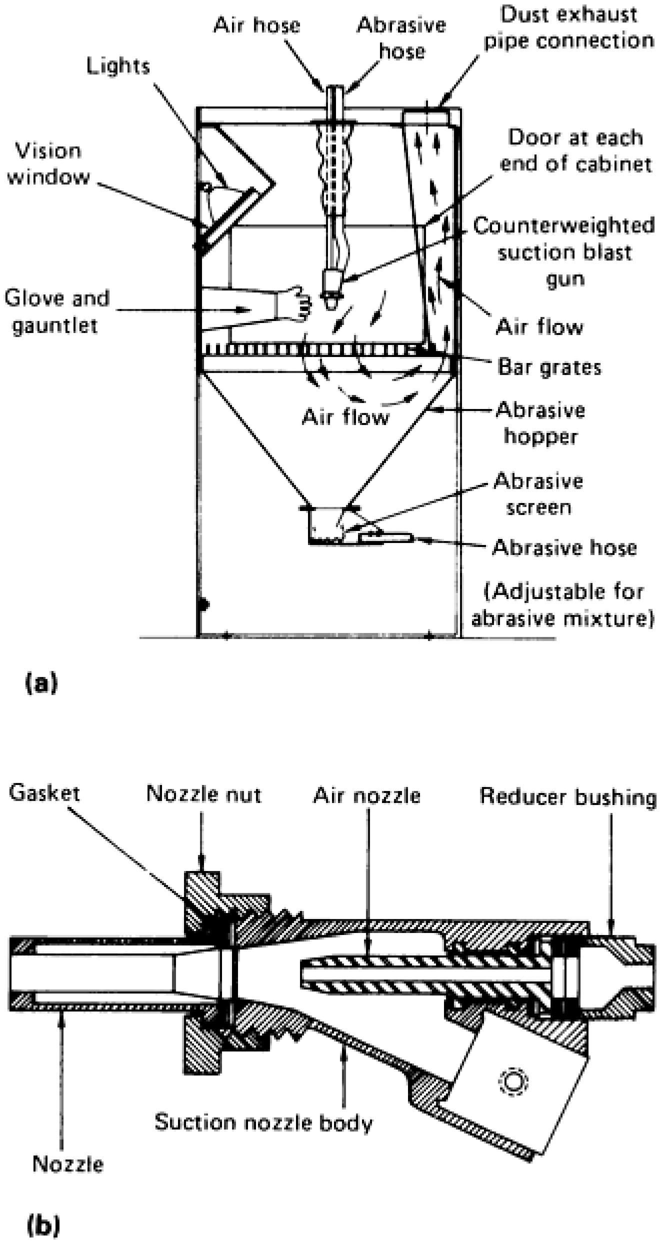


Fig. 3 Suction blast equipment (a) cabinet. (b) Nozzle assembly

Figure 3(b) illustrates a suction blast nozzle assembly. The nozzle in the suction cabinet is an induction nozzle that creates a blasting mixture by the siphon effect of the air discharged through the nozzle body. This effect pulls abrasive through the abrasive hose from the cabinet hopper, and the blast mixture is formed within the nozzle body. Because only compressed air flows through the air nozzle, the air consumption remains constant. The air nozzle is cast of a wear-resistant alloy. The nozzle can be used until considerably enlarged without affecting the efficiency of the blast. This cannot be done in a direct-pressure blast nozzle without seriously affecting air consumption. The amount of abrasive or the mixture of air and abrasive can be controlled in the suction cabinet by changing the relative position of the end of the abrasive hose to the abrasive flowing from the cabinet hopper.

Equipment for Dry Blast Cleaning

Dry blast cleaning is probably the most efficient and environmentally effective method for abrasive cleaning and finishing. Proper ventilation helps maintain a clean work area. No settling ponds or chemical treatment are required. Dust collectors provide dust disposal that is clean and simple, using sealed containers. Dry-blast systems need only be kept dry and can be started and stopped with minimum startup or shutdown operations. Several types of equipment are available

for dry blast cleaning, and equipment selection is primarily based on the type of parts to be blasted and the relative throughput required.

Cabinet Machines. A high percentage of dry blast cleaning is performed using cabinet machines. A cabinet houses the abrasive-propelling mechanism, such as a centrifugal wheel or compressed air nozzle(s), holds the work in position, and confines flying abrasive particles and dust. Cabinets are available in a wide range of sizes, shapes, and types to meet various cleaning, production, and materials handling requirements. Cabinet machines may be designed for manual, semiautomatic, or completely automated operation to provide single-piece, batch, or continuous-flow blast cleaning.

The table-type machine (Fig. 4) contains a power-driven rotating worktable. Within the cabinet, the blast stream is confined to approximately half the table area. The unit shown is self-contained and mounted on the floor. The work is positioned on the slowly rotating table, and the abrasive particles are propelled by an overhead centrifugal wheel. When the doors are closed, blast cleaning continues for a predetermined time. Some table-type machines are designed with one or more openings in the cabinet. These openings are shielded by curtains and permit continuous loading and unloading or movement of parts during the blast cycle.

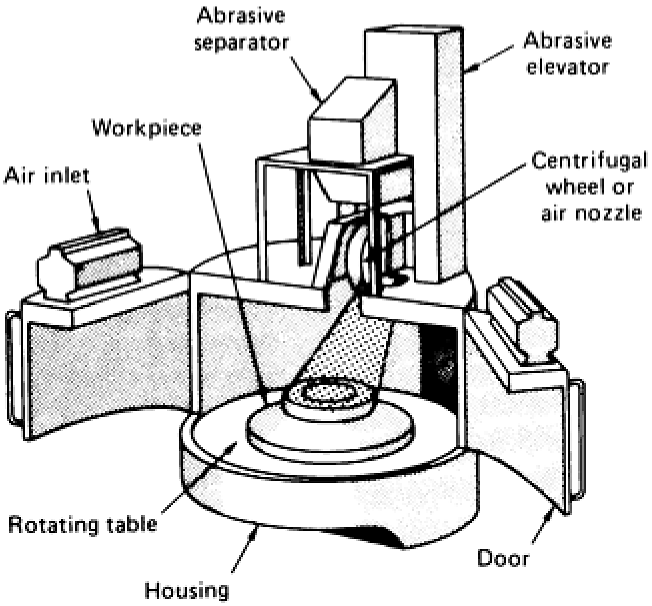


Fig. 4 Table-type blast cleaning machine. The centrifugal wheel propels the abrasive particles.

Removal of the contaminants and fines is performed with an airwash separator, as shown in Fig. 5. Spent abrasive and contaminants are fed by a belt and bucket elevator to the helicoid conveyor. The abrasive is screened in the rotary screen, falls in a vertical curtain, and passes under a swinging baffle. The abrasive is then subjected to a controlled cross-flow of air, which cleans it and removes foreign contaminants and fines. Finally, the abrasive gravitates to a storage hopper and is ready for reuse, while contaminants are routed to disposal.

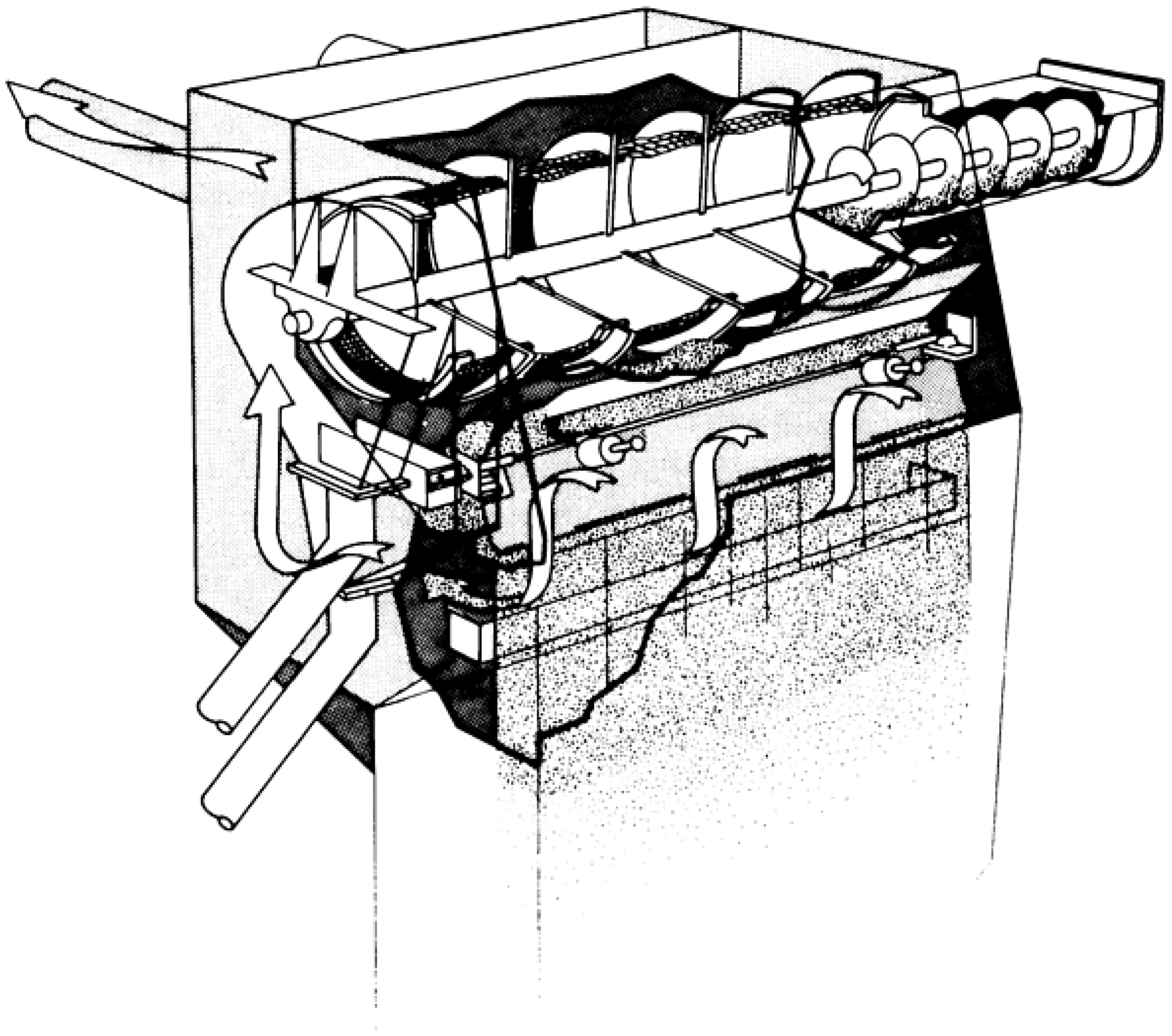


Fig. 5 Airwash separator

Continuous-flow machines equipped with proper supporting and conveying devices are used for continuous blast cleaning of steel strip, coil, and wire. These machines are also used to clean castings and forgings at a high production rate, making use of flat face or skew rolls, monorails, and other continuous work-handling mechanisms.

A continuous centrifugal blast cleaning machine, equipped with a monorail, is shown in Fig. 6. In operation, the work is loaded outside the blast cabinet and is conveyed into it through a curtained vestibule, which can be designed with 90° turns to reduce the escape of flying abrasive particles. The conveyor indexes the work to the center of each blast station and rotates it for complete blast coverage. If the workpiece contains intricate pockets, it may be indexed to an off-center position and be slowly conveyed past the blast in a manner that most effectively exposes the pockets to the abrasive stream. To minimize cycle time, the work is moved at an accelerated rate between blast stations. As it is conveyed and rotated on a return passageway that follows along the back of the cabinet, the work is exposed to additional cleaning and acts as a barrier to protect the cabinet walls from wear. Continuous-flow machines incorporate abrasive recycling facilities and an exhaust system for removing dust and fines.

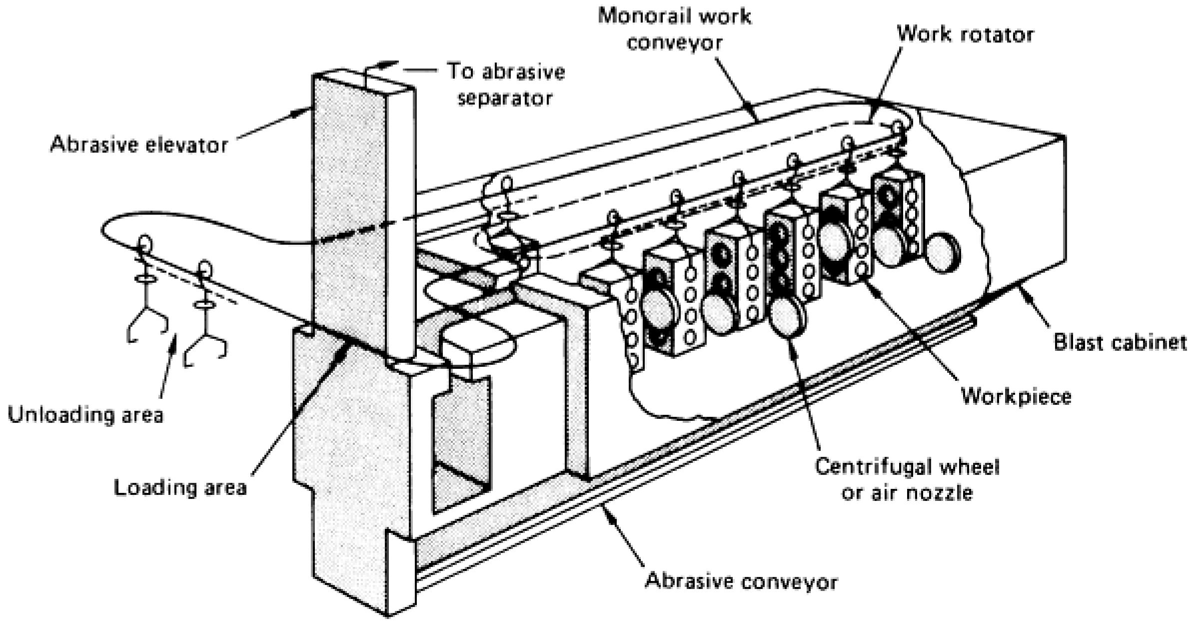


Fig. 6 Continuous centrifugal blast cleaning machine

Blasting-tumbling machines (Fig. 7) consist of an enclosed endless conveyor, a blast-propelling device or devices, and an abrasive recycling system. These machines simultaneously tumble and blast the work. They are made in various sizes to accommodate work loads from 0.03 to 2.8 m^3 (1 to 100 ft^3). The work usually is loaded into the conveyor by means of a skip-bucket loader. As the conveyor moves, it gently tumbles the work and exposes all workpiece surfaces to the abrasive blast. At the end of the cleaning cycle, the conveyor is reversed and the work is automatically discharged from the machine.

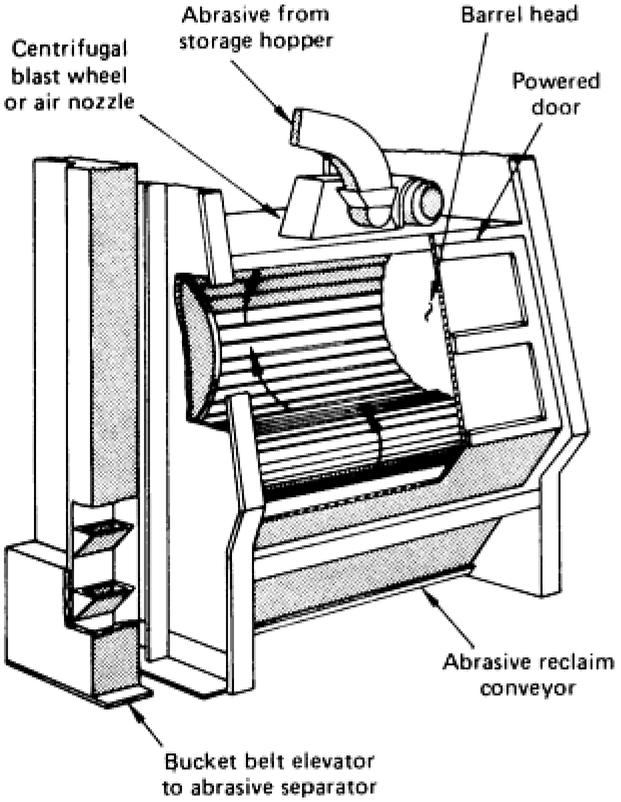


Fig. 7 Blasting-tumbling machine

Blasting-tumbling machines are used for cleaning unmachined castings, forgings, and weldments whose size, shape, and material permit them to be tumbled without damage. This equipment is not used for cleaning parts after machining, because tumbling damages machined surfaces. Blasting-tumbling machines remove dry contaminants such as sand, rust, scale, and welding flux, and they provide surface preparation for enameling, rubber bonding, electroplating, or etching before galvanizing. Blasting-tumbling machines can be integrated into automatic systems for high production rates. An example is the presort and tote box loader work-handling system shown in Fig. 8. Automatic vibrating feeder conveyors are also available to feed single or multiple machines in lieu of skip-bucket loaders.

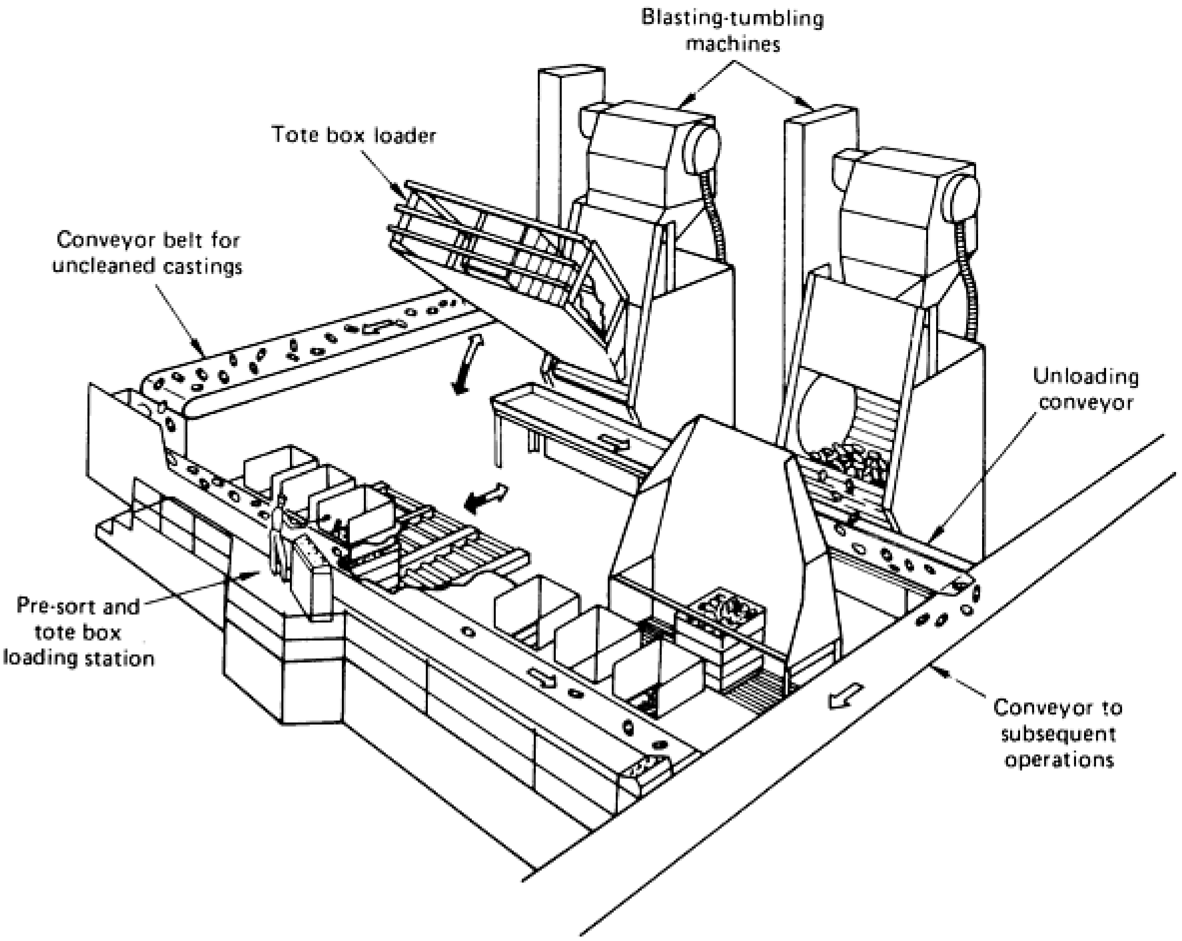


Fig. 8 Presort and tote box loader work-handling system. The sorter operates the tote box shuttle to and from the blasting-tumbling machine.

Portable Equipment. When parts to be cleaned are too large to be placed in blasting machines, portable equipment, such as air blast equipment, can be brought to the workpiece. A low-cost sand usually is used, because it is difficult to reclaim or recirculate the abrasive with portable equipment. Also, it is necessary to prevent random scatter of flying particles.

Portable recycling equipment is a new development in air pressure blasting. This equipment uses a pressurized media hose contained within a larger, evacuated hose. After impact, the media are returned through the outer hose to the central unit for reclaiming and recycling. A brush baffle prevents escape of media at the part surface. With this equipment, large external jobs may be done with specialized media without environmental problems.

Microabrasive blasting is another portable air blasting method. Both the abrasive particle size and nozzle opening are very small. Particle sizes are normally 10 to 100 μm (0.4 to 4 mils) and nozzle openings are 0.4 to 1.2 mm (0.015 to 0.045 in.) in diameter. The tungsten carbide nozzle tips are usually screwed into a pencil-shaped handpiece. Microabrasive blasting is normally a handheld operation for precision deburring, cleaning, or surface preparation. The design of the handpiece and the size of the abrasive particle allow a large degree of control in pointing the blast at the work surface. This is advantageous in deburring or cleaning blind orifices, intersecting slots, or internal bores with irregular surfaces. Microabrasive blasting is not effective for gross material removal or for covering large areas. Dryness and uniformity of particle classification are very critical, and abrasives cannot be reused. Because of the small nozzle size and the types of applications, abrasive usage is not excessive and nonreclamation is reasonable. In continuous-duty operation, 0.2 to 0.5 kg ($\frac{1}{2}$ to 1 lb) of abrasive is consumed per hour.

Ventilation. To ensure adequate ventilation of abrasive blast cabinets, a fabric filter dust collector is generally used with properly designed duct work. The fabric filters are generally equipped with exhaust fans on the clean-air side of the dust collector. This location is preferred because it eliminates erosion of the exhaust fan parts.

Two primary styles of fabric filter collectors are used. The first and oldest is the mechanical shaker type, in which an eccentric style drive activates pivoting racks from which the filters are suspended, providing periodic filter cleaning. A second type is the pulse jet, which uses tubular filter bags made of natural fibers or synthetic felt with an internal support cage of heavy wire and a venturi. Dust and foreign material accumulate on the outer surfaces of the bag and are removed by a short-time, high-pressure pulse of compressed air into the top opening of the venturi. Both types of fabric filters can be designed for light or heavy dust loadings and have throughput capacities from 2.83 m^3/s (100 ft^3/min) to several thousand cubic meters per second. The newest type of filter system uses a cartridge in lieu of a fabric tube. The cartridge is either paper- or fabric-based and is also cleaned by compressed-air pulsing.

Maintenance. Abrasive blasting machines are essentially self-destructive, and every effort must be made to protect components from the violent action of the abrasive. Machine interiors should be protected with wear-resistant cast or alloy metal liners or with heavy rubber mats or sheets to prevent erosion of metallic surfaces. High-velocity particles usually bounce from the rubber without damage to either the rubber or the abrasive. If the rubber receives the full impact of the blast, it will require periodic replacement.

Following are typical maintenance schedules that have proved satisfactory for the principal types of abrasive blasting machines:

Centrifugal wheel machines: weekly

- Check blades and wheel for wear. An unbalanced wheel can cause bearing wear and shaft bending. Install new blades if needed, check wheel balance, and test for cleaning pattern.
- Check for loose buckets on elevator belt; loose buckets may catch on the elevator shaft.
- Check sprocket at top and bottom of elevator shaft for wear and broken teeth.
- Check for wear on top plates of machine, rubber table tops, and table rings.
- Check for leaks in ventilation ducts.
- Check entire machine for possible wear holes through which abrasive might escape.
- Check rubber flaps at opening of machine for wear and escaping abrasives.

Automatic air blast machines: daily

- Check all nozzles and air jets for wear and proper flow.
- Check media and air hoses for leaks.
- Check table plates and rubber table tops for wear.
- Check suction lines for leaks.
- Check belts and chain for wear or slippage.
- Check shear pin; replace if necessary.

Hand air blast machines: daily

- Check nozzles and air jets for wear and proper flow.
- Check the following for leaks: media and air hoses, door gaskets, roof bellows and gauntlets, suction lines.
- Check gun bodies for uneven wear.
- Check suction lines for leaks.

Cycle Times for Dry Blast Cleaning

The amount of abrasive blasting required for a specific application depends on the workpiece material, the surface finish requirements, and the performance characteristics of the blast equipment. No dependable formula exists for establishing minimum blasting cycles; the amount of blasting time required to produce a given result in a given machine is established by trial. Table 2 lists abrasives, equipment, and cycles that have been used for dry blasting a number of materials or products for specific purposes.

Table 2 Abrasives, equipment, and cycles used for dry blasting

Material or product	Reason for blasting	Abrasive		Equipment				
				Type	Horse-power	Nozzle diameter		Blasting cycle
		Type	Size No.			mm	in.	
Ferrous metals								
Cast iron	Prepare for zinc impregnation	Iron grit	G80	Air, table[(a)]	. . .	6	$\frac{1}{4}$	1 h
	Remove molding sand	Steel shot	S230	Wheel, barrel	15	. . .	. . .	10 min
Cold rolled steel	Remove graphite for painting	Iron grit	G80	Wheel, barrel	15	. . .	. . .	10 min
				Air, table[(a)]	. . .	6	$\frac{1}{4}$	40 min
Gray iron exhaust manifolds, bearing caps	Clean for machining	Malleable iron shot	S460	Wheel, tumble[(b)]	80	. . .	. . .	1500 pieces/h
Gray iron motor blocks and heads	Remove sand and scale after heat treatment	Steel shot	S460	Wheel, blast cabinet[(c)]	500	. . .	. . .	6 s
Hardened steel screws	Remove heat treat scale	Iron grit	G80	Wheel, barrel	10	. . .	. . .	5 min

Material or product	Reason for blasting	Abrasive		Equipment				
				Type	Horse-power	Nozzle diameter		Blasting cycle
		Type	Size No.			mm	in.	
Hot rolled steel	Prepare for painting	Iron grit	G80	Air, table[(a)]	. . .	6	$\frac{1}{4}$	1 h
Malleable iron castings	Prepare for galvanizing	Steel grit	G50	Wheel, barrel	40	. . .	. . .	15 min
Pole-line hardware	Prepare for galvanizing	Steel grit	G50	Wheel, barrel	40	. . .	. . .	15-20 min
Round steel bar	Etch for adhesive coating	Iron grit	G80	Air, blast room	. . .	6	$\frac{1}{4}$	2 min
Soil pipe fittings	Remove molding sand	Steel shot	S330	Wheel, barrel	30	. . .	. . .	181 kg (400 lb) in 5 min
Steel drums	Prepare for painting	Iron grit	G80	Air, blast room	. . .	6	$\frac{1}{4}$	4 min
Steel rod	Clean for wiredrawing	Steel grit	G40	Wheel, continuous[(d)]	80	. . .	. . .	0.2-1.5 m/s (40-300 ft/min)
Steel screws	Prepare for plating	Iron grit	G80	Air, barrel[(a)]	. . .	8	$\frac{5}{16}$	2 min
Structural steel	Prepare for painting	Steel grit	G40	Wheel, continuous[(d)]	80	. . .	. . .	0.02 m/s (30 ft/min)
Weldments (steel)	Remove scale, welding flux, and splatter for painting	Steel grit	G25	Wheel, barrel	30	. . .	. . .	136-272 kg (300-600 lb) in 7 min
Engine parts for rebuilding	Remove paint, scale, and carbon deposits	Glass beads	60-100 mesh	Air	. . .	6	$\frac{1}{4}$	5-20 min
Nonferrous metals								

Material or product	Reason for blasting	Abrasive		Equipment				
				Type	Horse-power	Nozzle diameter		Blasting cycle
		Type	Size No.			mm	in.	
Aluminum	Produce frosted surface	Sand	50	Air, barrel	. . .	6	$\frac{1}{4}$	20 min
	Prepare for painting	Iron grit	G80	Wheel, barrel	15	. . .	. . .	5 min
Bronze	Produce frosted surface	Sand	50	Air, barrel	. . .	6	$\frac{1}{4}$	20 min
Aluminum and bronze	Prepare and condition surface	Glass beads	20-400	Air	. . .	6	$\frac{1}{4}$	5-20 min
Nonmetallic materials								
Clear plastic parts	Produce frosted surface	Sand	50	Air, barrel	. . .	6	$\frac{1}{4}$	15 min
Hard rubber	Improve appearance	Sand	50	Air, barrel	. . .	6	$\frac{1}{4}$	20 min
Molded plastic parts	Remove flash	Walnut shells	. . .	Wheel, barrel	10	. . .	. . .	8 min
Phenolic fiber	Produce frosted surface	Sand	50	Air, barrel	. . .	6	$\frac{1}{4}$	30 min
	Prepare for painting	Sand	50	Air, barrel	. . .	6	$\frac{1}{4}$	20 min

(a) Four air nozzles.

(b) Two wheels, 40 hp each.

(c) Ten wheels, 50 hp each.

(d) 4 wheels, 20 hp each

Applications and Limitations of Dry Blast Cleaning

Virtually all metals can be cleaned by at least one of the available abrasive blasting processes, but the abrasive medium must be carefully selected for soft, fragile metals and their alloys, such as aluminum, magnesium, copper, zinc, and beryllium. Otherwise, abrasive blasting may result in severe surface damage.

In some instances, abrasive blast cleaning induces residual compressive stresses in the surface of the workpiece. This is especially true with steel shot or glass beads. Although these stresses are highly desirable in terms of fatigue strength, they are detrimental to electrical components, such as motor laminations, because they alter electrical and magnetic characteristics.

Blasting at high pressures with a large particle size may produce warping in thin sections of steel and other metals as a result of induced stresses.

The blasting of extremely hard and brittle materials may result in chipping and excessive media consumption.

The corrosion resistance of stainless steels may be adversely affected by the adherence of dissimilar metals on the matte surface that is produced by abrasive blasting with metallic media. If this is a concern, grit blasting should be followed by chemical cleaning, or a stainless steel medium should be used.

Abrasive blasting usually roughens highly finished surfaces, particularly those of low hardness, so it is unsuitable for cleaning parts for which dimensional or surface finish requirements are critical.

The peening effect of abrasive particles may distort flat parts, particularly those with a high ratio of surface area to volume, such as clutch disks, long thin shafts, and control bars.

Even when the application of abrasive blast cleaning is known to be advantageous for a specific part, the particular abrasives and process selected should be entirely compatible with part requirements. For example, because small fragile parts may break in a tumbling operation, they should be processed in a stationary position on a rotating table or in conveyor equipment.

Shields or caps made of abrasion-resistant rubber compounds, sheet metal, or plastics are used to protect threaded sections from the abrasive blast. The tooth profiles of gear teeth may be protected from excessive blasting by positioning them in a way that controls their exposure to the blast.

Baffles and reflectors may be used to direct abrasive particles to certain areas, such as undercuts, that should not be exposed to the severity of direct impingement.

Because it is usually difficult to adjust velocities of mechanical cleaners, a finer shot or grit size may be selected to modify cleaning characteristics.

Type of Soil. Mechanical dry blasting does not readily lend itself to the removal of viscous or resilient soils such as grease, oil, or tar. These materials not only resist the blast action but also cling to, or coat, the abrasive material and components of the abrasive-recycling system. In time, such soils disrupt proper recycling, reclamation, and airwash separation of the reusable abrasive. Therefore, parts coated with oil or other viscous soils must be thoroughly degreased, or scrubbed and dried, before the mechanical dry blast operation.

Dry surface soils, such as sand, scale, rust, paint, weld spatter, and carbon, are readily removed by the dry blast action. These friable contaminants are compatible with airwash separation for reclamation of usable abrasive. Dry contaminants can be present on a surface in any quantity. Sand cores and molding sand are removed by the centrifugal blast method during core-knockout operations. Large castings are processed with portable equipment, and small castings are processed in batch-type machines.

On a limited or intermittent production basis, air or wet blast methods can be used to remove soils that are not removable by wheel blasting. (Wet blasting is described later in this article.) For example, an air blast nozzle may be used with soft agricultural abrasives, which absorb viscous soils, to clean oily or greasy surfaces. Because the initial cost of the abrasive is relatively low, the material can be discarded when it becomes contaminated or saturated. This method is often used by maintenance personnel for cleaning motors and gear reducers. New technology involving the use of baking soda aggregate is being developed as an additional potential cleaning solution.

Workpiece Shape. Parts of virtually any shape can be cleaned by some method of abrasive blasting, although complex parts with deep recesses or shielded areas present special problems. For example, it is often difficult for the abrasive to make contact with all surfaces of deep blind pockets with a velocity sufficient to loosen the soil to be removed. When direct impingement is impossible, deflection of the abrasive particles by means of baffles sometimes solves the problem. For effective cleaning of the inside surfaces of pipe, special air blast nozzles and lance air blast equipment must be used to deliver the abrasive with adequate velocity. Even these techniques have practical limitations, depending on the diameter and length of the pipe.

A second problem encountered in the cleaning of pockets or recessed areas is the buildup of abrasive in these areas. An accumulation of abrasive shields the surface from further blast action and interferes with cleaning. This problem is usually solved by positioning the work in a manner that permits the abrasive particles to drain by means of gravity. This positioning change may necessitate a corresponding change in the positioning of blast equipment. Cylinder blocks and valve bodies are typical examples of parts with recesses that catch and retain accumulations of abrasive.

Workpiece Size. The size of parts that can be cleaned by the centrifugal blast wheel method is limited principally by the size of the enclosure and the number of wheel units that can be applied economically. Wheel units are maneuverable to only a limited extent. Therefore, as part size increases, it is necessary to rotate or convey the part in a manner that properly exposes it to the available blast units. Castings and weldments 6 m (20 ft) in diameter, 5 m (16 ft) high, and weighing up to 136 tonnes (150 tons) have been cleaned in mechanical blast rooms. These rooms are equipped with a rotary table and several centrifugal wheel units operating simultaneously. During cleaning, such extremely large parts frequently require repositioning to expose all surfaces to the blast. Intricately shaped large parts may also require auxiliary air blast touch-up cleaning.

Various types of continuous blast machines are used for the cleaning of repetitive work. These machines vary in size and design in accordance with the application and type of work-handling equipment required. Rolled steel products, such as sheet, strip, wire, rod, and structural shapes, lend themselves to continuous mechanical blasting at moderate production rates. For example, rolled strip up to 1830 mm (72 in.) is mechanically blasted on a continual basis, to reduce the time required for acid pickling.

Structural shapes, including the largest sections rolled commercially, can be cleaned on continuous-roll conveyor machines equipped with multiple wheel units for coverage of all surfaces. The equipment is used for the removal of mill scale and rust before welding and painting. Hot-rolled rod and bar shapes are cleaned on single- or multiple-nozzle or wheel machines to remove surface scale and prepare the surface for drawing or cold heading.

By virtue of the flexibility provided by operator manipulation of blast hose nozzles, air blast equipment is widely used for cleaning extremely large parts and assemblies. Railroad cars, for example, can be reconditioned inside and outside by this method. Large storage tanks and vessels also are cleaned with air blast equipment, using inexpensive abrasives such as sand, slags, and natural minerals that need not be reclaimed or in conjunction with the reclaiming equipment previously described in this article.

In contrast, parts as small as 10 to 13 mm ($\frac{3}{8}$ to $\frac{1}{2}$ in.) in diameter can be satisfactorily cleaned by abrasive blasting. Usually, these small parts are most efficiently handled in mechanical or air blasting equipment, either barrel machines or combination blasting-tumbling units. Auxiliary devices, such as wire cages or baskets, may be used to prevent very small parts from being lost in the abrasive.

Mixed Work Loads. In blasting with either fixed nozzles or centrifugal wheels, it is always more economical to process loads made up of parts of about the same size. Mixing large and small parts in the same load is basically inefficient, because it wastes abrasive, wastes power, and frequently results in overblasting some parts and underblasting others, although parts can be mixed within reasonable limits. In job shop operations, especially, a varied production mix can be

cleaned in a single tumbling and blasting operation. However, parts with thin sections that may bend or seriously distort should not be processed with parts that are relatively compact.

Quantity and Flow of Work. Continuous airless blast cleaning equipment is generally used for medium- to high-production cleaning applications. However, there are no actual quantity limitations. For the most economical use of continuous blast equipment, the work being cleaned must be repetitive and similar in size and shape, and the quantity of work flowing through the blast cleaning machines must be uniform and constant.

Monorail conveyor equipment should be operated with all work hangers fully loaded and few gaps in the production flow. This type of equipment usually is designed so that conveyor speeds can be regulated or index times varied to match work flow requirements, and so that the feeding of abrasive into the blast wheels can be regulated to suit work flow conditions. Automated conveyor equipment for cleaning gray iron motor blocks and similar parts is capable of cleaning from 400 to 600 workpieces per hour.

Continuous blasting-tumbling barrel machines also require a steady flow of work of relatively uniform size and shape. A constant level of work in the blast chamber makes the operation more economical and promotes uniform cleaning. In cleaning medium-size gray iron castings, these barrels have a capacity of over 23 tonnes (25 tons) per hour. If a steady flow of work cannot be maintained, it is economical to stockpile work until a sufficient accumulation is available. Barrel blasting machines, some table machines, and spinner hanger machines are suited to this type of operation.

Newer continuous process machines have been introduced that convey product via wire mesh belt or vibrating tracks. They are generally better suited for lower-volume or lower-tonnage applications. Die cast aluminum and zinc products represent ideal opportunities for use of these types of machines.

Miscellaneous Applications. Dry abrasive blasting has proven useful in applications in which cleaning is of only secondary importance. One automotive manufacturer blasts induction hardened transmission pins with chilled iron grit to permit rapid visual inspection and segregation of improperly hardened pins. After blasting, hardened surfaces have a markedly shiny appearance and unhardened surfaces appear dull. The same inspection technique is used by a manufacturer of rolling-mill rolls to determine uniformity of heat treatment of the roll surface. A manufacturer of carburized gears uses the technique to detect areas of decarburization and case leakage.

In some applications, dry abrasive blasting supplements other inspection techniques. Aircraft quality investment and sand castings are blasted before magnetic-particle inspection to reduce or eliminate glare caused by polishing or machining. Defects are more readily detected on the dull blasted surface.

Abrasives for Dry Blast Cleaning

The materials used in dry abrasive blast cleaning can be categorized as metallic grit, metallic shot, sand, glass, and miscellaneous. Hardness, density, size, and shape are important considerations in choosing an abrasive for a specific application. The selection of the type and size of the blast cleaning material will depend on the size and shape of the parts to be cleaned, the finish desired, and the treatment or operation that may follow blast cleaning. The success of blast cleaning operations depends primarily on judicious selection of method and abrasive medium. The surfaces, especially ferrous surfaces, tend to be very active following abrasive cleaning, and any subsequent operation such as plating or painting should be performed as soon as possible after abrasive cleaning.

Metallic abrasive media consist of grit, shot, and cut wire.

Grit consists of angular metallic particles with high cutting power. Grit is usually made of crushed, hardened cast steel shot, which may be tempered, or of chilled white cast iron shot, which may be malleabilized. Size specifications for cast grit are shown in Table 3. In general, three hardnesses are offered in steel grit: 45, 56, and 65 HRC. The screen distribution and the velocity of the grit impacting on the part surfaces control the finish. Usually, grit blast produces a brighter finish than shot blast. Applications for grit include removal of heavy forging and heat-treat scale, removal of rust, and controlled profiling of workpieces before bonding or coating. Hard grit is also used to provide a gripping surface on steel mill rolls.

Table 3 Size specifications for cast grit (SAE J444)

Size No.	Screen tolerances[a]	Screen opening	
		mm	in.
G10	All pass No. 7	2.82	0.1110
	80% min on No. 10	2.00	0.0787
	90% min on No. 12	1.68	0.0661
G12	All pass No. 8	2.38	0.0937
	80% min on No. 12	1.68	0.0661
	90% min on No. 14	1.41	0.0555
G14	All pass No. 10	2.00	0.787
	80% min on No. 14	1.41	0.0555
	90% min on No. 16	1.19	0.0469
G16	All pass No. 12	1.68	0.0661
	75% min on No. 16	1.19	0.0469
	85% min on No. 18	1.00	0.0394
G18	All pass No. 14	1.41	0.0555
	75% min on No. 18	1.00	0.0394
	85% min on No. 25	0.711	0.0280
G25	All pass No. 16	1.19	0.0469
	70% min on No. 25	0.711	0.0280
	80% min on No. 40	0.419	0.0165
G40	All pass No. 18	1.00	0.0394

	70% min on No. 40	0.419	0.0165
	80% min on No. 50	0.297	0.0117
G50	All pass No. 25	0.711	0.0280
	65% min on No. 50	0.297	0.0117
	75% min on No. 80	0.18	0.0070
G80	All pass No. 40	0.419	0.0165
	65% min on No. 80	0.18	0.0070
	75% min on No. 120	0.12	0.0049
G120	All pass No. 50	0.297	0.0117
	60% min on No. 120	0.12	0.0049
	70% min on No. 200	0.074	0.0029
G200	All pass No. 80	0.18	0.0070
	55% min on No. 200	0.074	0.0029
	65% min on No. 325	0.043	0.0017
G325	All pass No. 120	0.12	0.0049
	20% min on No. 325	0.043	0.0017

(a) Minimum cumulative percentages (by weight) allowed on screens of numbers and opening sizes as indicated

Shot**,** normally made of the same materials as grit, is usually in the form of spherical particles. Shot removes scale, sand, and other surface contaminants by impact. Size specifications for cast shot are indicated in Table 4. Steel shot is the most widely used metallic abrasive medium and is least destructive to the components of the abrasive blast system. The matte finish produced by steel shot on metal surfaces can be controlled by the screen distribution of the operating mix and the velocity of shot impacting on part surfaces.

Table 4 Cast shot size specifications for shot peening or blast cleaning (SAE)

Screen No.	Screen size		Screen opening[a]	Passing[a], %
	mm	in.		
7	2.82	0.111	780	All pass
8	2.38	0.0937	660	All pass
10	2.00	0.0787	780	85 min
			550	All pass
			460	All pass
12	1.67	0.0661	780	97 min
			660	85 min
			460	5 max
			390	All pass
14	1.41	0.0555	660	97 min
			550	85 min
			390	5 max
			330	All pass
16	1.19	0.0469	550	97 min
			460	85 min
			330	5 max
			280	All pass
18	1.00	0.0394	460	96 min
			390	85 min

			280	5 max
			230	All pass
20	0.841	0.0331	390	96 min
			330	85 min
			230	10 min
			170	All pass
25	0.711	0.0280	330	96 min
			280	85 min
			170	All pass
30	0.590	0.232	280	96 min
			230	85 min
			110	All pass
35	0.500	0.0197	230	97 min
			110	10 max
40	0.419	0.0165	170	85 min
			70	All pass
45	0.351	0.0138	170	97 min
			70	10 max
50	0.297	0.0117	110	80 min
80	0.18	0.007	110	90 min
			70	80 min

120	0.124	0.0049	70	90 min

(a) Screen opening sizes and screen numbers with maximum and minimum cumulative percentages allowed on corresponding screens

Cut wire is available from aluminum, zinc, steel, or stainless steel primary metal. Cut wire deforms into rounded particles during usage or conditioning processes prior to sale; it is used frequently in the same manner as cast shot. Table 5 shows the specifications relating standard size numbers for cut steel wire shot to diameter and minimum hardness.

Table 5 Specifications for cut steel wire shot (SAE J441)

Size No.	**Diameter of wire**		**Minimum hardness, HRC**
	mm	**in.**	
CW-62	1.59±0.05	0.0625±0.002	36
CW-54	1.4±0.05	0.054±0.002	39
CW-47	1.2±0.05	0.047±0.002	41
CW-41	1.0±0.05	0.041±0.002	42
CW-35	0.89±0.03	0.035±0.001	44
CW-32	0.81±0.03	0.032±0.001	45
CW-28	0.71±0.03	0.028±0.001	46
CW-23	0.58±0.03	0.023±0.001	48

Nonmetallic abrasive media include sand, glass, agricultural products, and plastic and nylon. Table 6 lists physical properties and comparative characteristics of a variety of nonmetallic abrasives.

Table 6 Physical properties and comparative characteristics of nonmetallic abrasives

Description	**Glass beads[(a)]**	**Coarse mineral abrasives[(b)]**	**Fine angular mineral abrasives[(c)]**	**Organic soft grit abrasives[(d)]**	**Plastic abrasives**
Physical properties					

Shape	Spherical	Granular	Angular	Irregular	Cylindrical (diameter/length = 1)
Color	Clear	Tan	Brown/white	Brown/tan	Nylon: white, polycarbonate: orange
Specific gravity	2.45-2.50	2.4-2.7	2.4-4.0	1.3-1.4	Nylon: 1.15-1.17, polycarbonate: 1.2-1.65
Free silica content	None	100%	<1%	None	None
Free iron content	<1%	<1%	<1%	None	None
Hardness (Mohs)	5.5	7.5	9.0	1.0	R-110 to R-120
Media comparisons					
Toxicity	None	High	Low	Low/none	None
Metal removal	Low/none	High	High	None	Deburring only
Cleaning speed	Medium/high	High	High	Low	Low
Peening ability	High	None	None	None	None
Finish achieved	Range (various matte)	Rough anchor	Various matte	Smooth	Smooth
Surface contamination	None	Medium	Medium	Medium/high	Low to none
Suitability for wet blasting	High	Low	Low	Low	Low
Suitability for dry blasting	High	High	High	High	High
Standard size ranges	20-325	8-200	80-325	60-325	0.76 by 0.76 mm (0.030 by 0.030 in.)
	U.S. mesh	U.S. mesh	U.S. mesh	U.S. mesh	1.1 by 1.1 mm (0.045 by 0.045 in.) 1.5 by 1.5 mm (0.060 by 0.060 in.)
Consumption rate	Low	High	Medium	High	Very low
Cost comparison	Medium	Low	High/medium	High/medium	High/medium

(a) Glass beads are used for cleaning, finishing, light-to-medium peening, and deburring.

(b) Coarse mineral abrasives such as sand are used where metal removal and surface contamination are not considered.

(c) Fine angular mineral abrasives such as aluminum oxide are used in cleaning when smooth finish and surface contamination are not important.

(d) Organic soft grit abrasives, for example, walnut shells, are used in light deburring and cleaning of fragile items.

(e) (e)Plastic abrasives such as nylon and polycarbonate are used to deflash thermoset plastic parts and deburr finished machine parts.

Sand. This term is applied to diverse nonmetallic abrasives, in addition to ordinary silica sand. These materials are used when it is necessary to protect the surface of the workpiece from metallic contamination. They may be either natural materials, such as garnet, novaculite, dolomite, pumice, and flint quartz, or manufactured materials such as aluminum oxide, silicon carbide, and slag. The natural materials are lowest in initial cost; the manufactured materials, although somewhat more expensive than natural sands, cost less than metallic abrasives.

Glass is available as angular particles (ground glass) or spherical particles (glass beads) ranging in size from approximately 1 mm (0.039 in.) to less than 40 μm (0.0016 in.). The particles are usually made from soda-lime-silica glass with a hardness of about 500 HK (100 g load), equivalent to 46 to 50 HRC. Ground glass is effective for deburring and relatively aggressive finishing. Glass beads produce a fine matte appearance and clean without removing base metal. Size and roundness specifications for glass beads are given in Table 7.

Table 7 Standard size and roundness specifications for glass beads (MIL-G-9954A)

U.S. standard screen	Bead size	Roundness, minimum, %	Passing, %
10	1	60	100
12	1	60	95-100
	2	60	100
14	1	60	0-15
	2	60	95-100
	3	65	100
20	1	60	0-5
	2	60	0-15

	3	65	95-100
	4	70	100
30	2	60	0-5
	3	65	0-15
	4	70	95-100
	5	70	100
40	3	65	0-5
	4	70	0-15
	5	70	95-100
	6	80	100
50	4	70	0-5
	5	70	0-15
	6	80	95-100
	7	80	100
60	5	70	0-5
	7	80	95-100
	8	80	100
70	6	80	0-15
	8	80	95-100
	9	80	100
80	6	80	0-5

	7	80	0-15
	9	80	95-100
	10	90	100
100	7	80	0-5
	8	80	0-15
	10	90	95-100
	11	90	100
120	8	80	0-5
	9	80	0-15
	11	90	95-100
	12	90	100
140	9	80	0-5
	12	90	95-100
	13	95	100
170	10	90	0-15
	13	95	95-100
200	10	90	0-5
	11	90	0-15
230	11	90	0-5
	12	90	0-15
325	12	90	0-5

	13	95	0-15
400	13	95	0-5

Miscellaneous Materials. Mild abrasive action is provided by the use of such agricultural products as crushed walnut or pecan shells, rice hulls, rye husks, corncobs, and sawdust. Plastic and nylon media are also widely used for special purposes. Recent developments include the use of more environmentally attractive media such as CO_2 pellets and wheat starch.

Selection of abrasive for a specific application is influenced by the type of surface contamination to be removed, size and shape of the workpiece, surface finish specified, type and efficiency of cleaning equipment, and required production rate. Type, size, and hardness of metallic abrasives recommended for some typical applications are given in Table 8. In addition to the recommendations in this table, the following general observations relating to the performance of abrasive particles may be helpful:

- The smaller the abrasive particle, the finer the surface finish and the faster the surface coverage.
- The larger the abrasive particle, the greater the impact.
- In general, the harder the abrasive particle, the faster its cleaning action.
- The larger or harder the abrasive, the greater the wear on the equipment.

Table 8 Selection of abrasive

Application	Recommended abrasive[(a)]			
	Type	Nominal diameter		Hardness HRC
		mm	in.	
Blasting of ferrous metals				
Removal of light scale[(b)]	Shot or grit	0.2-0.71	0.007-0.028	30-66[(c)]
Removal of heavy scale[(b)]	Shot or grit	0.71-2.0	0.028-0.078	45-66
Cleaning of castings	Shot or grit	0.43-2.0	0.017-0.078	30-66[(c)]
Blasting of nonferrous metals				
Frosted appearance only	Grit	0.1-0.43	0.005-0.017	50-66
Preparation for other surface finishes	Shot or grit	0.2-0.71	0.007-0.028	30-66[(c)]

(a) Cast iron or cast steel.

(b) For phosphating or painting.

(c) Cast steel abrasive usually is not available in a hardness of less than 40 HRC.

Replacement of Abrasive. Production of a uniformly abraded surface depends on maintaining a uniform working mix of abrasive in the machine at all times. Metal surfaces treated with hard grit are more sensitive to a change in working mix than those treated with a soft grit or with shot. A program that includes testing and continuous gradual replacement of the abrasive is recommended. The working mix contains more abrasive fines than new abrasive. Examples of screen analyses of new and used abrasives are given in Table 9.

Table 9 Screen analysis of three metal abrasives

Screen No.	Screen size		Abrasive remaining on screen, %	
	mm	in.	New abrasive	Working mix
G25 cast steel grit				
16	1.19	0.0469	Trace	None
20	0.841	0.0331	82	23
30	0.589	0.0232	16	33
40	0.419	0.0165	1	19
50	0.297	0.0117	Trace	17
70	0.21	0.0083	Trace	6
Pan	. . .	. . .	Trace	2
G40 cast steel grit				
16	1.19	0.0469	None	None
20	0.841	0.0331	19	None
30	0.589	0.0232	76	18

40	0.419	0.0165	4	51
50	0.297	0.0117	Trace	26
70	0.21	0.0083	Trace	5
Pan	. . .	. . .	Trace	Trace
S280 cast steel shot				
16	1.19	0.0469	None	None
20	0.841	0.0331	40	27
30	0.589	0.0232	58	56
40	0.419	0.0165	1	11
50	0.297	0.0117	1	5
70	0.21	0.0083	None	1
Pan	. . .	. . .	None	None

A practical method of maintaining a reasonable degree of consistency of the working mix is to keep a uniform level of abrasive in the supply tank, bin, or hopper. This is accomplished by adding new abrasive periodically, usually at least once every 2 h. If surface finish requirements are more critical, hourly additions of new abrasive may be needed. The total tonnage of abrasive required to fill the machine to operating capacity also may affect the frequency of additions. When surface finish requirements are critical, the use of an automatic abrasive replenisher is indicated. This device maintains the abrasive level in the blasting machine by automatically feeding abrasive from a supply hopper. Consumption is gradual; therefore, replenishment should be equally gradual.

For control purposes, a representative sample of the abrasive used in the machine should be analyzed periodically. The frequency of these tests depends largely on surface finish and production requirements. Dust fines should be removed from the mix by an air separating system; proper performance of a separating device depends on a uniform flow of air through the separator and on maintenance of uniform abrasive sizes and quantities.

Control of Contaminants. After the abrasive medium makes contact with the workpiece, it is returned to a storage hopper for reuse. Coarse and fine contaminants picked up in the process are removed as the medium is returned to the hopper. Coarse contaminants include tramp metal, fins, core wire, core nails, slag, sand lumps, large flakes of rust and scale, and flash. These are usually removed by screening the abrasive mix through wire mesh, perforated plate, or expanded metal. Automatic rotary screens are preferred over stationary tray-type screens.

Fine contaminants include sand, fine mill scale and rust particles, metallic dusts, and disintegrated abrasive particles. Buildup of fine contaminants reduces blast efficiency, and a high sand content results in excessive wear of centrifugal blast wheel parts. Fine contaminants are removed from the mix by a current of air. In an expansion chamber, the heavier fine particles resist an upward turn of the air current and drop into the settling area to be discharged as refuse. Lighter

particles remain suspended in the air current and are carried out through the ventilating lines to the dust collector or exhaust.

In many blast cleaning operations, small metallic particles resulting from the wearing or breaking down of abrasives assist in scouring small crevices or valleys. If such fines are to be retained, separators must be adjusted accordingly.

Wet Blasting

Wet blasting differs from dry blasting in that the abrasive particles used are usually much finer and are suspended in chemically treated water to form a slurry. The slurry, pumped and continually agitated to prevent settling, is forced by compressed air through one or more nozzles, which are directed at the work.

Applications

In further contrast to dry blasting, wet blasting is not intended for the gross removal of heavy scale, coarse burrs, or soil, but is intended to produce only relatively slight effects on the workpiece surface. Wet blasting is most commonly used for:

- Removing minute burrs on precision parts
- Producing satin or matte finishes
- Inspection finish ground, hardened parts
- Removing fine tool marks from hard parts
- Removing light mill scale or machining marks in preparation for plating
- Removing surface oxide in preparation for soldering of electronic components and printed circuits
- Removing welding scale

Many small parts, including hypodermic needles and electronic components, are deburred by wet blasting. The application of wet blasting to large parts is limited to the cleaning and finishing of forging dies from which a minimum of metal removal is desired; dies weighing up to 90 tonnes (100 tons) have been wet blasted. Many cutting tools are wet blasted after final grinding.

Precleaning. In most instances, precleaning must precede wet blasting to prevent contamination of the recirculating slurry. Grease, protective coatings, and heavy oils may be removed by conventional degreasing methods. Heavy rust and dry soils may be removed by dry blasting. A very light layer of rust may be removed from machined parts by wet blasting without precleaning. However, in general, the finer the abrasive used in the wet blast slurry, the greater is the need for precleaning to prevent contamination of the slurry.

Abrasives for Wet Blasting. Many different kinds and sizes of abrasives can be used in wet blasting. Sizes range from 20-mesh (very coarse) to 5000-mesh (much finer than face powder). Among the types of abrasives used are organic or agricultural materials such as walnut shells, baking soda, and peach pits; novaculite, silica, quartz, garnet, and aluminum oxide; other refractory abrasives; and glass beads.

The organic or agricultural materials are used for mild blasting only. Novaculite, a soft type of silicon dioxide (99.46% silica; Mohs hardness, 6 to 6.5), is used to remove very light burrs and produces a fine matte finish. The silicas are slightly more aggressive than novaculite and are used to remove larger burrs and scale. Quartz is still more aggressive than silica and lasts longer; it is used for the rapid removal of tenacious burrs and scale.

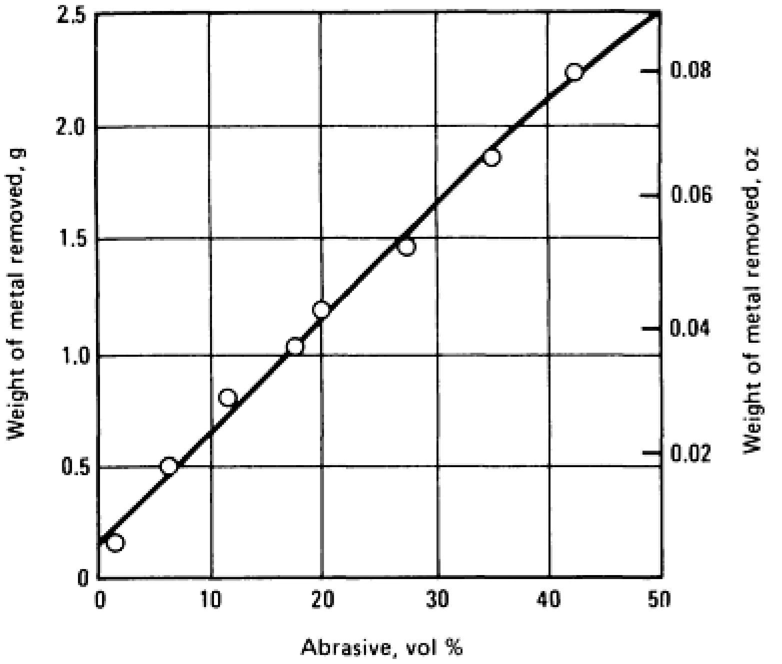
Garnet abrasives are highly aggressive and have long life; for a comparable mesh size, garnet will produce a rougher surface finish than will silicon dioxide. Aluminum oxide, silicon carbide, and other artificial abrasives are the most aggressive and erosive. Round glass shot (beads) composed of 72% silicon dioxide, 15% sodium monoxide, 9% calcium oxide, and 1% alumina produce a brighter finish and provide the most peening action. The high ricocheting property of glass beads is of value in blasting areas that are hard to reach. Table 10 describes various abrasives used in wet blasting and lists typical applications.

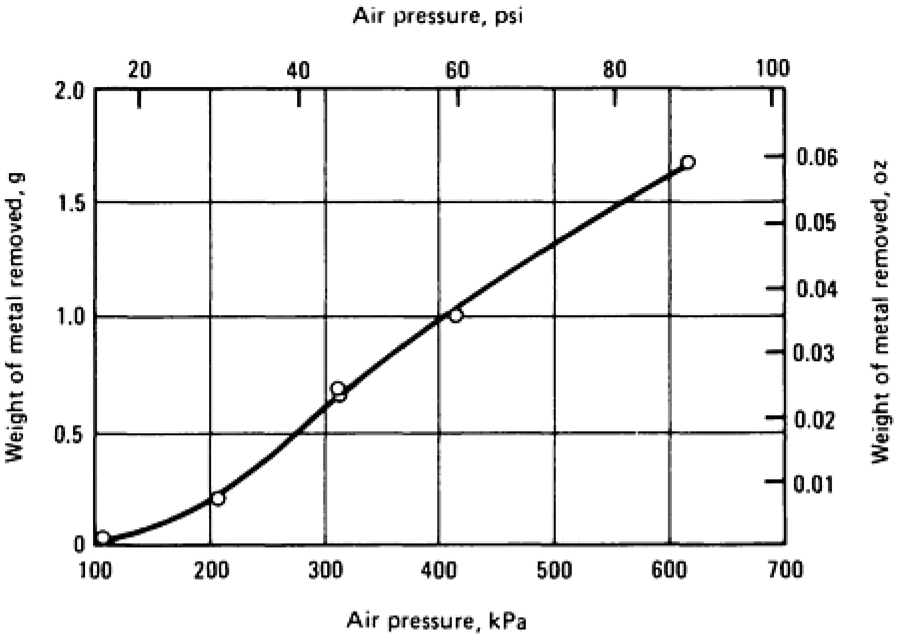
Table 10 Characteristics and typical applications of abrasives used in wet blasting

Abrasive	Mesh size	Characteristics and applications
Silica	40-80	Fast-cutting. Used for deburring steel and cast iron, removing oxides from steel. Close tolerances cannot be held
Silica	80	Fast-cutting. Used for deburring steel and cast iron, roughening surfaces for plastic bonding or rough plating. Has peening action. Tolerances cannot be held
Quartz (ground)	80	Very fast-cutting. Used for removing heavy burrs, light or medium scale, excessive rust. Can be used on nickel alloy steels. Tolerances cannot be held
Novaculite	100	Fast-cutting. Used for cleaning carbon from piston and valve heads: deburring brass, bronze, and copper. Can be used on crankshafts. Tolerances cannot be held
Quartz (ground)	100, 140	Fast-cutting. Used for blending-in preliminary grind lines on steel, brass and die castings; removing medium-hard carbon deposits; blasting radii of 0.1 to 0.3 mm (0.005 to 0.010 in.)
Silica	140	Used for removing small burrs from steel, copper, aluminum, and die castings; rough cleaning of dies and tools, removing metal. Tolerances cannot be held
Novaculite	325	Slow-cutting. Used in first stage for cleaning master rods and glass, and in second stage for cleaning aluminum pistons, crankshafts, impellers, valves. Holds tolerances to 0.06 mm (0.0025 in.)
Aluminum oxide	400	Fast-cutting. Used on stainless steel and on zinc and aluminum die castings. Excellent for oil-contaminated surfaces
Novaculite	1250	Used in second stage for cleaning crankshafts, impellers, rods, pistons, valves, gears and bearings. Also for polishing metals, tools, dies and die castings. Tolerances can be held
Novaculite	5000	Used for obtaining extra-fine surfaces on parts
Glass beads	20-400	Used for removing scale or discoloration after heat treating, removing oxide from jet-engine and electronic components. Produces peening effect

Liquid Carriers. The liquids most commonly used to carry the abrasive particles are water-containing additives such as rust inhibitors, wetting agents, and anticlogging and antisettling compounds. In a few applications, such as in the manufacture of spark plugs, petroleum distillates have been used as abrasive carriers for the removal of oil residues and fine chips and burrs. In these instances, the use of water would create difficulties. Petroleum distillates, however, can be used only with specially designed wet blasting units because of the fire hazard.

The proportion of abrasive to liquid in the wet abrasive slurry can be varied over a wide range, although certain limitations apply. The use of a very small percentage of abrasive results in slight cleaning action, while too large a percentage of abrasive might result in the formation of a paste that could not be properly circulated. Proportions should be fixed at a predetermined level for each application, to ensure uniform cleaning action and production of a uniform finish. A range of 20 to 35% volume abrasive is satisfactory for most applications but may be modified because of particle size, surface tension, specific gravity, agitation, or the desired effect on the workpiece. Figure 9 illustrates the effects of three variables on metal removal during wet blasting of 1010 steel. Reclamation of wet abrasive is usually impractical. The mixture generally is used until its cleaning action becomes unsatisfactory and is then discarded.


2.5
2.0
1.5
1.0
0.5
0
0
10
20
30
40
50
0.08
0.06
0.04
0.02
Weight of metal removed, g
Weight of metal removed, oz
Abrasive, vol %


Air pressure, psi
20
40
60
80
100
2.0
1.5
1.0
0.5
0
100
200
300
400
500
600
700
0.06
0.05
0.04
0.03
0.02
0.01
Weight of metal removed, g
Weight of metal removed, oz
Air pressure, kPa

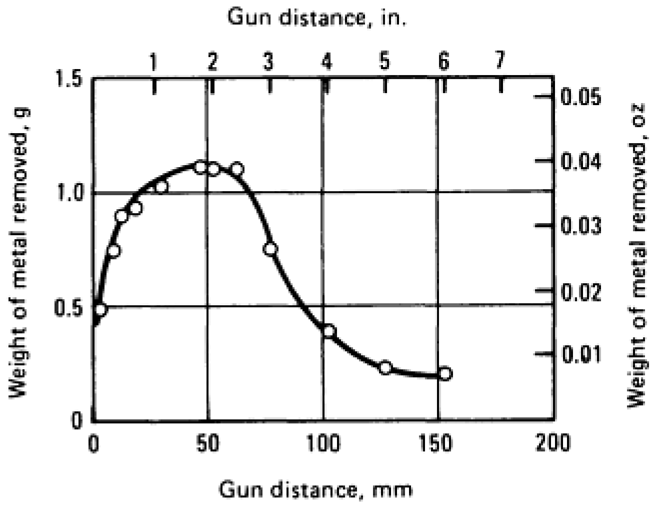

Gun distance, in.
1
2
3
4
5
6
7
1.5
1.0
0.5
0
0
50
100
150
200
0.05
0.04
0.03
0.02
0.01
Weight of metal removed, g
Weight of metal removed, oz
Gun distance, mm

Fig. 9 Effect of variables on amount of metal removed during wet blasting of 1010 steel

Equipment. Although equipment for wet blasting is often of special design for a particular application, several basic types of machines (Fig. 10) have been developed for general use, including:

- Cabinet-type machines
- Horizontal-plane turntable machines with tables of various diameters
- Vertical wheel-type machines
- Chain or belt conveyor machines
- Shuttle-type cabinets with cars and rail extensions
- Car-mounted, self-contained turning mechanisms for shafts or tubular parts

These basic types may be equipped with strippers, takeoff conveyors, and wash-rinse-dry stations. The blast guns may be mounted in a stationary position or be made to oscillate, depending on the application.

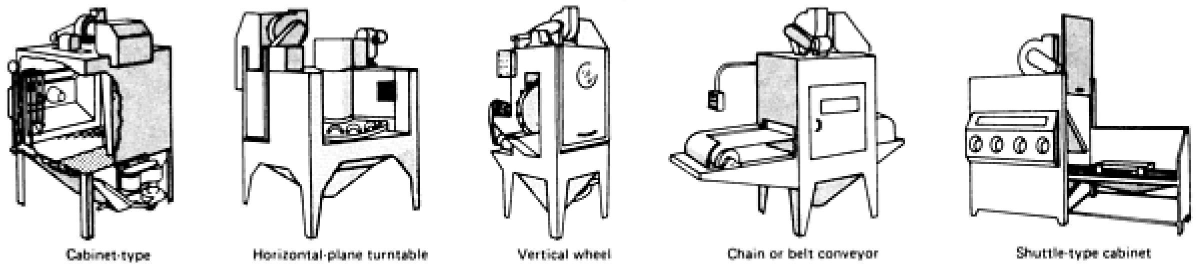


Fig. 10 Wet blasting machines

Combination blasting-tumbling cabinet-type machines also are available. These machines are made with an extension stand provided with rails so that a car-mounted tumbling barrel can be moved into the cabinet. The barrel, a self-contained unit, is provided with a driving mechanism for turning the barrel and oscillating the blast gun or guns inside the barrel. Barrels range in diameter from 305 to 660 mm (12 to 26 in.) and are perforated to allow the slurry to escape and recirculate.

Nozzles for wet blasting vary in form, shape, length, and diameter according to the type of abrasive used and the size of the parts to be blasted. The most common form is a cylindrical nozzle about 25 mm (1 in.) long, 13 mm ($\frac{1}{2}$ in.) inside diameter, and 19 mm ($\frac{3}{4}$ in.) outside diameter. It is made of low-carbon steel and is used in hand-operated cabinets for general cleaning purposes. This nozzle uses silicates or quartz in mesh sizes ranging from 100 to 300 and at blasting pressures of 550 to 620 kPa (80 to 90 psi), and it has an average life of about 40 h.

Special nozzles, such as fan-shaped types, usually are made of an alloy cast iron chilled to a high hardness, although some special nozzles are made of rubber.

Carbide nozzles are used in mechanized units that provide surface preparation for processes such as anodizing and phosphating. The higher cost of cylindrical carbide nozzles is justifiable in terms of long life and low maintenance. For special shapes, however, the cost of carbide is likely to be prohibitive. When used with fine abrasives, a cylindrical carbide nozzle has a life of several thousand hours. In one application, a carbide nozzle exhibited no measurable wear after 1000 h of service with 140-mesh quartz at a pressure of 620 kPa (90 psi).

A nozzle for wet blasting is considered to be worn out when its wall thickness has been so reduced as to be potentially damaging to the gun, or the blast pattern provides inadequate coverage of the workpieces.

The amount of air required for wet blasting depends on the diameter of the air-jet nozzle and the operating pressure. Figure 11 illustrates the cubic feet of air needed to operate air-jet nozzles 2.4 to 8 mm ($\frac{3}{32}$ to $\frac{5}{16}$ in.) in diameter at pressures from 70 to 690 kPa (10 to 100 psi). The data are based on operating a wet blasting gun with a slurry containing 40 vol% abrasive of 140-mesh.

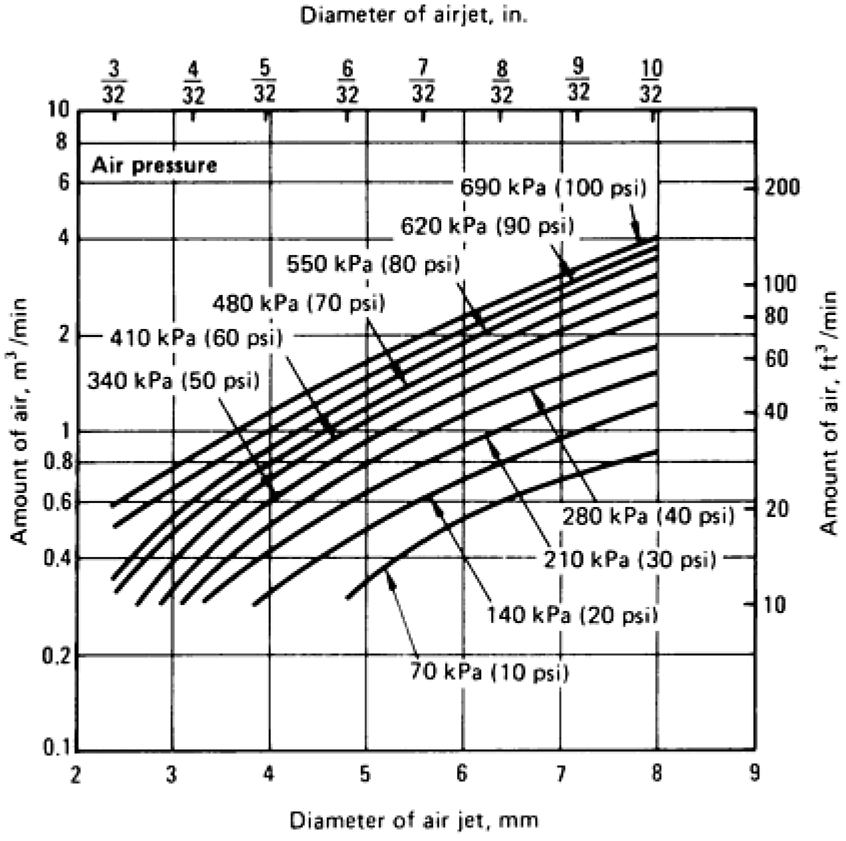


Fig. 11 Amount of air required for various sizes of air-jet nozzles at different operating pressures

Maintenance. Typical maintenance schedules for hand-operated wet blasting cabinets are as follows:

- *Weekly:* Wash filter and pump-intake strainer, making sure all foreign particles are removed; grease the pump follower.
- *Monthly:* Check pump packing gland for leaks and tighten if necessary.
- *Semiannually:* Remove wear plate from pump and inspect impeller and housing for wear; grease fan pillow-block bearings.

Health Hazards and Safety

Blast cleaning operations can be performed without risk to the health or safety of personnel if precautionary measures are followed rigorously. The health hazard that accompanies blast cleaning is silicosis, a disease of the lungs that results from the prolonged breathing of very fine particles of silica sand. In past years, improperly done sandblasting has been the cause of many cases of silicosis, which can be permanently disabling and even fatal. No matter how good the equipment, the operator should be examined by an accredited physician prior to employment and at least once a year thereafter.

Health Precautions. Air blasting of sand-free steel or iron castings and shot blasting of sandy castings produces enough fine silica to make the air dangerous to breathe. The blaster must be protected by a helmet supplied with air, special gauntlets, an apron, and often special leg protection. The blast room enclosure should be well lit (80 footcandles minimum illumination) and should provide ample clear space for walking and maneuvering by the operator. To meet

current environmental standards, it should include ventilation and dust collection equipment to clean the air that is drawn through. The air supplied to the worker (about 0.17 m^3/s, or 6 ft^3/min) should be clean, odorless, dry, and free from gaseous contaminants. If taken directly from the compressed-air receiver, it is likely to be wet and malodorous. Use of a carbon monoxide monitoring device with an audible alarm is a mandatory requirement in any application in which breathing air is produced for the operator.

Pickling and Descaling

Robert M. Hudson, Consultant

Introduction

OXIDE SCALE must be completely removed from hot-worked or hot-rolled steel before subsequent processing is initiated, in order to prevent wear on dies and rolls and avoid surface defects in the final product. This oxide scale originates during the hot working or hot rolling of steel, when the surface of the metal reacts with oxygen in the air to form oxides of iron, or mill scale. The scale actually consists of three iron oxides with different proportions of iron and oxygen. Hematite, Fe_2O_3, which contains 30.1% oxygen, is the outermost oxide in the scale layer, whereas wustite, FeO, with 22.3% oxygen, is the innermost oxide. Magnetite, Fe_3O_4, contains 27.6% oxygen; when all oxides are present, the middle layer in the scale is magnetic. At temperatures above 566 °C (1050 °F), wustite is the predominant oxide, but during cooling below 566 °C (1050 °F), a portion of it is transformed to iron and magnetite ($4FeO = Fe_3O_4 + Fe$). In cases of rapid cooling, which can occur with rod and bar, substantial amounts of wustite are retained in the cooled product. When cooling after hot rolling is relatively slow, as it is with coiled strip, magnetite is the main oxide constituent of the scale in the cooled product.

Pickling is the most common of several processes used to remove the scale from steel surfaces. The term *pickling* refers to the chemical removal of scale by immersion in an aqueous acid solution. The process originated in the late 1700s, when sheets of steel were descaled by immersion in vats of vinegar. Wide variations are possible in the type, strength, and temperature of the acid solutions used, depending on time constraints (batch vs. continuous operations), as well as the thickness, composition, and physical nature (cracks) of the scale. Pickling is applicable for many types of forgings and castings, for merchant bar, blooms, billets, sheet, strip, wire, and for tubing.

Pickling Solutions

For carbon steel, sulfuric acid (H_2SO_4) is used in most batch pickling operations, whereas hydrochloric acid has become the pickling agent of choice, as of 1994, for continuous operations with wire and strip. Hydrochloric acid (HCl) is also used for special purposes, such as etching before galvanizing or tinning. Nitric-hydrofluoric acid mixtures are used to pickle stainless steel. Hydrofluoric acid is sometimes used when pickling castings to remove sand.

Mixtures of hydrochloric and sulfuric acids have been used in batch pickling, often by adding rock salt (NaCl) to a sulfuric acid pickling bath. Such practices might be expected to give the bright, pickled steel surface characteristics associated with hydrochloric acid and to increase pickling rates, but not without some drawbacks. The proportion of HCl to H_2SO_4 that is required to achieve the rapid scale removal rate that is possible with HCl alone is too high to be economical, and the mixed acids cannot be properly handled by many of the spent pickle liquor disposal methods now in use (Ref 1).

Acids other than HCl or H_2SO_4 have been used to remove rust and scale from carbon steel. Citric acid, oxalic acid, formic acid, hydrofluoric acid, fluoboric acid, and phosphoric acid are all capable of removing mill scale from steel, but the rates of removal are generally not regarded as useful or economical for most commercial applications, especially continuous operations.

The mechanism of scale removal, or pickling, by mineral acids involves the penetration of acid through cracks in the scale, followed by the reaction of the acid with the innermost scale layer and base metal. The presence of hydrogen gas, which forms when acid reacts with the base metal, and the dissolution of FeO help detach the outer scale layer from the metal surface. This classical concept of pickling with H_2SO_4 is supported by experimental work and commercial practices that demonstrate substantial increases in scale removal rates when scale cracking is initiated by flexing, temper-rolling (of strip), or tension leveling (Ref 2).

The reaction of H_2SO_4 with FeO or with scale that is substantially Fe_3O_4 mixed with iron will form ferrous sulfate and water:

$$FeO + H_2SO_4 = FeSO_4 + H_2O \quad \textbf{(Eq 1)}$$

$$Fe_3O_4 + Fe + 4H_2SO_4 = 4FeSO_4 + 4H_2O \quad \textbf{(Eq 2)}$$

The reaction of sulfuric acid with base metal forms ferrous sulfate and hydrogen gas:

$$Fe + H_2SO_4 = FeSO_4 + H_2(g) \quad \textbf{(Eq 3)}$$

With hydrochloric acid, descaling primarily involves direct attack on the oxides. However, the penetration of acid through cracks in the scale does contribute to the scale removal process, although the magnitude of the effect resulting from enhanced scale cracking is somewhat less than it is with sulfuric acid (Ref 3). The reaction of HCl with FeO or with scale that is substantially Fe_3O_4 mixed with iron will form ferrous chloride and water:

$$FeO + 2HCl = FeCl_2 + H_2O \quad \textbf{(Eq 4)}$$

$$Fe_3O_4 + Fe + 8HCl = 4FeCl_2 + 4H_2O \quad \textbf{(Eq 5)}$$

The reaction of hydrochloric acid with base metal forms ferrous chloride and hydrogen gas:

$$Fe + 2HCl = FeCl_2 + H_2(g) \quad \textbf{(Eq 6)}$$

Sulfuric Acid Pickling. Sulfuric acid produces satisfactory results when used for batch pickling of carbon steel rod and wire (up to 0.60% C) and for continuous cleaning, if the iron concentration in the bath is less than 8 g/100mL. Table 1 lists the types of carbon and alloy steel products that are pickled in sulfuric acid and the ranges of acid concentrations and temperatures used.

Table 1 Solution concentrations and operating temperatures used for pickling carbon and alloy steel products

Product	Sulfuric acid concentration, wt%		Bath temperature			
			Minimum		Maximum	
	Minimum	Maximum	°C	°F	°C	°F
Bar, low-carbon	7	18	68	155	85	185
Bar, alloy	9	12	66	150	77	170
Billet, low-carbon	7	12	74	165	82	180
Billet, alloy	9	12	82	180	93	200
Pipe for galvanizing	7	15	71	160	88	190

Sheet for galvanizing	4	12	66	150	77	170
Sheet, tin plate (white pickle)	9	12	66	150	85	185
Strip, soft	6	12	77	170	88	190
Strip, alloy and high-carbon	7	12	66	150	77	170
Strip, continuous pickling	23	38	77	170	100	212
Tubing, low-carbon seamless	7	18	77	170	88	190
Tubing, high-carbon and alloy structural	9	18	71	160	93	200
Tubing (over 0.40% carbon)	9	18	60	140	71	160
Wire, soft	4	18	77	170	88	190
Wire, alloy and high-carbon	3	18	55	130	74	165
Fabricated parts (for tinning):						
Initial pickle	5	10	66	150	88	190
Final dip	(a)	(a)	. . .	. . .	38	100

(a) Concentrated hydrochloric acid, 1.14 to 1.16 sp gr

Commercial sulfuric acid is usually supplied at a concentration of 93 wt%, whereas hydrochloric acid is supplied at concentrations of 31 or 35 wt%. Prices for tank car lots of sulfuric and hydrochloric acids vary geographically within the United States. During 1993, costs were similar for 93 wt% sulfuric acid and 35 wt% hydrochloric acid. An advantage of using sulfuric acid is less fuming over pickling solutions. Disadvantages include darker surfaces and the production of smut, particularly on high-carbon steel, as well as a greater inhibiting effect on the sulfuric acid of iron salts in the bath.

Emissions from sulfuric acid pickling may include a spray (droplets of pickling solution resulting from acid attack on base metal that generates hydrogen gas); adequate ventilation must be provided to prevent localized corrosion of equipment and unsatisfactory working conditions.

Hydrochloric Acid Pickling. Hydrochloric acid is preferred for the batch pickling of hot-rolled or heat-treated high-carbon steel rod and wire. Continuous pickling operations also use hydrochloric acid to produce the very uniform surface characteristics required for both low- and high-carbon steel. The possibility of overpickling is minimized in these short-time operations. The acid also dissolves lead oxides that adhere to steel previously heat treated in molten lead baths.

Operating conditions for batch pickling in hydrochloric acid solutions typically involve acid concentrations of 8 to 12 g/100 mL, temperatures of 38 to 40 °C (10 to 105 °F), and immersion times of 5 to 15 min, with a maximum allowable

iron concentration of 13 g/100 mL. Operating conditions for continuous pickling in hydrochloric acid solutions typically involve acid concentrations of 2 to 20 g/100 mL, temperatures of 66 to 93 °C (150 to 200 °F), and immersion times of 1 to 20 s.

Hydrochloric acid offers a number of advantages, when compared with sulfuric and other acids. It consistently produces a uniform light-gray surface on high-carbon steel. The possibility of overpickling is less than it is with other acids. Effective pickling can be obtained with iron concentrations as high as 13 g/100 mL. Rinsing is facilitated because of the high solubility of chlorides. The cost of heating the bath for batch-type operations is less than it is with sulfuric acid because of lower operating temperatures. The chief disadvantage of hydrochloric acid is the necessity for a good fume-control system.

Emissions from hydrochloric acid pickling include hydrogen chloride gas and must be adequately vented to prevent localized corrosion of equipment and unsatisfactory working conditions.

Other Acid Mixtures. Excessive contamination of the pickling bath by oiled steel results in nonuniform descaling and staining of the steel. To avoid this problem, oiled steel should be degreased before pickling. When pickling either oiled or degreased steel, the use of a wetting agent in the acid solution increases the effectiveness and efficiency of the bath, thereby reducing immersion time. Many commercial pickling inhibitors are formulated with a wetting agent.

Annealing smut and heavy-metal ions can be removed from the surface of steel to be cold drawn, porcelain enameled, or tin plated by adding sodium ferrocyanide to the acid pickling solution. A solution of sulfuric and hydrofluoric acids can be used to pickle castings that have burned sand embedded in the surface. The relative concentration of each acid is determined by whether the primary objective is sand removal or scale removal.

Determination of Acid and Iron Concentrations in Pickling Baths. Plants frequently report acid and iron-salt concentrations in weight/volume (w/v) units of grams per 100 milliliters (g/100 mL). Although these units are sometimes loosely referred to as "percent," concentrations in g/100 mL must be divided by the density of the solution in grams per milliliter (g/mL) to convert to true weight percent (weight/weight, or w/w, units). For this purpose, approximate equations for calculating densities have been developed from published data on sulfuric acid-ferrous sulfate solutions (Ref 4, 5, 6, 7) and on hydrochloric acid-ferrous chloride solutions (Ref 8, 9):

$$D = 0.9971 + (6.33 \times 10^{-3})\, C_{H_2SO_4} + (9.90 \times 10^{-3})\, C_{FeSO_4} \qquad \text{(Eq 7)}$$

$$D = 0.9971 + (4.46 \times 10^{-3})\, C_{\mathrm{HCl}} + (8.15 \times 10^{-3})\, C_{FeCl_2} \qquad \text{(Eq 8)}$$

where D is expressed in g/mL at 25 °C (77 °F) and the concentrations, C, of H_2SO_4, ferrous sulfate ($FeSO_4$), HCl, and ferrous chloride ($FeCl_2$) are expressed in g/100 mL.

Equipment for the analysis of pickling solutions should be installed near the pickling operation to monitor acid concentration and to test the solutions at regular intervals. Testing after each acid addition and once or twice during an 8 h shift might be sufficient for batch operations. For continuous operations, which often involve continuous additions of acid, more frequent testing is required, at least once every 2 h. Titration methods for acid and iron concentrations in solutions are widely used. The calculations follow from the stoichiometric relationships between the reactants and products.

With sulfuric acid solutions, add 75 to 100 mL of distilled water and two or three drops of methyl orange indicator to a 5 mL sample. A burette containing a 1.02 N sodium hydroxide solution is used to titrate until the red color changes to yellow. The sample solution should be agitated during the titration. Each milliliter of sodium hydroxide solution is equivalent to 1 g H_2SO_4 per 100 mL of pickling solution. The concentration of H_2SO_4 in g/100 mL is determined by:

$$C_{H_2SO_4} = (\text{mL NaOH} \times N \times 0.0490 \times 100)/\text{mL sample} \qquad \text{(Eq 9)}$$

where N is the normality of the NaOH solution. With hydrochloric acid solutions, an analogous procedure is used. If a 1.37 N sodium hydroxide solution is used to titrate, each milliliter of this solution is equivalent to 1 g HCl per 100 mL of pickling solution. The concentration of HCl in g/100 mL is determined by:

$$C_{HCl} = (\text{mL NaOH} \times N \times 0.0365 \times 100)/\text{mL sample} \quad \textbf{(Eq 10)}$$

To determine the concentration of iron in either sulfuric acid or hydrochloric acid pickling solutions, add 25 mL of distilled water and approximately 5 mL of concentrated sulfuric acid to a 5 mL sample and titrate with 0.895 N potassium permanganate to a purple end point. Potassium permanganate, an oxidizing agent, converts ferrous iron to ferric iron. Each milliliter of the potassium permanganate solution is equivalent to 1 g Fe/100 mL of pickling solution. The concentration of iron in g/100 mL is determined by:

$$C_{Fe} = (\text{mL } KMnO_4 \times N \times 0.0558 \times 100)/\text{mL sample} \quad \textbf{(Eq 11)}$$

where N is the normality of the $KMnO_4$ solution. To calculate the concentration of ferrous sulfate in a sulfuric acid solution and the concentration of ferrous chloride in a hydrochloric acid solution, the calculated concentration of iron is multiplied by the factors 2.72 and 2.27, respectively.

The determination of acid and iron concentrations in hydrochloric and sulfuric acid pickling solutions is often carried out with automatic titration equipment. Concentrations of acid and iron can also be estimated from conductivity and density measurements made on pickling solutions (Ref 10).

Mixtures of nitric and hydrofluoric acids are used to pickle stainless steel. Fluoride-selective electrodes are used to control hydrofluoric acid additions on some lines (Ref 11). If the nitric acid concentration is known, it can be subtracted from total acid to estimate hydrofluoric acid. The complexing ability of hydrofluoric acid in nitric-hydrofluoric acid solutions has been determined using an automatic process titrator in a technique that involves a known addition of ferric nitrate to a sample of pickling solution, followed by titrations to determine uncomplexed iron (Ref 12).

References cited in this section

1. R.M. Hudson, Pickling of Hot-Rolled Strip: An Overview, *Iron Steelmaker,* Vol 18 (No. 9), 1991, p 31-39
2. R.M. Hudson and C.J. Warning, Pickling Hot-Rolled Steel Strip: Effect of Strip Velocity on Rate in H_2SO_4, *Met. Fin.,* Vol 82 (No. 3), 1984, p 39-46
3. R.M. Hudson and C.J. Warning, Effect of Strip Velocity on Pickling Rate of Hot-Rolled Steel in Hydrochloric Acid, *J. Met.,* Vol 34 (No. 2), 1982, p 65-70
4. *Handbook of Chemistry and Physics,* 46th ed., Chemical Rubber Publishing Co., 1966
5. H. Holtzman and L. May, Specific Gravities of Ferrous Sulfate Solutions, J. Amer. Chem. Soc., Vol 73, 1951, p 852
6. A.P. Belopol'skii and S.Y. Shpunt, System $FeSO_4$-H_2SO_4-H_2O at Temperatures 50-90 °C, *J. Appl. Chem., USSR,* Vol 14, 1941, p 716-733
7. W. Bullough, T.A. Canning, and M.I. Strawbridge, The Solubility of Ferrous Sulfate in Aqueous Solutions of Sulfuric Acid, *J. Appl. Chem., London,* Vol 2, 1952, p 703-707
8. *Lange's Handbook,* 11th ed., McGraw-Hill, 1973, p 10-97
9. R.M. Hudson and C.J. Warning, Minimizing Fuming During Pickling With Hydrochloric Acid, *Sheet Met. Ind.,* Vol 46 (No. 8), 1969, p 523-525
10. G. von der Dunk and B. Meuthen, The Use of Chemical and Physical Methods in the Control of Sulfuric Acid and Hydrochloric Acid Pickling Baths, *Stahl und Eisen,* Vol 82 (No. 25), 1962, p 179-196 (Brutcher Translation 5802)
11. K. Lindroos, Determination of Free Hydrofluoric and Nitric Acid in Stainless Steel Pickling Baths, *Analyst,*

Vol 112, 1987, p 71

12. J.K. Burdick, B.J. Meneghelli, and K.S. Fletcher III, On-Line Determination of Hydrogen Fluoride in a Mixed Acid Stainless Steel Pickling Bath, *Iron Steel Eng.,* Vol 69, 1992, p 32-34

Inhibitors

Inhibitors are added to acid pickling solutions in order to:

- Minimize acid attack on the base metal with excessive loss of iron
- Avoid pitting associated with overpickling, which contributes to poor surface quality
- Reduce acid solution spray resulting from hydrogen that forms when acid attacks steel
- Lower acid consumption
- Minimize the risk of hydrogen embrittlement

When used at appropriate concentrations, inhibitors should not appreciably affect the rate of scale or rust removal.

A number of additives have been used in pickling solutions to inhibit acid attack on metals. Natural products, such as bran, gelatin, glue, byproducts from petroleum refining and coal coking, and wood tars were initially used. Modern inhibitors are largely formulations of wetting agents with mixtures of active synthetic materials, including nitrogen-base compounds (pyridine, quinidine, hexamethylene tetramine, and other amines or polyamines), aldehydes and thioaldehydes, acetylenic alcohols, and sulfur-containing compounds such as thiourea and thiourea derivatives (Ref 13). Frequently, two or more active ingredients provide a synergistic effect, whereby the mixture is more effective than the additive effect of the individual components. A good inhibitor should not exhibit "breakout," which is sludge that deposits on the work, a characteristic of many of the natural products formerly used. It should be stable at the temperature of the pickling bath and should not emit offensive odors. Modern inhibitors used with sulfuric acid often contain thiourea or a substituted thiourea with an amine. Most of the newer inhibitors developed for use with hydrochloric acid contain amines or heterocyclic nitrogen compounds as active ingredients.

In sulfuric acid pickling, the ferrous sulfate buildup in a worked pickling bath also inhibits the activity of the acid and reduces the effectiveness of the solution for cleaning and brightening the steel. Most steels are reactive with acid and require inhibited solutions. Steels with high phosphorus contents (0.03% or above) are particularly prone to overpickling. Inhibited acid solutions are generally used in continuous strip lines and in oil well drilling operations to clean the internal surfaces of pipes. Although the immersion times during continuous strip pickling are substantially shorter than in batch operations, an excessive loss of base metal would occur during a line stop if inhibitors were not used. This would not only be objectionable because of the roughened overpickled surface, but also because of the effect on critical final-gage requirements of the product.

In commercial practice, inhibitor concentrations are usually expressed in terms of percent by volume of the makeup acid used, because most inhibitors are liquids. For example, if an addition of 0.9 L (0.25 gal) of inhibitor is made with 380 L (100 gal) of concentrated acid, then the concentration of inhibitor is said to be 0.25 vol% of the acid. Additions are best made proportional to the acid additions to pickling tanks or to the acid volume in large storage tanks or truckload shipments of acid. A poor method of introducing inhibitor to pickling solutions is by adding inhibitor to the bath at certain time intervals that are not related to actual acid additions. Before inhibitor additions are made, the bath may be underinhibited, and just after additions are made, the bath might be overinhibited.

It is generally agreed that the primary step in the action of inhibitors in acid solutions is adsorption onto the metal surface. The adsorbed inhibitor then acts to retard the cathodic and/or anodic electrochemical processes of the corrosion. When inhibitor concentrations are much below recommended levels, the adsorbed layer of inhibitor on the steel surface may be incomplete, which can result in preferential attack on unprotected areas.

To help control inhibitor concentrations in pickling solutions, inhibitor manufacturers have proposed the inclusion in their formulations of various materials that can be used as tracers in determining inhibitor concentration. One scheme involved the use of fluorescent dyes and colorimetric analyses. However, because of color changes in the dye with time, this approach has not proven satisfactory. Another possibility is the inclusion of phosphates or phosphoric acid, which can be detected in either sulfuric or hydrochloric acid pickling solutions by colorimetric procedures. Inclusion of lithium salts with subsequent analyses by neutron activation or atomic absorption spectrometry also has been tried. For amine-based inhibitors, concentrations in pickling solutions can be estimated by determining the nitrogen concentration in the solution

and comparing it with the known nitrogen concentration in the neat inhibitor. Analyses can be made by the Kjeldahl method, or if the inhibitor contains simple amines rather than heterocyclic amines, by using an ammonia selective ion electrode with suitable standards.

Before a new inhibitor is introduced in a plant, some laboratory tests should be made to identify concentration dependence of inhibition under conditions appropriate for a particular operation. The degree of acid attack on the base metal can be measured by determining the weight loss or hydrogen evolution from a steel specimen of known size and weight that is immersed for a specified time in a solution containing known amounts of acid, iron salts, and inhibitor at a temperature typical of use. Results of inhibitor testing are often expressed as percent inhibition, defined as: 100 × [(weight loss, uninhibited) -- (weight loss, inhibited)] divided by (weight loss, uninhibited). This relationship is useful when a number of inhibitors are being compared under a selected set of conditions. A value of 90% inhibition, associated with proper usage of an effective inhibitor, implies that the corrosion rate is only 10% of the rate when no inhibitor is used.

For plain carbon steels containing less than 0.40% C, and for batch pickling baths that contain 10 to 14 wt% sulfuric acid (1.82 sp gr) and operate at 71 °C (160 °F) or higher, strong inhibitors are used at concentrations of 0.25 to 0.50 vol% raw acid in the tank. When the concentration of ferrous sulfate reaches 30 wt%, the solution should be discarded, because this level of iron salt slows down the pickling process and may cause smut to form on the surface of the product. When iron levels approach this concentration in batch pickling with sulfuric acid, further additions of inhibitor may not be required.

Plain carbon steels containing 0.40% C or more are pickled in similar baths with somewhat lower temperatures (60 to 66 °C, or 140 to 150 °F) and with ferrous sulfate concentrations of less than 20 wt%. With hydrochloric acid, strong inhibitors are used at concentrations of 0.125 to 0.25 vol% of raw acid. Because pickling rates in both sulfuric acid and hydrochloric acid tend to decrease when the pickling solution contains high levels of iron (higher levels are tolerable with HCl), especially when coupled with low acid concentration, commercial pickling bath additives, or accelerators, are sometimes used to enhance pickling rates. These proprietary materials are usually formulated with inhibitors to prevent excessive base-metal attack by the acid during scale dissolution.

Uninhibited acid solutions are often used for pickling high-alloy steels, because more chemical action is required to remove the oxide. Alloy or plain carbon steels used in forming flat and shaped sections are sometimes etched by uninhibited acid solutions to produce a surface that retains the die lubricant during cold working. These solutions are used also for conditioning steel with slivers and sharp corners, as well as steel that is ground before coating for additional cold working. If an inhibitor is used when pickling alloy steels, concentrations that are somewhat less than those recommended for plain carbon steels are suggested.

Reference cited in this section

13. R.M. Hudson and C.J. Warning, Effectiveness of Organic Compounds as Pickling Inhibitors in Hydrochloric and Sulfuric Acid, *Met. Fin.,* Vol 64 (No. 10), 1966, p 58-61, 63

Precleaning

Alkaline precleaning before acid pickling is beneficial for removing soils that do not readily react with acid, such as grease, oil, soaps, lubricants, and carrier coatings. A buildup of such materials in a pickling bath interferes with the pickling action, especially when the pickling time is short (20 s or less). A typical alkaline cleaning solution contains 20% sodium hydroxide, 30% organic chelating agents, 45% complex phosphates, and 5% surface-activating agents. The concentration of the cleaner in the precleaning solution is 30 to 45 g/L (4 to 6 oz/gal), and the operating temperature of the solution ranges from 82 °C (180 °F) to boiling. After immersion in the cleaning solution, the work is rinsed in water at room temperature.

Chelating Agents. Lubricants used in cold-drawing operations contain compounds of calcium, zinc, magnesium, iron, or some other metal. Removal is facilitated when alkaline cleaners containing chelating agents are used. Chelates react with the metal ion to form a soluble metal chelate. Chelates include citric acid, ethylene diamine tetraacetic acid, gluconic acid, and nitrilotriacetic acid. Although all chelating agents react in a similar manner, certain chelates have a greater affinity for specific metal ions. The solution must contain an adequate amount of chelate and be of the proper pH (usually, basic) for effective cleaning. Chelates must be stable with respect to the particular environment (oxidizing or reducing, acid or alkaline).

A procedure for determining the chelating power of the alkaline cleaning formula consists of mixing 10 mL of filtered cleaning solution with 10 mL of distilled water and 10 drops of saturated 5% ammonium oxalate solution. This mixture is then titrated carefully with a 2% solution of calcium chloride until one drop of the latter produces a faint, permanent turbidity. The number of milliliters of 2% calcium chloride required is equivalent to the chelating power.

Equipment

Storage Tanks for Acid. Hydrochloric acid can be stored in rubber-lined steel tanks or glass-fiber-reinforced polyester-resin tanks. Polyester-glass linings in steel tanks are not recommended, because permeation of acid through pinholes in the lining could result in attack on the steel. Hydrofluoric acid (70%) is usually stored in plastic-lined tanks, although low-carbon steel can be used at temperatures up to 38 °C (100 °F) if properly passivated. Concentrated nitric acid (94.2% or higher) is best stored in tanks made of 3003 aluminum. For less concentrated nitric acid, tanks should be of type 304L stainless steel (type 304 annealed stainless for nonwelded construction) or 15 to 16% high-chromium iron. Dilute sulfuric acid is more corrosive to iron and steel than more concentrated acid. A 93.2% sulfuric acid can be stored in iron tanks over a wide range of temperatures, but a 77.7% sulfuric acid must be stored below 38 °C (100 °F). A $\leq$74.4% sulfuric acid cannot be stored in unlined iron tanks or carried through unlined iron pipes. A glass or phenolic lining, among others, can be used.

Batch Pickling Tanks and Auxiliary Equipment. Construction materials for pickling tanks include wood, concrete, brick, plastic, and steel. Acid-resistant linings provide protection for the outer shell of the tank and are commonly made from natural, pure gum, or synthetic rubber. Acid-resistant brick is used to line the sides and floor of the tank. Bricks are mortared with poured sulfur cement or an acid-resistant resinous cement. Drainage lines should be made of vitrified tile caulked with an acid-resistant cement. Figure 1 shows the materials used in constructing a 3.5 to 4.4 Mg (3.9 to 4.9 ton) capacity tank for the pickling of coiled steel. In a batch pickling operation, bar product to be pickled is placed in tiers on crates and racks made of an acid-resistant material, such as Monel metal. Coils of strip, rod, or wire are pickled by passing a C-hook or chain through the open center. The holders are raised and lowered by an overhead crane.

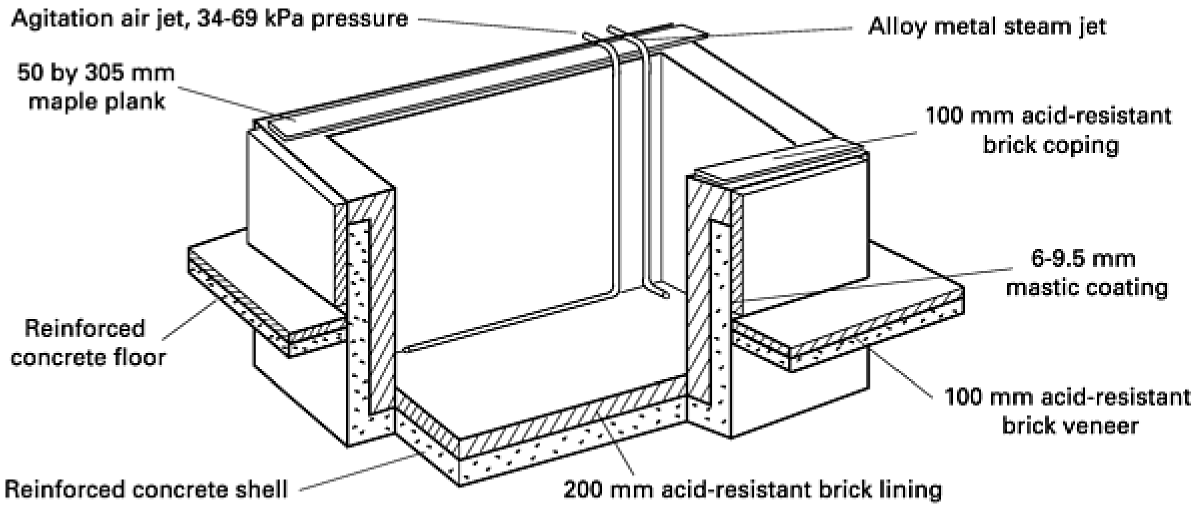


Fig. 1 Materials used in construction of 3.5 to 4.4 Mg (3.9 to 4.9 ton) capacity tanks for pickling coils of steel

After pickling, the product should be rinsed with high-pressure cold-water sprays to remove excess acid solution. It should then be placed in a hot-water rinse tank with sufficient overflow to ensure that the pH is not less than 5 or 6.

Heating Methods and Temperature Control. In the past, the most widely used method of heating pickling solutions was the direct injection of live steam through steam jets. Although steam so introduced does provide some agitation of the solution, the steam condensate dilutes the pickling solution, requiring higher amounts of acid to be added to maintain concentration. Steam sparging also increases the volume of spent pickle liquor. Better heating methods include coil steam heat, heat interchangers, and, for small installations, electric immersion heaters. Heating equipment must be made of acid-resistant materials, such as carbon, lead alloy, stainless steel, or zirconium for use with sulfuric acid. Carbon and polytetrafluoroethylene-covered heat exchangers should be used with hydrochloric acid. Acid-resistant

indicating and regulating temperature-control instruments are available for pickling solutions. Heaters can be centrally located or, in the case of continuous pickling, placed at strategic intervals along the tank.

Continuous-Strip Pickling Lines. A few pickling lines make use of vertical towers in which one or two hydrochloric acid spray columns are used (Ref 14, 15). The acid spray columns are assembled and sealed in sections made of fiber-glass-reinforced polyester, with a tower height of 21.3 to 45.7 m (70 to 150 ft). The tank sections are made from rubber-lined steel. After use, acid flows into a sump and is returned to the circulating tank. The composition of the acid in the recirculation tank is typically maintained at 11 g/100 mL HCl and 13% $FeCl_2$. It is passed through a carbon-block heat exchanger and delivered to the sprays at 77 °C (170 °F). Most lines of this type have acid-regenerating facilities. Entry and exit coil handling are similar to the more common horizontal lines.

Continuous-strip pickling lines with horizontal pickling tanks are capable of handling coils that are welded head to tail. The entry section comprises a coil conveyer, one or two uncoilers, one or two processors, one or two shears, and a welder. Processors are integral with the uncoiling equipment and consist of a mandrel, hold-down roll, and a series of smaller-diameter rolls. As the strip is flexed through the processor, some cracking occurs in the scale layer, although not nearly as much as that imparted by a temper mill. Proper welding and weld trimming is essential to avoid strip breaks in the line. The section prior to the pickling tanks uses bridles for tensioning the strip; a strip accumulator, either in the form of wet looping pits or, for more modern lines, a coil-car accumulator; and, for many lines, a temper mill to crack the scale on the surface of the strip. A stretch leveler can replace the temper mill and not only effectively cracks the scale, but also contributes to superior strip shape.

The pickling section usually contains three or more tanks. So-called "deep tanks" are typically 1.22 m (4 ft) in depth and up to 31.3 m (90 ft) in length. Acid tanks are steel shells with layers of rubber bonded to the steel. The rubber is protected from abrasion by a lining of silica-base acid-proof brick. Most lines have a cascade flow of pickling solutions countercurrent to the direction of strip movement. When fresh acid is added to the last tank, it will contain the highest concentration of acid. Acid concentrations will decrease from the last tank to the first tank, from which the spent pickle liquor is discharged. A rinse section follows the pickling section.

An especially effective rinsing method used on many continuous lines is the cascade rinse system (Ref 16). Several rinse compartments are used, and fresh water is added to the last compartment. The solution in that compartment cascades over weirs into the preceding compartments. The excess overflows from the first compartment and is sent to the waste-water treatment plant (a portion can be used for makeup water in the pickle tanks). Each compartment contains less acid than the previous compartment. At the exit end of the line, there are usually an exit strip accumulator, steering rolls, a strip inspection station, dual side trimmers, an oiler, and two coilers. Pickling lines must have fume scrubbers to capture emissions/spray from the pickle tanks.

In some modern lines, the pickling solution is contained in shallow tanks with liquid depths of approximately 0.41 m (16 in.) and lengths up to approximately 36 m (118 ft). Although they involve a cascade system, the solution in each tank is recirculated through a heat exchanger. During a line stop, the pickling solution can be rapidly drained from shallow tanks into individual storage tanks and then pumped back when the line starts up. Lines with deep tanks usually have strip lifters provided to remove the strip from the acid solution during an extended line stop. Tank covers may be made from fiberglass or polypropylene. Some lines have squeegee rolls, covered with acid-resistant rubber, located above and below the strip at each tank exit to minimize acid carryover from one tank to another.

Maximum speeds in modern lines in the pickling section can be as high as 305 to 457 m/min (1000 to 1500 ft/min). Although sustained operation at such speeds is limited by other aspects of coil handling, the selection of pickling tank acid concentrations and temperatures must be such that complete scale removal is achieved during periods of high-speed operation. The combination of a pickling line and a cold reduction mill in tandem represents a new state of the art in continuous processing facilities (Ref 17). Another type of strip pickling line suitable for plants with moderate production requirements is the push-pull type, which has many of the features of the continuous-type lines, but no welder (Ref 18). Turbulent-flow, shallow-tank, continuous-strip lines that claim to provide more effective pickling action than conventional lines have been developed (Ref 19).

References cited in this section

14. Spray Tower Pickles Steel, *Iron Age*, Vol 190, 4 Oct 1962, p 78-79

15. D.E. Poole, Hydrochloric Acid Pickling of Steel Strip, *J. Met.*, Vol 17, 1965, p 223-224

16. J.B. Hodsden and W.L. Van Kley, Cascade Rinse System at Inland's 63-in. Continuous Strip Pickling Line, *Iron Steel Eng.,* Vol 51 (No. 3), 1974, p 49-53
17. N.L. Samways, Modernization at Pittsburg to Make USS-POSCO More Competitive, *Iron Steel Eng.,* Vol 64 (No. 6), 1987, p 21-29
18. G. Kuebler, Pushing for Pickling Productivity, *33 Metal Producing,* Vol 30 (No. 9), 1992, p 28-31
19. F.G. Pempera and F.W. Delwig, Turbulent Shallow-Type Pickling Lines, *Iron Steel Eng.,* Vol 65 (No. 3), 1988, p 33-36

Effect of Process Variables on Scale Removal in Sulfuric Acid

The composition of scale on hot-rolled strip is primarily influenced by the cooling rate after coiling. When pickling with sulfuric acid, this is important because conditions that increase the amount of FeO in the scale (rapid cooling) render it more easily pickled (Ref 20, 21). With hydrochloric acid, the solubility of Fe_3O_4 is significantly greater than it is in sulfuric acid (Ref 22). Therefore, the relative amounts of FeO versus Fe_3O_4 in the scale layer are of less importance with hydrochloric acid. As the coiling temperature after hot rolling is increased, the scale thickness increases and pickling rates decrease (Ref 23).

The degree to which pickling rates are affected by concentrations of sulfuric acid and ferrous sulfate, as well as by temperature, is illustrated in Fig. 2 and 3. These bench-scale tests were made with specimens cut from the center and tail end of a hot-rolled coil (2.0 mm, or 0.080 in., thickness) of low-carbon drawing-quality steel. The respective scale thicknesses were 2.6 mg/cm^2 (0.00475 mm, or 0.000187 in.) and 5.2 mg/cm^2 (0.00953 mm, or 0.000375 in.). As might be expected, specimens with thicker scale required longer immersion times for scale removal than specimens with thinner scale under the same bath conditions. The time to remove scale decreased with increases in temperature from 80 to 100 °C (175 to 212 °F) and with increases in acid concentration from 5 to 25 g/100 mL. With sulfuric acid, increases in the concentration of ferrous sulfate exert an inhibiting action that increases the time for scale removal. The effect is greater when acid concentrations are 10 g/100 mL or lower. Pickling efficiency in a bath decreases with time, unless fresh acid additions are made, because the acid concentration drops while the ferrous sulfate concentration increases. Increased agitation in the bath increases the pickling rate. When specimens with thick scale are pickled in acid solutions of 10 g/100 mL or lower, increases in inhibitor concentration tend to slow down the pickling action.

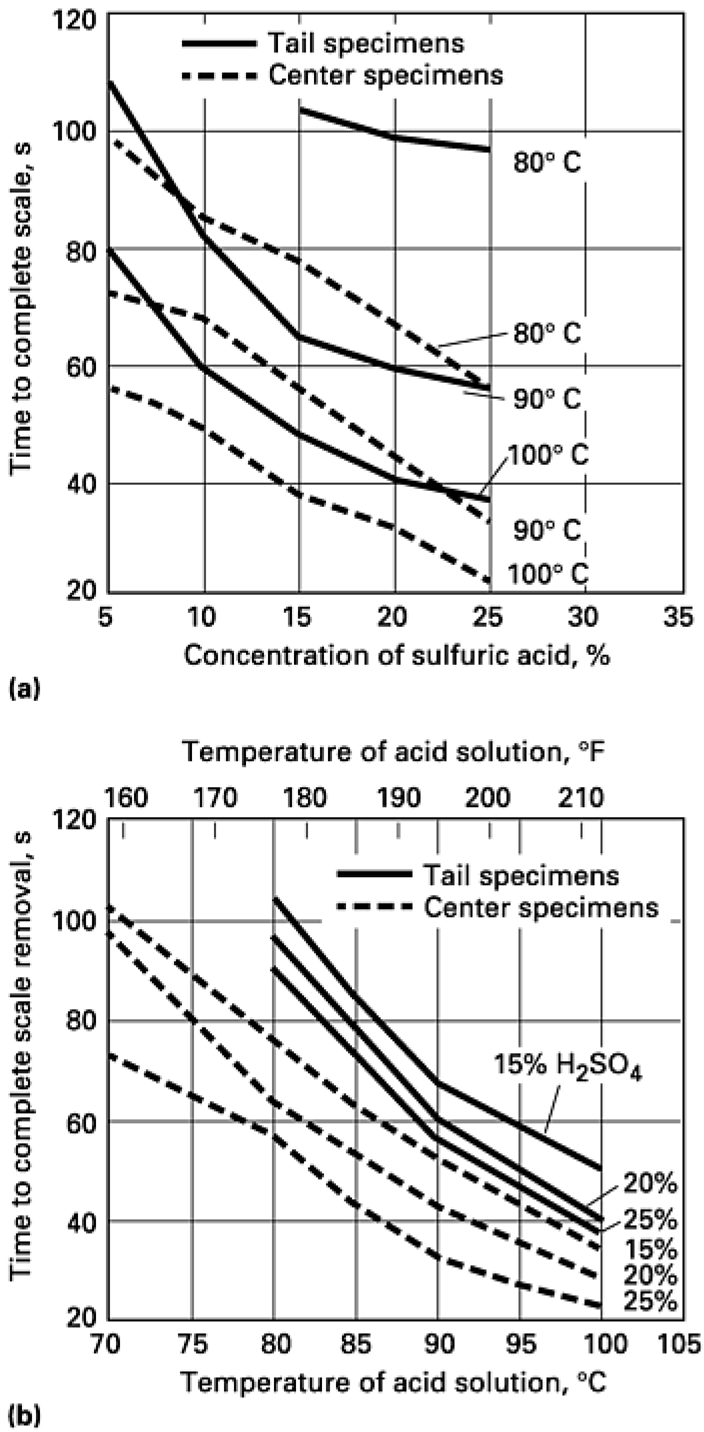
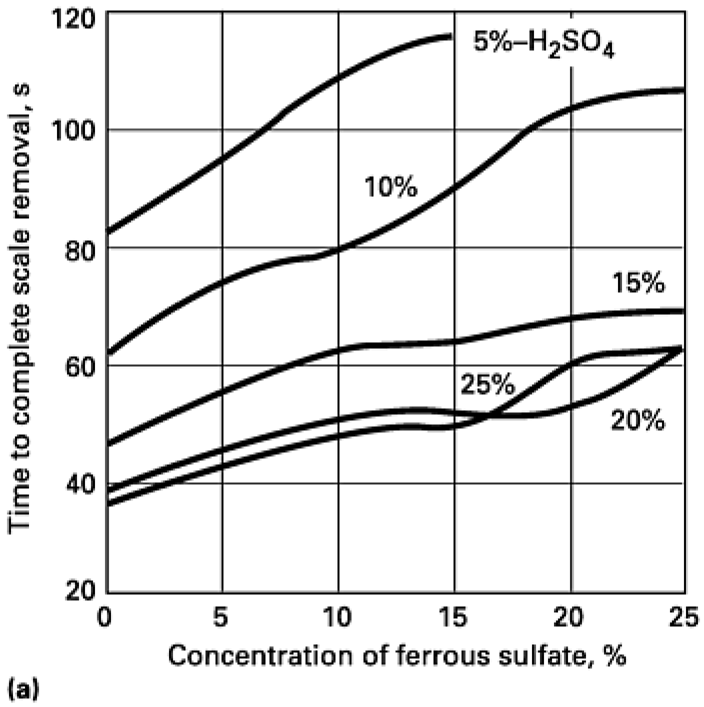


Fig. 2 Effect of acid concentration (a) and temperature of acid solution (b) on pickling time required to remove scale from sheet steel, 2 mm (0.080 in.) thick



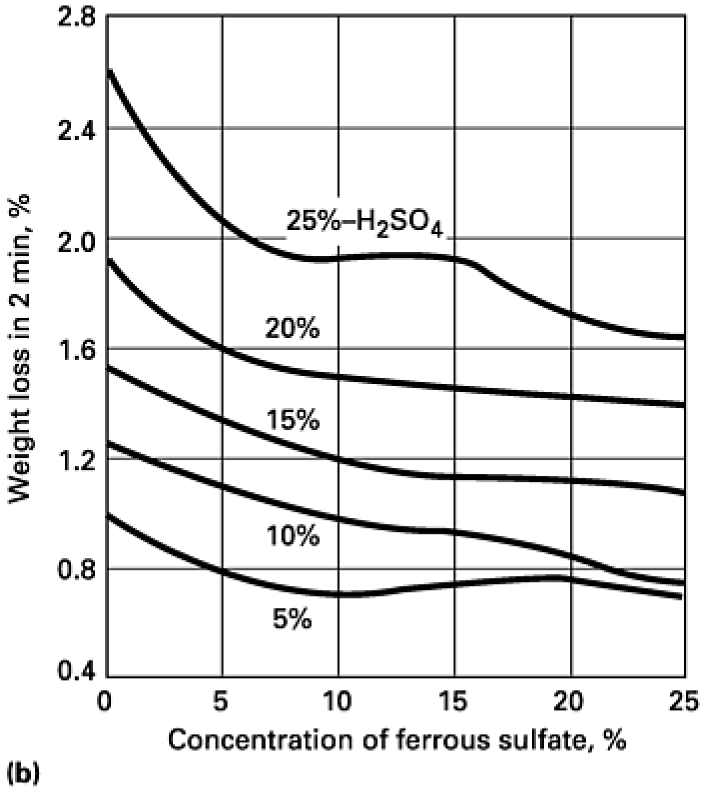


Fig. 3 Inhibiting action of ferrous sulfate on low-carbon drawing-quality sheet pickled for 2 min in sulfuric acid solutions of concentrations indicated. (a) Pickling time for complete scale removal. (b) Weight loss

In a separate bench-scale study (Ref 24), it was found that the influence of temper mill scale breaking (cracking the scale by imposing moderate room-temperature deformation to the workpiece) on the descaling time of hot-rolled strip in sulfuric acid solutions is pronounced. Descaling time is frequently half or less the amount required in a given solution without temper mill scale breaking, as illustrated in Fig. 4. The results of bench-scale experiments (unstirred solutions) with a commercial hot-rolled low-carbon steel with a scale weight of 3.4 mg/cm^2 (0.0062 mm, or 0.00024 in.) are also shown in Fig. 4. For nontemper-rolled material, descaling times were decreased as the temperature increased from 82 to 105 °C (180 to 220 °F). The pickling times achieved by increasing the temperature from 93 to 105 °C (200 to 220 °F)

were about the same as those that resulted from maintaining the temperature at 93 °C (200 °F) and using temper mill scale breaking (3%) before pickling.

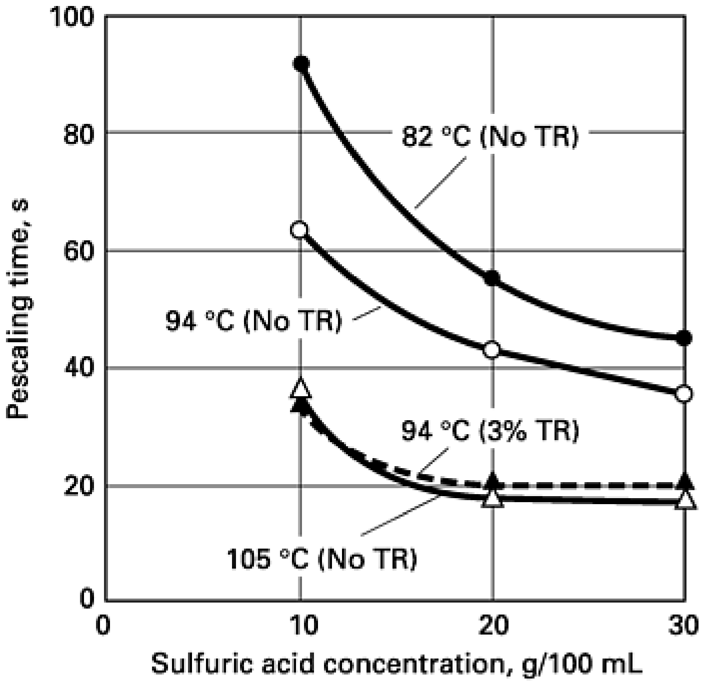


Fig. 4 Effect of solution temperature on pickling time for hot-rolled low-carbon steel; comparison with temper mill scale breaking. All solutions contained 15 g $FeSO_4$/100 mL. TR, temper rolled

Because the reductions in strip thickness introduced by temper rolling are relatively small, the effect of strip thickness profiles must be considered when used on pickling lines. *Crown* is an increase in thickness of the rolled center of strip as compared with the edges. For strip with some crown and feather edges, if the amount of reduction used for temper mill scale breaking is based on the center area with crown, then the thinner edge areas may not receive enough reduction to effectively crack the scale and enhance pickling. Commercial experience indicates that stretch leveling is at least as effective in cracking the scale as the use of a temper mill.

Decreases in pickling rates caused by increases in ferrous sulfate concentration were found to be less pronounced for more concentrated acid solutions. The time required for scale removal in tests at 93 °C (200 °F) was not affected by inhibitor usages up to 0.25 vol%, based on concentrated acid, but did increase when usages exceeded 0.50 vol% (0.25 or 0.50 gal inhibitor, respectively, per 100 gal concentrated acid).

The effect of strip speed, as well as the combined effects of acid and iron concentration, temperature, inhibitor usage, and degree of scale breaking on the pickling process was determined by using an apparatus constructed to simulate the motion of strip through a continuous-strip pickling line. Steel specimens were mounted on a cylindrical holder that could be rotated through a pickling solution. The solution was contained in a holder that had baffles to minimize bulk movement of the solution (Ref 2). Over the range of acid concentrations from 10 to 30 g/100 mL, descaling times were lowered by increases in strip speed from 0 to 30.5 m/min (0 to 100 ft/min), but the magnitude of the effect was not as great as that associated with hydrochloric acid solutions (which will be discussed below.) Only small decreases in descaling time were observed from 30.5 to 122 m/min (100 to 400 ft/min). Data obtained at a strip velocity of 122 m/min (400 ft/min), summarized in Table 2, should be pertinent to commercial continuous pickling in which line speeds can range from 1.5 to 6 m/s (300 to 1200 ft/min) or higher. Laboratory tests made with a well-stirred solution (mechanical stirring of 500 rev/min or greater) should give similar results to those in Table 2.

Table 2 Laboratory pickling tests using sulfuric acid solutions to remove scale from hot-rolled ingot cast steel

Temperature		Sulfuric acid concentration, g/100 mL	Ferrous sulfate concentration, g/100 mL	Time to remove scale, s			
°C	°F			0%[a]	1.5%[a]	3%[a]	4.5%[a]
82	180	10	15	90	. . .	. . .	. . .
82	180	20	15	55	. . .	. . .	. . .
82	180	30	15	45	. . .	. . .	. . .
93	200	10	10	55	. . .	. . .	. . .
93	200	20	10	30	. . .	. . .	. . .
93	200	30	10	30	. . .	. . .	. . .
93	200	5	15	. . .	. . .	15	. . .
93	200	10	15	70	20	10	10
93	200	20	15	50	15	10	5
93	200	30	15	40	15	10	5
93	200	10	20	70	. . .	. . .	. . .
93	200	20	20	40	. . .	. . .	. . .
101	214[b]	10	15	40	. . .	. . .	. . .
103	217[b]	20	15	30	. . .	. . .	. . .
106	222[b]	30	15	20	. . .	. . .	. . .

(a) Degree of temper mill scale breaking in percent temper rolled.

(b) Solutions were at the boiling point during the test.

The time required to remove scale from hot-rolled strip in stirred sulfuric acid solutions is significantly decreased by temper mill scale breaking. For nontemper-rolled material, pickling at temperatures near the solution boiling point (as high as 105 °C, or 222 °F) resulted in scale removal times that were about half those found at 82 °C (180 °F). At 93 °C

(200 °F), a typical solution temperature on commercial continuous-strip lines that use sulfuric acid, the benefit to be derived by temper mill scale breaking is much greater than would be achieved if the steel were pickled at higher temperatures without temper rolling. Without temper mill scale breaking, the time required to remove the scale was lowered by increasing the acid concentration from 10 to 30 g/100 mL and decreasing the ferrous sulfate concentration from the 15 to 20 g/100 mL range to 10 g/100 mL. An effective commercial inhibitor, even when used at twice the recommended concentration (0.25 vol% based on the makeup H_2SO_4), did not affect descaling rates. However, an effective accelerator does increase scale removal by as much as 30%.

References cited in this section

2. R.M. Hudson and C.J. Warning, Pickling Hot-Rolled Steel Strip: Effect of Strip Velocity on Rate in H_2SO_4, *Met. Fin.,* Vol 82 (No. 3), 1984, p 39-46
20. J.P. Morgan and D.J. Shellenberger, Hot Band Pickle-Patch: Its Cause and Elimination, *J. Met.,* Vol 17 (No. 10), 1965, p 1121-1125
21. C.W. Tuck, The Effect of Scale Microstructure on the Pickling of Hot-Rolled Steel Strip, *Anti-Corros. Methods Mater.,* Vol 16 (No. 11), 1969, p 22-27
22. B. Meuthen, J.H. Arnesen, and H.J. Engell, The System HCl-$FeCl_2$-H_2O and the Behavior of Hot-Rolled Steel Strip Pickled in These Solutions, *Stahl und Eisen,* Vol 85, 1965, p 1722
23. L. Hachtel, R. Bode, and L. Meyer, Influence of the Coiling Temperature on the Pickling Behavior of Mild Steel Hot Strip, *Stahl und Eisen,* Vol 104 (No. 14), 1984, p 645-650
24. R.M. Hudson and C.J. Warning, Factors Influencing the Pickling Rate of Hot-Rolled Low-Carbon Steel in Sulfuric and Hydrochloric Acids, *Met. Fin.,* Vol 78 (No. 6), 1980, p 21-28

Effect of Process Variables on Scale Removal in Hydrochloric Acid

The effect of hydrochloric acid and ferrous chloride concentrations, solution temperature, and scale breaking on pickling rates was studied in a series of laboratory tests with nonstirred solutions (Ref 24). It was found that the time required for scale removal decreases with increases in acid concentration and with increases in temperature. For an ingot-cast low-carbon steel with a scale thickness of 3.6 mg/cm^2 (0.0066 mm, or 0.00026 in.), test data for nontemper-rolled specimens in solutions that contain from 1 to 14 g HCl/100 mL and up to about 30 g $FeCl_2$/100 mL at temperatures of 66 to 93 °C (150 to 200 °F) can be summarized by an empirical equation:

$$\log t = A + B \log C_{HCl} + D (T_F + 459)^{-1} \quad \textbf{(Eq 12)}$$

where t is time in seconds for scale removal, C_{HCl} is acid concentration in g/100 mL, and T_F is the solution temperature in degrees Fahrenheit. For this steel, A = -2.22, B = -0.87, and D = 2824. From a limited number of tests made with specimens subjected to temper mill scale breaking, it was concluded that the times calculated by this equation are lower by approximately 10%. Inhibitor usages up to 0.50 vol% based on free acid did not affect time for descaling. The influence of iron buildup in hydrochloric acid solutions on pickling rate was not nearly as pronounced as the effect of iron buildup in sulfuric acid solutions.

In a subsequent study (Ref 3), the effect of strip speed on pickling time in hydrochloric acid was investigated. It was found that the time for scale removal decreased with an increase in strip velocity from 0 to ~1.3 m/s (0 to ~250 ft/min) (Fig. 5). As strip speeds were increased from 1.3 to 4 m/s (250 to 800 ft/min), there was no further decrease in descaling time. As expected, times were lowered by temperature increases from 66 to 93 °C (150 to 200 °F). The observed velocity effects for hydrochloric acid were greater than those observed for pickling in sulfuric acid, probably because of the depletion of acid that occurs near the steel surface during pickling in an unstirred bath and the higher acid concentrations usually used with sulfuric acid. Because descaling time in hydrochloric acid does not change for strip velocities above 1.3 m/s (250 ft/min), a number of tests carried out at 2 m/s (400 ft/min) are believed pertinent to continuous operations in which speeds can range from 1.5 to 6 m/s (300 to 1200 ft/min) or higher. These results were summarized by an empirical equation of the same form as that developed from still-bath data, except that A = -4.46, B = -0.56, and D = 3916. Similar equations have been obtained for other steels where coefficients A and B are negative and D is positive. For slow-pickling steels, A becomes less negative, whereas for fast-pickling steels, A becomes more negative. Equations of this type are useful for predicting the effect of changes in hydrochloric acid concentration and temperature on pickling time.

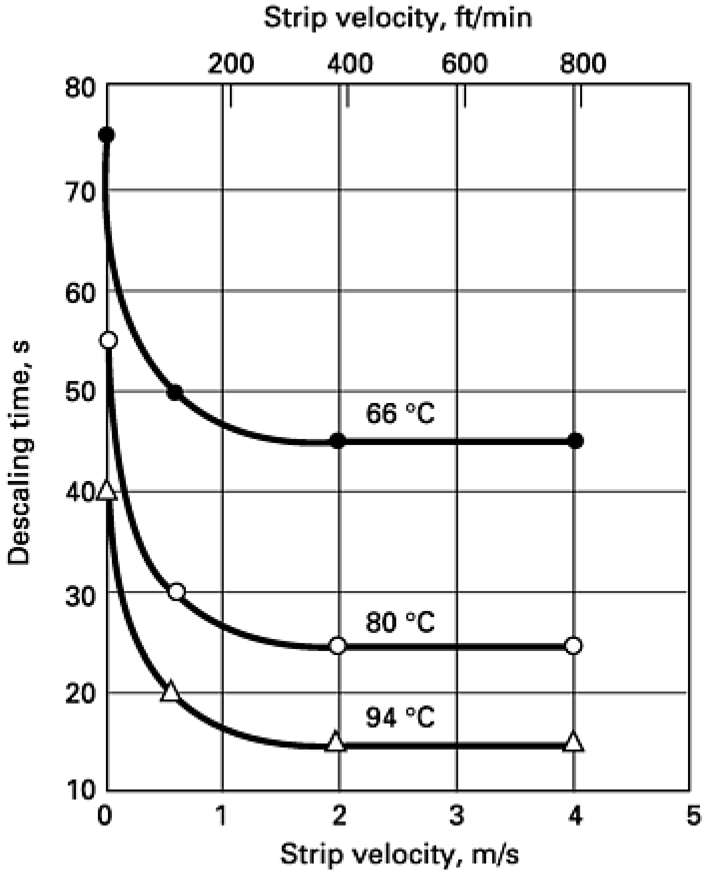


Fig. 5 Effect of strip velocity on descaling time of hot-rolled low-carbon steel in 4 g hydrochloric acid/100 mL, 22.7 g $FeCl_2$/100 mL

The effect of solution concentration and temperature on pickling has been studied in well-stirred hydrochloric acid solutions for aluminum-killed continuous-cast hot-rolled steels subjected to low coiling temperatures (LCT) of 566 to 593 °C (1050 to 1100 °F) and high coiling temperatures (HCT) (721 °C, or 1330 °F) after various degrees (up to 5%) of temper mill scale breaking (Ref 1). The average scale thickness on these steels was, respectively, 3.5 mg/cm^2 (0.0063 mm, or 0.00025 in.) and 5.0 mg/cm^2 (0.0090 mm, or 0.00036 in.). Pickling tests were made on temper-rolled and nontemper-rolled material at temperatures of 66 and 88 °C (150 and 190 °F) in uninhibited solutions that contained from 2 to 16 g HCl/100 mL and with 16 to 18 g $FeCl_2$/100 mL. The time required for complete removal of scale during pickling of nontemper-rolled LCT and HCT steels is shown in Fig. 6. The time required for complete removal of scale during pickling of these steels after 3% temper rolling is shown in Fig. 7. The data can be summarized using equations of the type mentioned above. Decreases in time for scale removal, going from 0 to 3% temper mill reduction, are much greater than the decrease in time associated with an increase in temper mill reduction from 3 to 5% (Table 3).

Table 3 Comparison of pickling times required for scale removal from hot-rolled AK-CC steels, as influenced by HCl concentration, solution temperature, degree of temper mill scale reaking and hot strip mill coiling temperature

Calculated from prediction equations developed for these steels. Solutions contained from 16 to 18 g $FeCl_2$/100 mL.

Temperature		Hydrochloric acid concentration, g/100 mL	Steel[a]	Time to remove scale, s		
°C	°F			0%[b]	3%[b]	5%[b]
65	150	2	LCT	52	34	25

65	150	6	LCT	28	18	13
65	150	10	LCT	20	13	10
65	150	16	LCT	16	10	7
65	150	2	HCT	114	43	22
65	150	6	HCT	61	23	12
65	150	10	HCT	46	17	9
88	190	2	LCT	25	19	16
88	190	6	LCT	13	10	8
88	190	10	LCT	10	8	6
88	190	2	HCT	42	27	20
88	190	6	HCT	22	14	11
88	190	10	HCT	17	11	8

(a) Based on hot strip mill coiling temperature. LCT, low coiling temperature; HCT, high coiling temperature.

(b) Degree of temper mill scale breaking in percent temper rolled

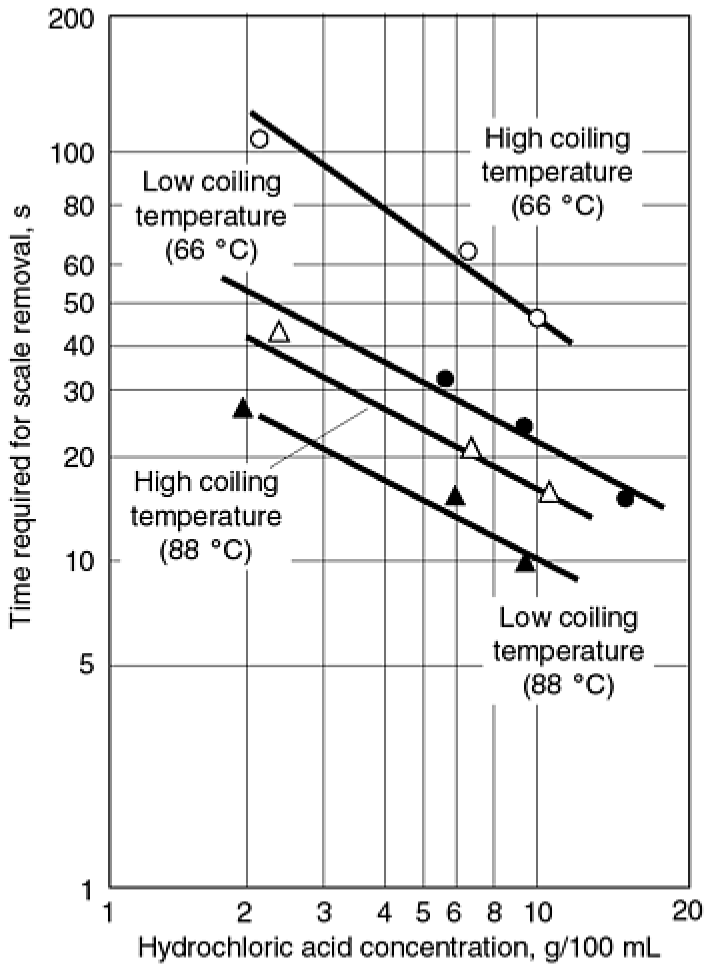


Fig. 6 Influence of acid concentration and solution temperature on time required for scale removal from hot-rolled strip, where strip was not subjected to temper mill scale breaking

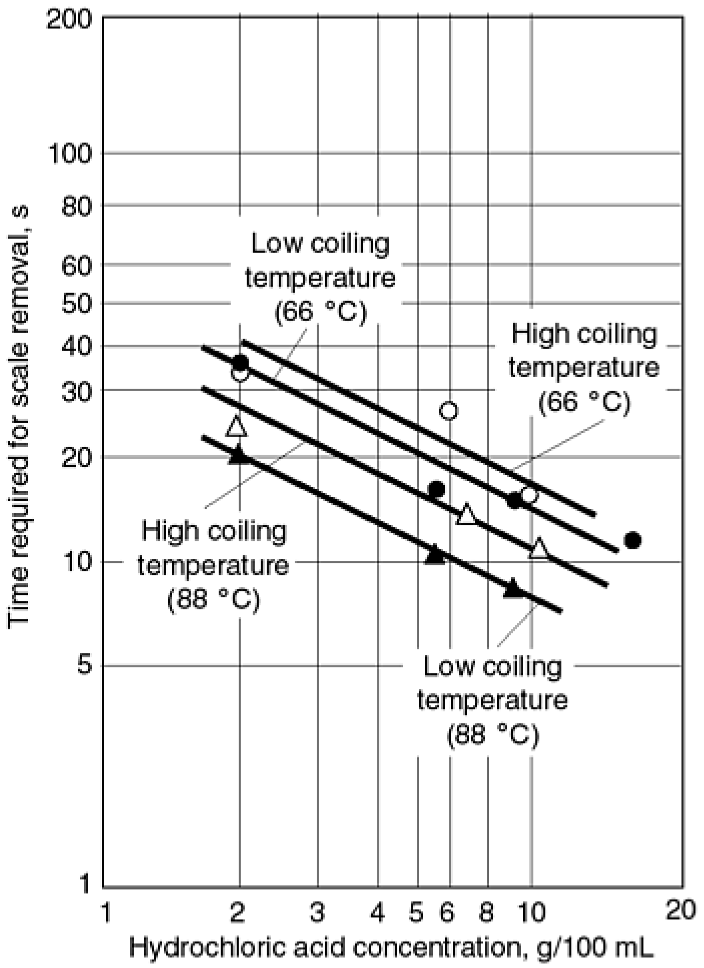


Fig. 7 Influence of acid concentration and solution temperature on time required for scale removal from hot-rolled strip, where strip was subjected to temper mill scale breaking (3% reduction)

For both LCT and HCT steels, the relative importance of degree of temper mill scale breaking is much greater for a solution temperature of 66 °C (150 °F) than it is for 88 °C (190 °F). Without scale breaking, the time required for scale removal under the same conditions of acid concentration and solution temperature is substantially longer for the HCT steel than for the LCT steel. With adequate scale breaking (3% or more reduction), and when using acid concentrations and temperatures that are favorable for pickling LCT material, commercially useful pickling rates can be achieved for HCT material.

References cited in this section

1. R.M. Hudson, Pickling of Hot-Rolled Strip: An Overview, *Iron Steelmaker,* Vol 18 (No. 9), 1991, p 31-39
3. R.M. Hudson and C.J. Warning, Effect of Strip Velocity on Pickling Rate of Hot-Rolled Steel in Hydrochloric Acid, *J. Met.,* Vol 34 (No. 2), 1982, p 65-70
24. R.M. Hudson and C.J. Warning, Factors Influencing the Pickling Rate of Hot-Rolled Low-Carbon Steel in Sulfuric and Hydrochloric Acids, *Met. Fin.,* Vol 78 (No. 6), 1980, p 21-28

Batch Pickling

Carbon steel rod, wire, and pipe are usually batch pickled in sulfuric acid solutions. Rod ranging from 5 mm (0.200 in.) to over 17 mm (0.675 in.) in diameter in coils weighing from 136 kg (300 lb) to more than 454 kg (1000 lb) can be pickled using one to ten coils at a time. With wire, especially for diameters below 3 mm (0.100 in.) the packing effect makes it difficult for the acid solution to penetrate and contact all wraps uniformly. To promote better cleaning of wire, the coil sizes can be restricted and the coils bounced during the pickling operation. Bar flats are held apart with separators

to improve solution contact. The heavy scale on patented rod (0.40% C, or higher) can also be removed by pickling for a sufficient time in sulfuric acid.

In one plant that batch pickles bar stock, the makeup solution contains 14 to 15 g/100 mL sulfuric acid and is operated at 60 °C (140 °F) until the concentration of acid drops to about 7 g/100 mL. Fresh acid is added to increase the concentration to about 12 g/100 mL, and the bath is operated until the concentration decreases to about 6 g/100 mL. The temperature is gradually increased during this period to about 68 °C (155 °F). Inhibitors are used at concentrations up to 0.5 vol% of the free acid present. When the iron content in solution reaches about 8 g/100 mL, the solution is no longer used.

Most iron and steel castings are cleaned by mechanical methods, such as shot blasting, sand blasting, and tumbling. When pickling is used, the castings are cleaned in solutions containing sulfuric and hydrofluoric acids. The concentration of each acid depends on whether the primary purpose is to remove sand or scale. Increased hydrofluoric acid is needed to remove embedded sand from the casting surface, whereas sulfuric or hydrochloric acids are sufficient for simple scale removal. Table 4 gives the operating conditions for pickling iron and steel castings. Before being pickled, castings must be free of oil, grease, and other contamination. After being removed from the pickling solution, castings are rinsed thoroughly in hot water. Residual heat permits self-drying, but drying can be accelerated by using a fan. If the shape of the castings hinders drying, then the process can be completed in a baking oven.

Table 4 Operating conditions and solution compositions for pickling iron and steel castings

Operating variable[(a)]	Sand removal	Scale removal
Sulfuric acid, %	5	7
Hydrofluoric acid, %	5	3
Water, %	90	90
Temperature[(b)], °C (°F)	66-85 (150-185)	49 to over 85 (120 to over 185)
Average immersion time, h	4	4

(a) Percentages by volume.

(b) 49 °C (120 °F) is for slow pickling, 66 to 85 °C (150 to 185 °F) is for average pickling speed, and over 85 °C (185 °F) is for fast pickling.

Stainless steel products should be free of oil, grease, or other soils that can contaminate the pickling solution. Heating the steel to a temperature under 540 °C (1005 °F) to burn off contaminants such as light oils is sometimes used as a cleaning method before pickling. However, some austenitic stainless steels are sensitized when heated at 400 to 900 °C (750 to 1650 °F) and may undergo intergranular corrosion. If alkaline precleaning is used, then adequate rinsing is required before pickling. Precleaning is not required if oxide or scale is the only soil on the surface. Forgings and castings usually are not pickled, but forgings can be pickled as an inspection procedure to determine the presence of surface defects. If pickling is necessary, then castings and forgings are pickled by the procedures used for rolled forms of stainless steel.

Pickling cycles for the 300-series austenitic stainless steels are given in Table 5. The lower immersion time values are for pickling the lower-alloy steels, whereas the upper values are for the more highly alloyed steels, such as types 309, 310, 316, 317, and 318. The immersion time in the acid solutions can be reduced substantially by prior treatment of the

material in a salt descaling bath. Electrolytic pickling in sodium sulfate is also used as a pretreatment. Pickling cycles for the low-carbon 400-series stainless steels are given in Table 6. As with 300-series steels, immersion time can be reduced by pretreatment. The higher-carbon grades of 400-series stainless steels are pickled as indicated in Table 6, except that the immersion time in the sulfuric and nitric acid solutions is reduced to 5 to 20 min and 5 to 10 min, respectively.

Table 5 Sequence of procedures for pickling 300-series stainless steels

Cycle	Solution composition[(a)], vol%	Operating temperature		Immersion time[(b)], min
		°C	°F	
Sulfuric acid dip	15-25 H_2SO_4[(c)]	71-82	160-180	30-60
Water rinse[(d)]	. . .	Ambient	Ambient	. . .
Nitric-hydrofluoric acid dip	5-12 HNO_3, 2-4 HF	49 max	120 max	2-20
Water rinse[(d)]	. . .	Ambient	Ambient	. . .
Caustic permanganate dip[(e)]	18-20 NaOH, 4-6 $KMnO_4$[(f)]	71-93	160-200	15-60
Water rinse[(d)]	. . .	Ambient	Ambient	. . .
Sulfuric acid dip	15-25 H_2SO_4[(c)]	71-82	160-180	2-5
Water rinse[(d)]	. . .	Ambient	Ambient	. . .
Nitric acid dip	10-30 HNO_3	60-82	140-180	5-15

(a) Acid solutions are not inhibited.

(b) Shorter times are for lower-alloy steels; longer times are for more highly alloyed types, such as 309, 310, 316, 317, and 318.

(c) Sodium chloride (up to 5 wt%) may be added.

(d) Dip or pressure spray.

(e) Sometimes used to loosen scale.

(f) Percent by weight.

(g) Boiling water may be used to facilitate drying.

Table 6 Sequence for pickling low-carbon 400-series stainless steels

Cycle	Solution composition[a], vol%	Operating temperature		Immersion time
		°C	°F	
Sulfuric acid dip	15-25 H_2SO_4[b]	71-82	160-180	5-30 min
Water rinse[c]	. . .	Ambient	Ambient	. . .
Caustic permanganate dip[d]	18-20 NaOH, 4-6 $KMnO_4$[e]	71-93	160-200	20 min to 8 h[f]
Water rinse[c]	. . .	Ambient	Ambient	. . .
Sulfuric acid dip	15-25 H_2SO_4[b]	71-82	160-180	2-3 min
Nitric acid dip	30 HNO_3	Ambient	Ambient	10-30 min

(a) Acid solutions are not inhibited.

(b) Sodium chloride (up to 5 wt%) may be added.

(c) Dip, pressure hose, or spray. High-pressure spray or jets are more effective for removing scale and smut.

(d) Sometimes used to loosen scale.

(e) Percent by weight.

(f) Immersion time may exceed this range.

(g) Boiling water may be used to facilitate drying.

Precipitation-hardenable stainless steels, such as 17-7 PH, AM-350, and AM-355, can be pickled in the annealed condition in a manner similar to that for the 300-series grades. In the precipitation-hardened condition, the high hardness and the nature of the structure make the steel susceptible to strain cracking during pickling. Therefore, the immersion times during pickling should be as short as possible. For precipitation-hardenable steels in the fully hardened condition, grit blasting to remove scale, followed by passivation in a 30 to 50% nitric acid solution, is recommended.

Control of Process Variables. The immersion time required to pickle a particular product can best be determined by trial. The influence of temperature on pickling time and iron buildup in pickling solutions is pronounced and therefore temperature control is important. Because the rate of pickling also increases in proportion to the concentration of the acid, periodic testing of the solution is important. Rinse tanks of the overflowing variety should have a sufficient flow of fresh water, so that acid buildup indicated by low pH readings does not occur. If rinse tanks are not of the overflowing variety, then they should be frequently monitored to determine how often they should be dumped.

Solutions containing sulfuric acid and iron can either be diverted to the pickling of other material or discarded when the iron content reaches 5 to 7 wt%. Nitric-hydrofluoric acid solutions are discarded when the iron content reaches 5 wt%, whereas nitric acid solutions are discarded when iron reaches 2 wt%. The caustic permanganate solution (Tables 5 and 6) is desludged every 3 to 5 mo, and makeup materials are added to it. Analytical procedures and sampling of these solutions are described in many texts on chemical analysis.

Continuous Pickling

Carbon Sheet and Strip. In a continuous-strip pickling line with three or more tanks, the concentration of acid is generally highest in the final tank and lowest in the initial tank from which the spent pickle liquor is discharged. Iron-salt concentrations are lowest in the final tank and highest in the initial tank. In one commercial line using sulfuric acid with four tanks and steam sparging for heating, typical acid concentrations in the tanks are 12, 15, 17, and 20 g/100 mL. Typical ferrous sulfate concentrations in these tanks are 20, 17, 14, and 12 g/100 mL. Tank temperatures are maintained at 93 to 99 °C (200 to 210 °F). If indirect heating had been used instead of steam sparging, then ferrous sulfate concentrations would have been higher.

In another commercial line using hydrochloric acid with four tanks and steam sparging for heating (tank temperatures of 82 to 88 °C, or 180 to 190 °F), typical acid concentrations in the tanks are 2, 3, 5, and 7 g/100 mL, and typical ferrous chloride concentrations are 21, 19, 16, and 14 g/100 mL. When indirect heating is introduced on this line, the acid concentrations are maintained at nearly the same levels, but the ferrous chloride concentrations become 34, 32, 26, and 20 g/100 mL. In another line using hydrochloric acid with three tanks and indirect heating (tank temperatures at 79 °C, or 175 °F), typical acid concentrations are 4, 12, and 16 g/100 mL, with ferrous chloride concentrations of 31, 16, and 6 g/100 mL.

To estimate the maximum line speed consistent with complete descaling under various tank conditions, the fact that there are different pickling rates for each tank must be considered. In a continuous-strip pickling line with four tanks, the effective immersed strip lengths are L_1, L_2, L_3, and L_4 (these lengths, measured in feet, are somewhat less than the tank lengths, especially for the initial and final tanks). If S is the line speed in feet per minute, then the time in seconds that strip is immersed in each tank is equal to each of these distances multiplied by $(60/S)$. If the temperature and solution composition are known for each tank, then the times required for complete descaling, *if carried out completely in a tank,* can be estimated from bench-scale test data that relates pickling time to tank concentration and temperature. These required pickling times can be designated as t_1, t_2, t_3, and t_4. For complete descaling to occur in a continuous-strip pickling line, the fractions of scale removed in each tank should total 1.00 or greater. These individual fractions are $(60L_1/S)/t_1$, $(60L_2/S)/t_2$, $(60L_3/S)/t_3$, and $(60L_4/S)/t_4$ for tanks 1, 2, 3, and 4, respectively. Imposing the condition that:

$$(60/S)\,[(L_1/t_1) + (L_2/t_2) + (L_3/t_3) + (L_4/t_4)] = 1 \qquad \textbf{(Eq 13)}$$

and multiplying both sides by S gives an expression for the line speed that is the *maximum* consistent with complete descaling under a particular set of conditions.

$$S_{max} = 60\,[(L_1/t_1) + (L_2/t_2) + (L_3/t_3) + (L_4/t_4)] \qquad \textbf{(Eq 14)}$$

If the calculation predicts a maximum line speed that is less than desired, then more aggressive tank conditions (higher acid concentration and/or temperature) should be adopted. If the calculation predicts a maximum line speed that is appreciably higher than that required or that can be mechanically sustained, then consideration should be given to adopting less aggressive tank conditions (lower acid concentration and/or temperature).

In one plant, strip from a continuous normalizing furnace exits into the air and the oxides formed are removed by pickling in two tanks that contain from 19 to 21 g H_2SO_4/100 mL with about 12 g $FeSO_4$/100 mL at 91 °C (195 °F). At the usual line speed of 0.61 m/s (120 ft/min), the total pickling time is about 60 s, and no difficulty is experienced in removing

scale under these conditions. A specimen of strip sampled after normalizing and before pickling was examined, and the scale was found to be predominantly FeO, the oxide most readily attacked by sulfuric acid.

Carbon Steel Rod and Wire. In one plant, steel rod of 5.56 mm (0.22 in.) diameter with from 0.6 to 0.8% C is continuous pickled with hydrochloric acid. A reverse-bend scale breaking operation precedes immersion for about 80 s in a 54 °C (130 °F) solution that contains from 12 to 15 g HCl/100 mL and from 3 to 30 g $FeCl_2$/100 mL. Rod sampled before and after scale breaking, but before pickling, was found to have about 80% of the scale removed by scale breaking.

In another plant, continuous pickling is used in connection with the continuous galvanizing of steel wire. Wire containing from 0.4 to 0.8% C is pickled in a 10 to 15 vol% solution of sulfuric acid (1.83 sp gr) at 71 to 82 °C (160 to 180 °F), spray-rinsed with cold water, pickled in a 40 to 50 vol% solution of hydrochloric acid (1.16 sp gr) at 54 to 60 °C (130 to 140 °F), spray-rinsed with cold water, fluxed and dried, and then dipped in molten zinc. Immersion time in each of the pickling solutions ranges from 16 to 32 s. Wire may have patenting scale or a light scale of lead oxide that is obtained from a molten lead bath following drawing.

Stainless Steel (SS) Strip. *Continuous-anneal pickle lines necessitate pickling times of several minutes or less, depending on the capabilities of the line and the grade being processed. Whenever possible, production should not be limited by the ability to pickle. Pickling practices should be adjusted to allow for desired production rates. Generally, practices should be selected that produce complete scale removal, minimum yield loss, and an acceptable pickled surface for the specific application. Overall surface cleanliness and corrosion test performance may influence customer definition regarding acceptable pickled surfaces.

Scales that form on stainless steels are more difficult to remove than those formed on carbon steels. Therefore, a single reducing acid, such as sulfuric or hydrochloric, is usually not effective. Pickle liquors used for stainless strip include sulfuric, sulfuric-hydrofluoric, nitric-hydrofluoric, and nitric acids. A typical pickling scheme could consist of a tub of sulfuric acid, followed by nitric-hydrofluoric acid, followed by nitric acid only. The most aggressive liquor is nitric-hydrofluoric acid. The oxidizing ability of nitric acid, coupled with the formation of strong fluoride complexes with iron, chromium, titanium, aluminum, and silicon, makes nitric-hydrofluoric acid an effective scale remover for stainless steels. Its use should be controlled as well as possible, because hydrofluoric acid is the most expensive acid commonly used, and because overpickling can result in excessive groundwater and air pollution.

Hot-Rolled SS Strip (Hot Bands). Hot-band scale is generally thicker and more irregular than scale produced from annealing after cold rolling. If hot bands are annealed after hot rolling and are then pickled, then the additional scale produced by annealing makes scale removal even more difficult. In either case, a common practice is to assist scale removal by using a scale breaker or by shot blasting before pickling. If shot blasting is used, then its effectiveness will depend on processing line speed, the shot type, impingement density and energy, and inherent fracturability of the scale itself. Generally, pickling can be carried out in sulfuric acid with or without hydrofluoric acid, followed by nitric-hydrofluoric acid. The acid concentrations, times, and temperatures, which must be determined empirically, will depend on the grade being processed, the processing line speed, and incoming scale characteristics. General conditions for 400- and 300-series hot bands are given in Table 7.

Table 7 Pickling conditions for hot-rolled stainless steel strip following shot blasting

Grade	Concentration (g/100 mL) and acid type	Temperature		Time, s
		°C	°F	
Ferritic	10-15 sulfuric plus 0-4 hydrofluoric	50-65	120-150	20-60
	5-10 nitric plus 0.2-1 hydrofluoric	50-65	120-150	20-60
Austenitic	10-15 sulfuric plus 0-4 hydrofluoric	50-70	120-160	20-60

	5-15 nitric plus 1-4 hydrofluoric	50-70	120-160	20-60

It is important to note that 400-series grades do not normally passivate in mixtures of nitric-hydrofluoric acid. Therefore, considerable base-metal yield loss can occur if pickling conditions are not well controlled when using this acid mixture. In addition, an increasing base-metal yield loss will increase airborne nitrogen oxides and acid consumption. Hydrofluoric acid, in particular, should be added either slowly and continuously or in small-volume increments, rather than in large, bulk volumes, which would substantially increase the acid concentration and the pickling rate. Pickling of 300-series grades is easier to control, because of base-metal passivation (that is, pickling will eventually stop when the clean base-metal surface passivates). The higher hydrofluoric concentrations required by 300-series grades makes it possible to make less frequent acid additions and to maintain control of the pickling process.

Because of short immersion times, the mechanism of scale removal is a combination of scale dissolution, undercutting of scale by acid attack of base metal, and mechanical removal of loose scale or smut by sprays and brushes after pickling. Therefore, effective sprays and brushing after pickling can have a significant effect on surface cleanliness. Scale that is removed by undercutting and that remains in the pickle liquor will usually dissolve.

Cold-rolled SS strip is normally annealed and pickled before shipment. The cold-rolled strip should be free of contaminants that could cause it to have a nonuniform appearance or pattern after annealing and pickling. Small quantities of clean rolling emulsion will burn off during annealing and should not cause problems. Annealing conditions will affect pickling practices for annealed cold-rolled materials. A consistent annealing furnace atmosphere will help produce a consistent scale that can, in turn, be removed using a consistent pickling practice. Uncontrolled cycling of the annealing atmosphere between oxidizing and reducing conditions can produce scale that is difficult to remove, resulting in unexplained loss of pickling.

Scale Conditioning Before Pickling. Scale produced by annealing after cold rolling is usually thinner than hot-band scale. Shot blasting is not normally used to fracture scale before pickling, because the surface would be roughened by this treatment. An oxidizing alkaline molten salt bath is an effective scale-conditioning method to use before pickling. The strip should contact the molten salt for at least 5 s at 455 to 470 °C (850 to 875 °F). Salt-bath conditioning may cut pickling yield loss in half for some grades, because milder pickling conditions can be used, such as the lower acid concentrations and temperature ranges given in Table 8. Benefits of a molten salt plus mild-acid descaling scheme, when compared with a strong acid only scheme, include better control of strip cleanliness and brightness, lower base-metal yield loss, higher line speeds where pickle tub length is limited, lower nitrogen oxide emissions, lower acid consumption, and reduced waste-disposal requirements. In some cases, the cost of salt-bath conditioning can be more than offset by savings in raw-acid costs, yield loss, and waste-disposal costs.

Table 8 Pickling conditions for cold-rolled stainless steel strip after annealing

Grade	Concentration (g/100 mL) and acid type	Temperature		Time, s
		°C	°F	
Ferritic	5-15 sulfuric plus 0-4 hydrofluoric	50-65	120-150	15-60
	5-10 nitric plus 0.1-1 hydrofluoric	50-65	120-150	15-60
	10-15 nitric only	50-65	120-150	15-60
Austenitic	10-15 sulfuric plus 0-4 hydrofluoric	50-65	120-150	15-60
	5-15 nitric plus 1-4 hydrofluoric	50-65	120-150	15-60

	10-15 nitric only	50-65	120-150	15-60

Acid Pickling Schemes. If scale has been preconditioned or if it is inherently easy to remove, then use of electrolytic sodium sulfate or electrolytically assisted sulfuric and nitric acids may be sufficient. Use of these liquors should result in less base-metal yield loss than would result if nitric-hydrofluoric acid were used, especially with 400-series grades. In some cases, combining electrolytic tubs with a mild nitric-hydrofluoric acid is effective.

Scales that are more difficult to remove require progressively harsher treatment with acids. Use of sulfuric acid, followed by nitric-hydrofluoric acid, followed by nitric acid only can usually be made effective. A good general approach is to develop practices that begin with less aggressive pickling conditions (low temperature, low acid concentrations, and minimum immersion times) and work toward more aggressive conditions as necessary.

Effects of Process Variables. The pickling rate in nitric-hydrofluoric acid will increase with temperature, hydrofluoric acid concentration, and, to a lesser extent, nitric acid concentration. For 300-series grades, increasing the nitric acid concentration much above 8 g/100 mL (w/v) may actually result in lower pickling rates in nitric-hydrofluoric acid solutions. For the efficient use of acids, spent pickle liquors should be high in metals and low in free-acid content. The most consistent pickling will be obtained if pickle liquors are maintained at steady-state conditions. For example, a 409-type SS might be pickled in 7 w/v nitric acid plus 0.5 w/v hydrofluoric acid plus 5 w/v metals at 60 °C (140 °F). Maintaining constant pickle tub chemistry can be achieved by operating in a feed-and-bleed mode, whereby acids and water are added at one end of a tub and spent pickle liquor overflows or is drained from the other end of the tub. Failure to add appropriate amounts of water along with concentrated pickling acids will result in eventual precipitation of metal salts in the pickle tub. In a nitric-hydrofluoric acid solution, the product of the percent of metal times the percent of hydrofluoric acid should not exceed 15.

Accelerators can be added to the above-mentioned acids at concentrations as low as 0.5 w/v, based on the volume of raw acid needed to increase the pickling rate by as much as 40%. These accelerators lower the interfacial tension between the steel and the acid and reduce the acid consumption by as much as 60%.

Note cited in this section

* The sections on stainless steels were prepared by Ronald D. Rodabaugh, ARMCO Inc.

Electrolytic Pickling

Electrolytic pickling is widely used commercially to remove superficial oxides from light-gage strip that is to be electroplated in high-speed continuous processing lines. Such pickling is usually carried out at ambient or room temperature, using a solution that contains from 5 to 10 wt% sulfuric acid with less than 2 g Fe/100 mL, with a coulomb density of about 805 C/m^2 (75 C/ft^2). Coulomb density is the product of current density and the treatment time. Depending on line speed, electrolytic pickling times in commercial electrotinning lines range from about 1 to 1.5 s. Current densities consistent with the conditions cited are usually less than 1075 A/m^2 (100 A/ft^2). For most electrotinning applications, the strip is the cathode during electrolytic pickling and the steel does not dissolve, nor is hydrogen gas generated on the surface. When the strip is the anode, some steel does dissolve, forming iron salts in the pickling solution. Because anodic pickling can form some carbon smut on the surface, an anodic pickling pass is often followed by a cathodic pass to promote a cleaner surface.

Hot-mill scale can also be removed from carbon steels by electrolytic pickling in a fraction of the time that chemical pickling requires, but at much higher current densities and somewhat higher solution temperatures than are required in the electrotinning application. The production of hydrogen at a steel cathode aids in scale removal both mechanically and by reducing the oxide film. Economic analyses, however, indicate that the excessive power costs associated with electrolytic pickling of hot-rolled carbon steel strip would render the method unfeasible, compared with chemical pickling. Electrolytic pickling might be considered for abnormally thick hot-mill scale or for scale layers on alloy steels that are difficult to remove by chemical pickling. Stainless steel has oxides in the scale that are especially difficult to remove during chemical pickling (chromium sesquioxide, Cr_2O_3, and iron chromite, $FeCr_2O_4$). Therefore, electrolytic pickling at current densities in excess of 1075 A/m^2 (100 A/ft^2) has been applied commercially. The electrolyte solution can be sulfuric acid or sodium sulfate.

Although sulfuric acid is used for either chemical pickling or electrolytic pickling, hydrochloric acid should only be used for chemical pickling. During electrolysis with hydrochloric acid, the anode reaction produces chlorine gas.

Pickling Defects

Pickling is frequently blamed for certain defects that appear during the pickling operation, but actually originate elsewhere. Some defects are the result of earlier operations, such as rolling, heat treating, or forging. Scratches introduced during hot rolling or pickling, as well as pickle its, both result in line-type surface imperfections that persist through subsequent processing stages. The effect of such defects on the surface properties of steel has been extensively studied (Ref 25, 26).

Underpickling results when the steel has not had sufficient time in the pickling tanks to become free of adherent scale. It occurs when the solution composition and temperature are not properly controlled. Small patches of scale that are not removed by pickling may persist through subsequent operations. Annealing in a reducing atmosphere will convert such scale to a reduced sponge-iron type of surface defect.

Overpickling causes porosity of the transverse surfaces and a roughening of the whole surface, accompanied by discoloration and a decrease in size and weight. Overpickling can be avoided by removing the material from the bath promptly when scale removal is complete. Inhibitors aid in preventing overpickling. For strip product, the undercutting of surface grains can result in pickup at hold-down boards at a cold mill and can lead to cold-mill scratches.

Pitting may be caused by overpickling, particularly when inhibitors are used, but in less-than-adequate amounts. Such pitting appears when material remains in the bath much longer than is necessary for complete scale removal. Pits caused by rolled-in scale, nonmetallic inclusions, or refractories in the rolling process are intensified during pickling. On heat-treated alloy steels and forgings, electrolytic pitting can occur, characterized by a patchwork of irregularly shaped pitted areas that are caused by an electrical potential between scaled areas and areas where scale has been removed from small areas before pickling. The use of inhibitors generally results in pitted areas of uniform depth. Without inhibitors, pitted areas are irregular in depth.

Hydrogen embrittlement occurs when cold-working operations follow too soon after pickling, because nascent hydrogen diffuses into the steel during pickling. Embrittlement of this type can be avoided by aging. Baking cleaned parts at 200 to 240 °C (390 to 465 °F) for 3 to 4 h may be necessary for high-strength steel (>1380 MPa, or 200 ksi). Cracking may occur on such embrittled steel within 4 h after pickling. Inhibitors help minimize this effect, but some that contain organic sulfur compounds may actually promote hydrogen pickup, even though they are highly effective in limiting base-metal loss (Ref 13).

Blistering is a defect on sheet and strip steel that is related to flaws in the steel caused by formation of gas pockets just beneath the surface during rolling when gaseous inclusions are present. Hydrogen formed in the pickling operation can penetrate these pockets to lift the surface, causing a blister.

Rusting can result on pickled product if rinsing is not thorough enough to maintain pickle salt and acid concentrations on the surface below levels that promote in-plant rusting. Threshold concentrations of chlorides (0.4 mg/m^2, or 0.04 mg/ft^2) and sulfates (0.6 mg/m^2, or 0.06 mg/ft^2) are associated with rusting on bare steel when relative humidities exceed 30% for chlorides or 50% for sulfates (Ref 27). Somewhat higher surface-concentration levels of chlorides or sulfates can be tolerated on material that is oiled after pickling, particularly if rust preventative inhibitors are present in the oil. Rinse additives are helpful in preventing stains on pickled product that is shipped or further processed without oiling.

Another source of contamination of pickled product is improper storage in areas subjected to acid spray from pickle tanks or to air-borne hydrogen chloride emissions. The vapor pressure of hydrogen chloride above solutions that contain hydrochloric acid and ferrous chloride increases with temperature. It also increases with increases in both acid and salt concentration. Water vapor losses above pickling baths are far greater than hydrogen chloride vapor losses. The vapor pressure of water over pickling solutions increases with temperature and decreases with increases of acid and iron-salt concentration. This last statement is true for both hydrochloric and sulfuric acid solutions.

References cited in this section

13. R.M. Hudson and C.J. Warning, Effectiveness of Organic Compounds as Pickling Inhibitors in Hydrochloric and Sulfuric Acid, *Met. Fin.,* Vol 64 (No. 10), 1966, p 58-61, 63
25. R.M. Hudson, Strip Surface Imperfections After Cold Reduction Resulting from Initial Scratches, *Iron Steelmaker,* Vol 14 (No. 1), 1987, p 30-42
26. R.M. Hudson and H.M. Alworth, Formability of Annealed Sheet and Black Plate as Affected by Scratches Before Cold Reduction, *Iron Steelmaker,* Vol 17 (No. 2), 1990, p 26-32
27. L.E. Helwig, Rusting of Steel Surfaces Contaminated With Acid Pickle Salts, *Met. Fin.,* Vol 78 (No. 7), 1980, p 41-46

Disposal of Spent Pickle Liquor

Spent pickle liquor (SPL) from sulfuric acid pickling may contain from 2 to 15 wt% H_2SO_4 and 5 to 20 wt% $FeSO_4$. Neutralization with a lime slurry produces a mixture of sparingly soluble gypsum ($CaSO_4$) and iron hydroxide that can be pumped to lagoons for settling and, eventually, disposed of as landfill. In a modification of this process, aeration is used to convert iron hydroxide to Fe_3O_4, forming a dense sludge and avoiding slimes or colloids that are difficult to handle. Hydrochloric acid SPL from continuous pickling lines typically contains from 1 to 4 g HCl/100 mL and from 20 to 30 g $FeCl_2$/100 mL. Neutralization of HCl SPL with lime produces highly soluble calcium chloride, which cannot be discharged to inland water systems. A process has been developed in which the calcium chloride solution is further treated with H_2SO_4 to precipitate gypsum and regenerate HCl, but this process is not in commercial use. In some areas of the United States, the underground rock formations are such that H_2SO_4 or HCl SPL can be injected into a deep well without affecting existing ground-water supplies. This method is no longer in wide use, because of concern that contamination of ground waters would eventually occur.

Because ferrous sulfate becomes less soluble as the temperature of the solution decreases or as the acid concentration increases, it can be recovered as crystals by cooling or concentrating H_2SO_4 SPL by evaporation. Recovery of the monohydrate $FeSO_4 \cdot H_2O$ from hot solutions is generally avoided. If it is produced, then the monohydrate can be roasted to produce sulfuric acid and iron oxide, but this process is generally not considered economically attractive. Recovery of the heptahydrate (copperas), $FeSO_4 \cdot 7H_2O$, utilizes a cold solution (-1 °C, or 30 °F) that is removed by centrifuging or by using a crystallizer from which solids can be removed. The solution contains sulfuric acid and lowered amounts of iron and water than exist in the SPL. The solution is then returned to the pickling tanks, thus effecting a recovery of the unreacted acid. Fresh acid additions must be made to the pickle tanks to maintain desired operating conditions. Use of this recovery method lowers overall acid consumption for pickling, compared with the amount required if no recovery system is used. The heptahydrate crystals are used in fertilizers and for water treatment.

Many commercial installations use this recovery method. Systems of this type can be operated on a batch or continuous basis. For a continuous basis, the amount of SPL withdrawn for treatment must be adjusted to the volume of the pickling solution. In addition, the recovery unit is sized so that the removal rate of iron from SPL equals the rate of iron entering the pickling solution from the pickling operation. A fairly constant iron content is maintained in the SPL.

An analogous process for removing iron from HCl SPL has been developed (Ref 28), and requires that either higher-than-conventional HCl concentrations be used in the pickling operation (probably coupled with lower solution temperatures) or that additions of concentrated HCl be made to the HCl SPL that is to be treated, so that ferrous chloride tetrahydrate crystals ($FeCl_2 \cdot 4H_2O$) form when the liquor is cooled below about -8 to -7 °C (18 to 20 °F) and to about -23 °C (-10 °F). Recovered crystals can be dissolved in water to prepare a solution suitable for use in water treatment.

A widely used process for complete regeneration (as high as 99% recovery) of HCl SPL involves spray roasting. The SPL is first concentrated by water evaporation. The concentrated SPL enters the roaster at a temperature ranging from 600 to 750 °C (1112 to 1382 °F). Free HCl and most of the water is evaporated and leaves the reactor with the combustion gases. Ferrous chloride reacts with the balance of water and oxygen to form hydrogen chloride and hematite:

$$2FeCl_2 + 1/2\ O_2 + 2H_2O = Fe_2O_3 + 4HCl \qquad \textbf{(Eq 15)}$$

Gases containing hydrogen chloride are washed with water to form an 18 to 20 wt% HCl solution. By-product Fe_2O_3 can be used as a pigment or, depending on purity, for magnetic tapes.

Ion exchange can be used to regenerate either H_2SO_4 or HCl from SPL. The SPL is pumped through an acidic ion-exchange bed, where the iron is stripped from the SPL and replaced by hydrogen ions. The iron-rich ion-exchange resin is

then regenerated with another acid. Although ion-exchange procedures are not being used for H_2SO_4 or HCl SPL, they are in commercial use for treating hydrofluoric-nitric acid SPL from the pickling of stainless steels (Ref 29).

At some plants, HCl SPL is treated on site with chlorine gas to convert ferrous chloride to ferric chloride, which is used in sewage and water-treatment plants. Other plants pay to have their SPL hauled to an authorized treatment site. This method is becoming increasingly expensive. Drawbacks include possible closings of some disposal sites and the continuing responsibility of the source for environmental damage associated with hauling SPL and its final disposal.

References cited in this section

28. J.C. Peterson and G.A. Salof, Process and Apparatus for the Low Temperature Recovery of Ferrous Chloride from Spent Hydrochloric Acid Pickle Liquors, U.S. Patent 5,057,290, 15 Oct 1991
29. J.C. McArdle, J.A. Piccari, and G.G. Thornburg, AQUATECH Systems' Pickle Liquor Recovery Process, *Iron Steel Eng.,* Vol 68 (No. 5), 1991, p 39-43

Safety

A number of safety practices should be followed during alkaline precleaning and acid-pickling operations. Employees handling chemicals should wash their hands and faces, both before eating and before leaving at the end of a shift. Only authorized employees familiar with chemical handling safety rules should be permitted to add the chemicals to pickling tanks. Face shields, chemical safety goggles, rubber gloves, and rubber aprons should be worn by employees who clean or repair tanks or make additions of chemicals. Hard hats and safety shoes also should be worn. If splashed or spilled chemicals contact body parts, then employees should wash immediately and thoroughly with cool water and report promptly to an emergency facility for treatment. An emergency shower with quick-opening valves that stay open should be available, as should eye-wash fountains. Any changes in working procedures or any unusual occurrences relating to the use of chemicals should be brought to the attention of supervisory personnel.

Safe practices in the use of alkaline and acid solutions should be followed. Alkalis should be added to water slowly, using a hopper or shovel. Adequate agitation should be provided after an alkali has been added, to ensure that the chemicals dissolve. To prevent eruption of the solution caused by rapid dissolving of the alkali, the temperature of the solution should not exceed 66 °C (150 °F) during additions. Acids should always be added to water, rather than water added to concentrated acid. When preparing a new solution, acid should be added to cold water, and the solution should not be heated until the acid has been added. Additions of acid to hot pickling solutions should be made with extreme caution. Materials should be carefully immersed in and withdrawn from acid solutions to avoid splashing. Adequate ventilation also should be provided in the vicinity of a pickling operation.

Classification and Selection of Finishing Processes

K. Subramanian, World Grinding Technology Center, Norton Company

Introduction

THE TERM *finishing* as used in this Section of the Handbook refers to a wide variety of processes used to generate surfaces with specific geometries, tolerances, and surface characteristics. The finishing methods described in the articles in this Section focus on material removal in one form or another to generate the desired surfaces. These surface generation methods are used usually to achieve certain functional or decorative characteristics of the surface. Other surface preparation processes such as cleaning, plating, coating, and surface modifications are covered in other sections in this Volume.

Most of the finishing methods described in this Section are carried out as the last operation in a series of industrial processes used to produce or manufacture parts or components. As an example, a cast product may need snagging or cutting off of gates and risers as the finishing operation before it is shipped for use or sent to the next component fabrication department. A forged shaft may be cut, machined, or otherwise finished before it becomes an industrial component for use in an assembly process. After heat treatment, bearing or gear components may be ground to desired tolerances and surface quality before they are assembled into finished bearings or a transmission, respectively. Computer parts such as microchips or magnetic heads may be ground, lapped, or polished before they are sent to assembly operations. Jet engine blades may have coolant holes drilled using electrical discharge machining or laser machining prior to their use in an assembly process to manufacture jet engines. The above are just a few of many applications in which finishing methods are used in a wide range of materials and industries. Thus, finishing methods play a key role in a number of engineering activities. It is beyond the scope of this Section to treat each process in detail, but the articles provide an overview of the various methods, their critical features, and the range of their application or use. This is supplemented by a large number of references that deal with each process in significant detail.

Technology Drivers for Finishing Methods

Engineering activity is usually driven by a few driving forces. These technology drivers are generally universal and are often found to be independent of geography. The scale or magnitude of these drivers may vary, depending on the local demands for quality, economic forces, and so on. Technology drivers for finishing methods are addressed briefly in the following paragraphs.

Tolerance in generic terms implies deviation from the nominal value. As it relates to finishing methods, tolerance refers to geometric dimensions and their deviation from the nominal. These may be used to measure linear dimensions such as thickness, length, and radius. They may also refer to surface features such as finish, form, flatness, and waviness. Extensive review of geometric dimensioning and tolerances may be found in a number of references (Ref 1, 2, 3).

Whichever tolerances are referred to, it is clear that one of the driving forces for finishing methods is to achieve improved or closer tolerances. As an example, finished parts of closer tolerances in a hydraulic pump help to achieve higher pump efficiency, which results in improved power steering performance and thus enhances the quality of an automobile. Closer tolerances in gears cause them to roll against other gears more readily while reducing sliding friction. This results in better gear efficiency, increased torque carrying ability, and lower noise level. These benefits have a wide range of applications in automotive components, jet engines, construction equipment, and so on. The trend for improvement in tolerances is constant, as shown in Fig. 1.

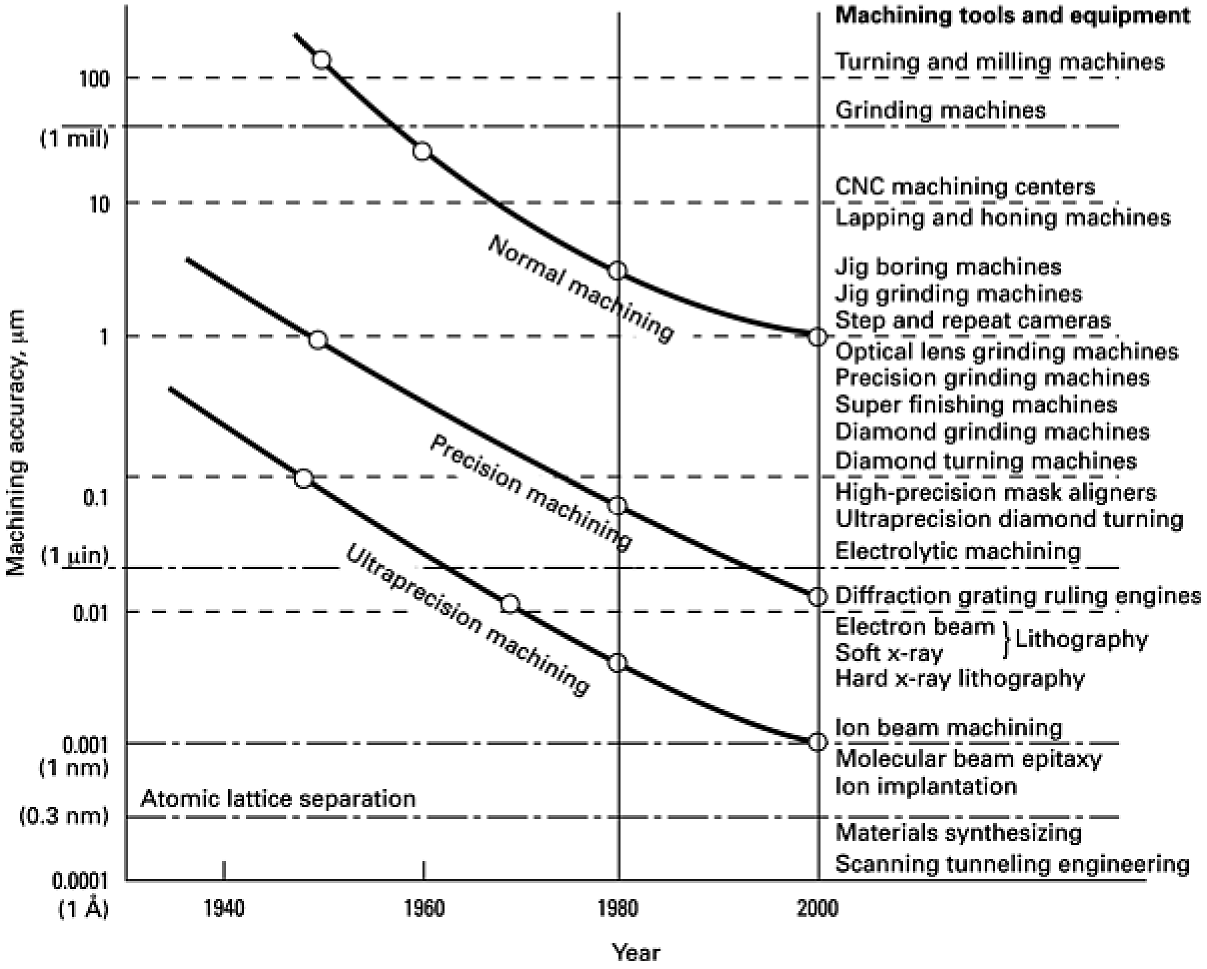


Fig. 1 Achievable machining accuracy. CNC, computer numerically controlled. Source: Ref 4, after Norio Taniguchi

Consistency. For a given tolerance of a finished part, it is critical to achieve them consistently over a batch of components. Consistency is established through the confidence limits arrived at through statistical process control. If a tolerance is viewed as a "set point" or location in geometric space, consistency defines the ability to stay close to the set point. Detailed discussions of statistical process control and methods of achieving consistency can be found in Ref 5, 6, and 7.

Finishing methods constantly strive to improve the consistency of their output (i.e., generated surfaces of required geometry and surface characteristics). Imagine that an improvement in the form accuracy or tolerances of a gear surface is achieved through a new or improved finishing method. This could result in significant improvement in the performance of the transmission in which the gear is used. The new process will become successful only when two conditions are met: the new process delivers the improved tolerances consistently and all other components in the transmission are manufactured consistently. If one of the consistency requirements is not met, the new transmission will not meet the higher performance levels and the new finishing method developed may not see the light of the day. Conversely, constant improvement in consistency is a key technology driver that closely follows improvement in tolerances of the finished components.

Surface Quality. Finishing methods result in generation of surfaces, which alters the surface layers of the work material. This alteration may change surface characteristics such as:

- Surface finish
- Fatigue strength
- Residual stress

- Retained strength

All finishing methods constantly strive to improve on these and other surface characteristics. Many of these topics are addressed in various articles in this Section. It is sufficient here to say that surface quality and its improvement is a key technology driver for finishing methods.

New materials such as high-silicon aluminum alloys, fiber-reinforced composites, metal matrix composites, ceramics, ceramic coatings, particle boards, and metallic glass constantly pose challenges for both innovation and improvements in finishing methods. Such new work materials are constantly introduced to achieve lower weight, higher strength-weight ratio, high-temperature resistance, or better operation under severe environments, or to achieve other unique performance improvements. These in turn influence the choice and improvements necessary in the finishing methods.

Productivity. Although this article has discussed technology drivers that relate to technical aspects of finishing methods, it is obvious that the results must be achieved at lower cost, to compete in the global marketplace. This requirement simply translates into improved productivity. All finishing methods seek to achieve higher productivity through incremental or small improvements in productivity or quantum improvements in new processes.

References cited in this section

1. Tolerancing and Metrology, Special Section, *Manufacturing Review*, Vol 6 (No. 4), Dec 1993
2. *Machinery's Handbook* (latest ed.), Industrial Press, Inc.
3. R. Komanduri, "Ultra Precision Machining," *Advanced Manufacturing Processes* (transcript of a video course), American Society of Mechanical Engineers, Sept 1993
4. P.A. McKewon, High Precision Manufacturing, *Ann. CIRP*, Vol 36 (No. 2), 1987
5. F.W. Breyfogle III, *Statistical Methods for Testing, Development, and Manufacturing*, John Wiley & Sons, 1991
6. P.M. Noaker, Wanted: SPC Detectives, *Manufacturing Engineering*, Nov 1991, p 66-71
7. E.E. Sprow, What Hath Taguchi Wrought?, *Manufacturing Engineering*, April 1992, p 57-60

Systems Approach for Finishing Methods

Every finishing method may be viewed as a manufacturing system consisting of four input categories: machine tool, processing tool, work material, and operational factors. These inputs result in microscopic or intrinsic process interactions that can be measured or monitored through macroscopic process variables. The interactions result in certain technical outputs or, when economic aspects are included, certain system outputs. The finishing method is shown as a system in Fig. 2.

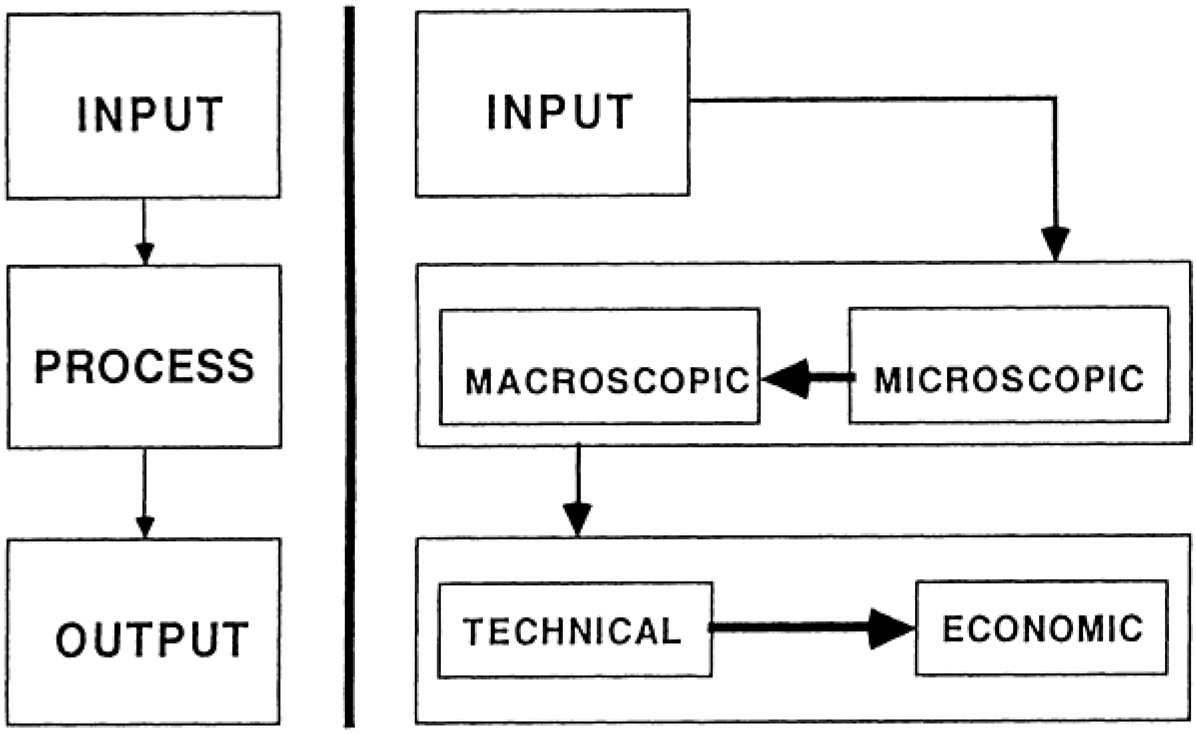


Fig. 2 Systems approach for the manufacturing process

When the microscopic process interactions are understood, the finishing method may be managed efficiently through casual relationships. Efficient achievement or quantum improvements of the technology drivers described above result when the four input elements are managed simultaneously to optimize the microscopic process interactions (Ref 8, 9). Whenever possible, the finishing methods outlined in this chapter are described in terms of the four input elements, key or governing microscopic interactions, characteristic macroscopic variables, and technical and economic outputs.

References cited in this section

8. K. Subramanian, Precision Grinding of Ceramics--A Systems Approach, *ACS Bulletin,* March 1994
9. K. Subramanian, "Advances in Manufacturing Processes through a Systems Approach," *Advanced Manufacturing Processes* (transcript of a video course), American Society of Mechanical Engineers, Sept 1993

Outline of Finishing Methods

In this Section, finishing as a surface generation process is broadly classified as follows.

"Finishing Methods Using Defined Cutting Edges." Many finishing processes use tools of well-defined geometry. Typical examples are turning, milling, and drilling.

"Finishing Methods Using Multipoint or Random Cutting Edges." As described in this title, many finishing processes use processing tools such as grinding wheels, abrasive belts, and abrasive slurries such that the surface generation process takes place between the work material and a number of cutting edges whose geometry is not precisely defined in each case.

"Nonabrasive Finishing Methods" are those in which surface generation takes place without any mechanical interaction between the processing tool and the work materials. These are generally described as nontraditional machining methods. Typical examples are electrochemical machining, electrical discharge machining, and laser machining.

"Mass Finishing Methods."The methods described in the articles mentioned above usually deal with only one or a few work materials or components at a time. However, a number of processes deal with surface modification of a large number of parts at the same time. Typical examples are tumbling and barrel finishing. Shot peening can be classified as a mass finishing method; however, because of its importance and unique characteristics, it is described in a separate article in this Section.

Every finishing method may be characterized as ultraprecision, precision, or rough, depending on the nature or scale of the output of the process, as shown in Fig. 3. The technology drivers described earlier push the advancements in all these methods, and the directions for such advancements are also shown in Fig. 3. The articles mentioned above describe these precision aspects and the trends for advancement in finishing methods.

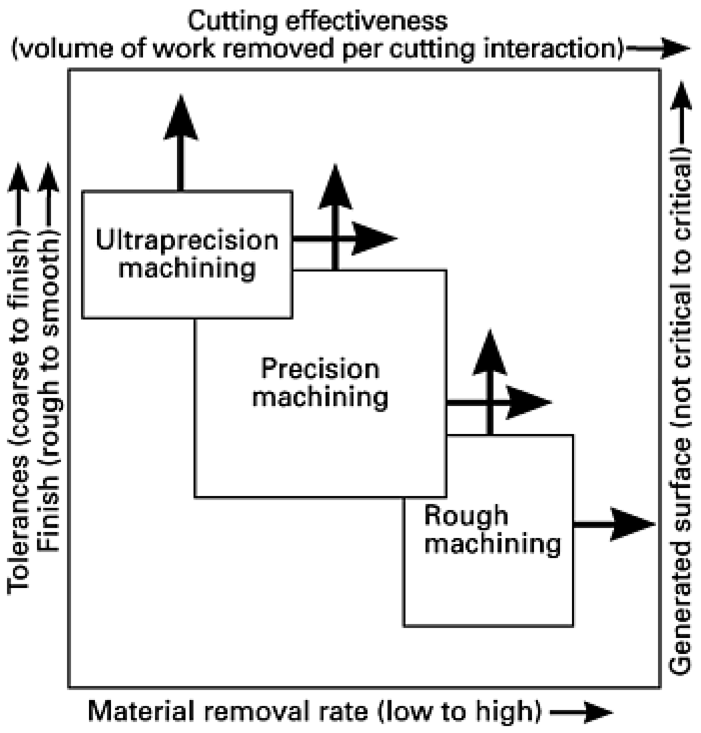


Fig. 3 Classification of finishing methods based on surface generation process and surface characteristics

Characteristics of Finished Surfaces

Surface generation is the primary output of all the methods described in this Section. It is natural, then, to address the characteristics of the generated surfaces and the methods used to measure them.

"Topography of Surface."One of the key characteristics of generated surfaces is the topography. Many contact and noncontact methods are used to measure surfaces, and a number of parameters are used to describe surface features, such as roughness, waviness, and bearing ratio.

"Microstructural Analysis of Finished Surfaces." Because finishing methods generate surfaces by material removal processes, they modify the microstructure of the work material through thermal and mechanical interactions. These results on the generated surfaces are measured and monitored through a number of methods.

"Residual Effects of Finishing Methods." Surface generation processes alter the geometry, topography, and microstructural aspects of finished surfaces. These in turn influence the behavior of the surface under various loads or forces (e.g., mechanical, optical, electrical, and magnetic properties).

Special Topics Related to Finishing Methods

In most finishing processes, thermomechanical interactions occur between the processing tool (cutting tool, grinding wheel, polishing pad, electron beam, etc.) and the work material in the presence of machine tool and operational factors.

Most of these interactions and their results are addressed in the articles mentioned above. However, a few topics common for all finishing methods deserve special attention.

"Thermal Aspects of Finishing Methods." Thermal interactions are one of the key types of microscopic interactions in all finishing methods. They are maximized in some applications and minimized in others. These interactions are strongly dependent on the process selected and the four input elements (machine tool, process tool, operational factors, and work material). General consideration of thermal interactions and their control is critical for any successful use of finishing methods.

"Selection, Application, and Disposal of Finishing Fluids." All finishing methods are carried out in the presence of an environment. Air or ambient conditions may be most common in dry finishing methods. All finishing methods that are carried out "wet" involve the use of a fluid whose function may be intrinsic to the process interactions, such as cooling effects and lubricating effects, or extrinsic, such as removal of the swarf and the thermal stability of the system. Environmental elements such as dielectric fluid play a critical role in electrical discharge machining. Whatever the role of the fluid used in the finishing methods, increasing attention will be paid to their use, maintenance, and proper disposal, and all these aspects of the fluids require special consideration.

"Influence of Work Material Properties on Finishing Methods." The microstructure, properties, and performance requirements of the work drive the selection of suitable finishing methods. Conversely, finishing methods influence the microstructure, properties, and performance of the surfaces generated on work materials. The final article in this Section describes these relationships and presents some guidelines relative to advanced materials.

Finishing Methods Using Defined Cutting Edges

V.C. Venkatesh and S. Enomoto, Gintic Institute of Manufacturing Technology, Nanyang Technological University, Singapore

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Introduction

THIS ARTICLE covers precision and ultraprecision finish machining techniques that make use of defined cutting edges, such as polycrystalline diamond (PCD) and cubic boron nitride (CBN) compacts. Grinding techniques are discussed in the article "Finishing Methods Using Multipoint or Random Cutting Edges" in this Volume. The turning, broaching, milling, drilling, and reaming processes discussed in this article are also covered extensively in *Machining,* Volume 16 of the *ASM Handbook* (Ref 1). The same volume provides in-depth information on machining fundamentals and cutting tool materials.

Reference

1. *Machining,* Vol 16, 9th ed., *Metals Handbook,* ASM International, 1989

Finish Turning

Much of the recent progress in turning has been made in precision and ultraprecision machining, and it is generally true that today's precision engineering will be tomorrow's general engineering. At present, the highest spindle speeds in conventional lathes are 2200 to 2400 rpm. For precision finishing cuts on steel and materials with similar properties, the highest spindle speeds should range from 3000 to 5000 rpm to give cutting speeds of 120 to 915 m/min (400 to 3000 ft/min). Fine stepless feeds are desirable to provide gradual entry of the tool into the workpiece, especially at high speeds. Inserts with chip control are essential, and it is not unusual for lathes to have slant beds and screw conveyors for continuous chip disposal. Machine tools must have high rigidity for finish turning that is carried out at high speeds (Ref 2).

The cutting tool materials widely used for finishing cuts are:

- Chemical vapor deposition ceramic (aluminum oxide) coated carbides
- Chemical vapor deposition triphase (TiC/TiCN/TiN) coated carbides
- Physical vapor deposition TiN (titanium nitride) coated carbides

- Cermets
- Ceramics (alumina-based and silicon nitride-based)
- PCD
- Polycrystalline CBN

These tool materials need to be used with specific work materials. Table 1 gives the cutting speeds, feeds, and depths of cut that correspond to some typical work materials.

Table 1 Depth of cut, feed rate, and cutting speed for finish turning of selected materials

Work material	Depth of cut		Feed rate		Cutting speed using indicated tool materials, m/min (ft/min)					
	mm	in.	mm/rev	in./rev	Ceramic-coated carbides	TiN (CVD coated)	TiN (PVD coated)	Cermets	Ceramics	PCD/CBN
Low-carbon and free-machining steel	0.5-2.5	0.02-0.1	0.15-0.28	0.006-0.011	185-455 (600-1500)	120-245 (400-800)	90-230 (300-375)	135-455 (450-1500)	245-915 (800-3000)	. . .
Medium-and high-carbon steel	0.25-2.5	0.01-0.1	0.15-0.3	0.006-0.012	150-410 (500-1350)	90-215 (300-700)	75-215 (250-700)	170-305 (450-850)	245-455 (800-1500)	. . .
Low-carbon alloy steel	0.25-2.5	0.01-0.1	0.15-0.3	0.006-0.012	135-335 (450-1100)	90-230 (300-750)	135-305 (450-1000)	75-185 (250-600)	230-425 (75-1400)	. . .
Medium-carbon alloy steel	0.4-2.5	0.015-0.1	0.08-0.2	0.003-0.008	150-275 (560-900)	60-120 (200-400)	55-130 (175-450)	325-750 (325-750)	230-410 (750-1350)	. . .
Hardened irons (400-525 HB)	0.08-1.5	0.003-0.6	0.08-0.3	0.003-0.012	. . .	. . .	. . .	. . .	60-185 (200-600)	CBN 25-120 (80-400)
Glasses and ceramics (200-250 HB)	0.12-1.2	0.005-0.050	0.12-0.25	0.005-0.1	. . .	. . .	. . .	. . .	. . .	PCD 230-1005 (750-3300)

For ultraprecision turning the lathes mentioned above are unsuitable. Among the tool materials indicated in Table 1 for finish machining, not even PCD or CBN compacts can be used for ultraprecision turning, only single-crystal diamonds and CBN. The machines need to have stiffness, which is provided by aerostatic bearings for the spindle and hydrostatic bearings for the bedway. The machine tool should be capable of giving feeds at the nanometer level for brittle materials, and this, combined with an equally fine depth of cut and moderately high speeds, enables the machining of brittle materials such as germanium and silicon. At such low feeds and depths of cut, brittle materials behave like ductile materials, and this mode of removal is known as ductile machining (Ref 3). Glass cannot be turned on these machines as yet, but this should be possible in the near future.

Pioneering work conducted at a number of institutions (Ref 3, 4, 5, 6, 7, 8, 9) has resulted in the development of ultraprecision lathes. Two typical machines are shown in Fig. 1. The cutting tools used are single-crystal diamonds. One mode of manufacture of these tools is chemical machining, in which the material removal rate ranges from 1 to 3000 $\mu m^3/s$ (Ref 9). The cube face of the single-crystal diamond is selected as the cutting edge to avoid cleavage, which occurs easily on the octahedral face. The cutting edge should show no nicks or chips at magnifications of 10,000×. By way of comparison, PCDs used for finish turning are inspected at 50×.

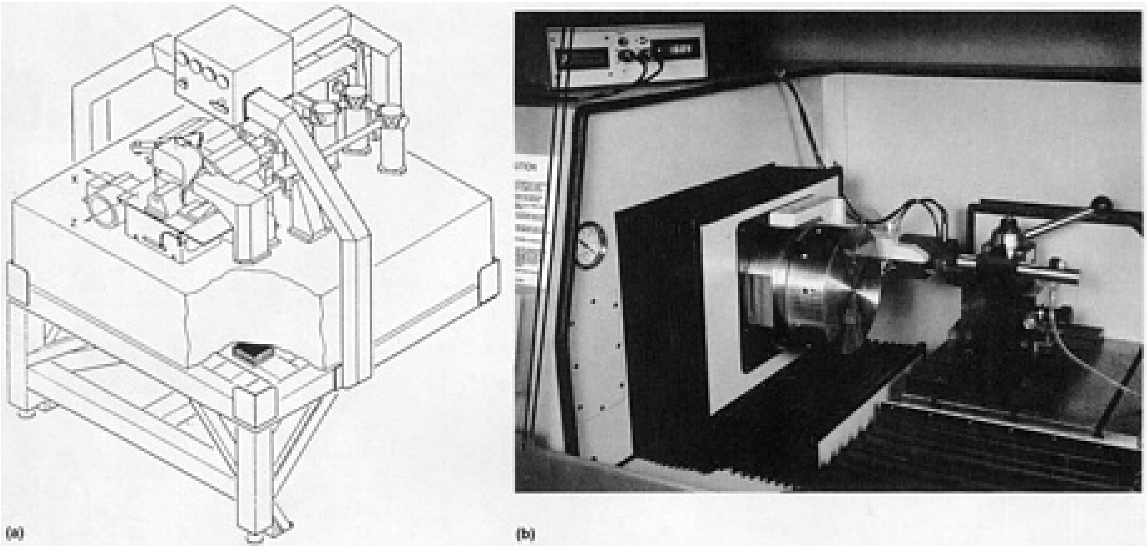

Fig. 1 Ultraprecision lathes. (a) Lawrence Livermore PAUL lathe. Source: Ref 3. (b) Rank Pneumo lathe. Source: Ref 5

Figure 2(a) shows a sketch of a single-crystal diamond/CBN tool. The cutting edge radius is around 50 nm; after wear it is about 350 nm (Fig. 2b). Brittle materials (such as silicon and its compounds, germanium used in aspheric lenses, and ceramics) and ductile materials (such as aluminum for computer hard disks and copper for laser printer mirrors) are easily machined with these tools. When they are used to finish germanium on an ultraprecision lathe, mirror-like surfaces with an average surface roughness (R_a) of 1 nm have been achieved. Even composites such as silicon-carbide-whisker-reinforced (SiC_w) aluminum have been successfully machined by single-crystal diamonds to R_a of 10 nm (Ref 9).

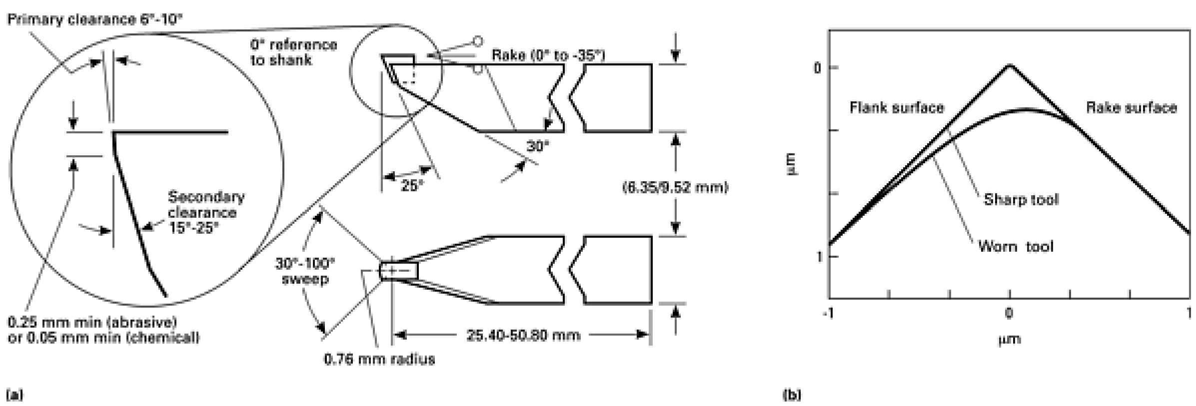

Fig. 2 Single-crystal diamond machining tools. (a) Schematic of a single-crystal diamond/cubic boron nitride tool (Ref 11). (b) Cutting edge radius on a single-crystal diamond before wear (50 nm) and after wear (350 nm). Source: Ref 8

Precision tolerances for silicon, germanium, aluminum, and copper are bilateral of the order of +20 nm for a linear dimension of 20 mm (0.8 in.). Ultraprecision tolerances are unilateral from +5 nm (lower) to +10 nm (upper) for a linear

dimension of 20 mm (0.8 in.). A typical product where these tolerances are easily achieved is the polygon mirror. These tolerances are not as easily achieved with SiC_w aluminum alloys because of the orientation of whiskers and heavy tool wear.

References cited in this section

2. F. Koenigsberger, *Design of Metal Cutting Machine Tools,* Pergamon Press, 1964, p 43-161
3. P.N. Blake and R.O. Scattergood, Ductile-Regime Machining of Germanium and Silicon, *J. Am. Ceram. Soc.,* Vol 73, 1990, p 949-957
4. J. Franse, J.W. Roblee, and K. Modemann, Dynamic Characteristics of the Lawrence Livermore National Laboratory Precision Engineering Research Lathe, *Precis. Eng.,* Vol 13 (No. 3), July 1991, p 196-202
5. D.E. Luttrell, Machining Non-Axisymmetric Optics, *Proceedings ASPE Annual Conference,* (Rochester, NY), 1990, p 31-34
6. W.J. Wills-Moren et al., Some Aspects of the Design and Development of a Large High Precision CNC Diamond Turning Machine, *Ann. CIRP,* Vol 31 (No. 1), 1982, p 409-414
7. M. Sawa et al., Development of an Advanced Tool-Setting Device for Diamond Turning, *Ann. CIRP,* Vol 42 (No. 1), 1993, p 87-90
8. K. Horia et al., A Study on Damaged Layer Remaining in Diamond Mirror Cut Surface, *Ann. CIRP,* Vol 41 (No. 1), 1992, p 137-140
9. C.J. Yuan, L. Geng, and S. Dong, Ultraprecision Machining of SiCw/Al Composites, *Ann. CIRP,* Vol 42 (No. 1), p 107-109
11. F. Mason, Atomic Machining of Diamond Tools, *Am. Mach.,* Vol 134 (No. 4), April 1990, p 49-52

Finish Broaching

Broaching is a typical multipoint process that makes use of several transverse cutting edges, which are pushed or pulled through a hole or over a surface to remove metal by axial cutting. Because a broach has roughing, semifinishing, and finishing teeth, the holes or surfaces produced have close tolerances. The dimensional accuracies and surface finishes for various materials are given in Table 2.

Table 2 Commonly broached materials and typical results

Metal	Heat treatment[(a)]	Hardness HRC	Tolerance		Finish	
			mm	in.	µm	µin.
2618-T61 Al	G	70 HRB	0.05	0.002	0.80-1.15	32-45
2014-T6 Al	G	70 HRB	0.058	0.0023	0.80	32
Ti-6Al-4V	E	36-38	0.019	0.00075	0.61-0.80	24-32
Stellite 31	B	32	0.05	0.002	2.00	80
SAE 51410 (type 410 SS)	H	32-36	0.05	0.002	1.60	63
Greek Ascoloy	I	32-38	0.025	0.001	0.80-1.07	35-42

Inconel	A	85 HRB	0.13	0.005	2.00	80
Inconel X	H	29	0.025	0.001	0.80	32
Timken 16-25-6	F	20-28	0.025	0.001	0.80-1.60	32-63
A-286	G	28-30	0.060	0.0024	0.80	32
		30-35	0.025	0.001	0.89	35
		32-38	0.015	0.0006	0.80	32
S-816	G	23-30	0.025	0.001	0.80-1.00	32-40
SAE 3310	E	20	0.25	0.010	1.60	63
SAE 9310	I	36-38	0.05	0.002	1.60	63
17-22A(S)	H	29-34	0.025	0.001	1.50	60
17-22A	H	35-40	0.075	0.003	. . .	. . .
SAE 9840	I	32-36	0.025	0.001	1.25	50
SAE 4130	I	32	0.013	0.0005	1.60	63
SAE 4140	I	25-29	0.05	0.002	0.80-1.60	32-63
SAE 4340	I	38	0.05	0.002	1.14-1.60	45-63
M2 tool steel	A	24-28	0.02	0.0008	0.80	32
EMS 544	. . .	40-47	0.025	0.001	0.75	30
Inconel 901	I	32-36	0.038	0.0015	1.60	63
René 41	G	40-42	0.060	0.0024	0.80	32
WAD 7823A	. . .	28	0.0076	0.0003	1.0-1.5	40-60
D-979	I	38-40	0.013	0.0005	1.50	60

EMS 73030	. . .	32-36	0.071	0.0028	1.60	63
M-308	. . .	36-38	0.060	0.0024	0.80	32
Chromoloy	. . .	31-32	0.10	0.004	0.80	32
PWA-682 (Ti)	. . .	34-36	0.025	0.001	0.80	32
Lapelloy	J	30-37	0.20	0.008	0.80	32
Type 303 SS	A	85 HRB	0.025	0.001	1.60	63
Type 304 SS	A	80-85 HRB	0.05	0.002	1.60	63
Type 403 SS	I	37-40	0.015	0.006	1.60	63
SAE 1010	D	60	0.025	0.001	0.75	30
SAE 1020	D	3-12	0.05	0.002	1.55-2.05	60-80
SAE 1037	I	15-20	0.0076	0.0003	1.60	30
SAE 1045	I	24-31	0.013	0.0005	. . .	. . .
SAE 1063	E	12-18	0.10	0.004	0.63-1.5	25-60
SAE 1070	E	5-10	0.05	0.002	0.71-1.5	28-60
SAE 1112	. . .	87 HRB	0.025	0.001	1.0-1.15	40-45
SAE 1145	C	13-18	. . .	. . .	1.25-2.5	50-100
SAE 1340	C	15-20	0.075	0.003	. . .	. . .
SAE 4047	C	8-15	0.05	0.002	1.5-2.0	60-80
SAE 5140	C	8-15	0.05	0.002	1.5-2.0	60-80
SAE 52100	D	25	0.013	0.0005	0.75	30
Gray cast iron	B	90 HRB	0.075	0.003	2.0-2.5	80-100

KP-7 cast iron	B	. . .	0.013	0.0005	3.20	125

SS, stainless.

Source: *Metal Cutting: Today's Techniques for Engineers and Shop Personnel,* McGraw-Hill, 1979

(a) Treatment or condition. A, annealed; B, as-cast; C, as-forged; D, cold finished; E, hot finished; F, stress relieved; G, solution and precipitation treated; H, air quench, furnace temper; I, oil quench, furnace temper; J, salt quench, furnace temper.

Further accuracy can be obtained by providing burnishing teeth on the same broach, thus extending its size, or by having a separate broach with burnishing teeth to be used as a second operation only when needed (Fig. 3). A burnishing broach not only increases accuracy but also provides a smoother, more wear-resistant surface. A burnishing broach produces a glazed surface, particularly in steel, cast iron, and nonferrous materials. The total change in diameter produced by a burnishing operation may be no more than 0.013 to 0.025 mm (0.0005 to 0.001 in.). Burnishing teeth are rounded; they do not cut the surface but rather compress and cold work it, improving both the R_a and R_t (total roughness) surface finish values. Burnishing tools, used when surface finish and accuracy are critical, are relatively short and are generally designed as push broaches. Burnishing buttons are sometimes included behind the finishing tooth section of a conventional broaching tool (Fig. 3). The burnishing section can be added as a special attachment or an easily replaced shell. These shells are commonly used to reduce tooling costs when high wear or tool breakage is expected. Burnishing tolerances range from 13 nm (lower) to 25 nm (upper).

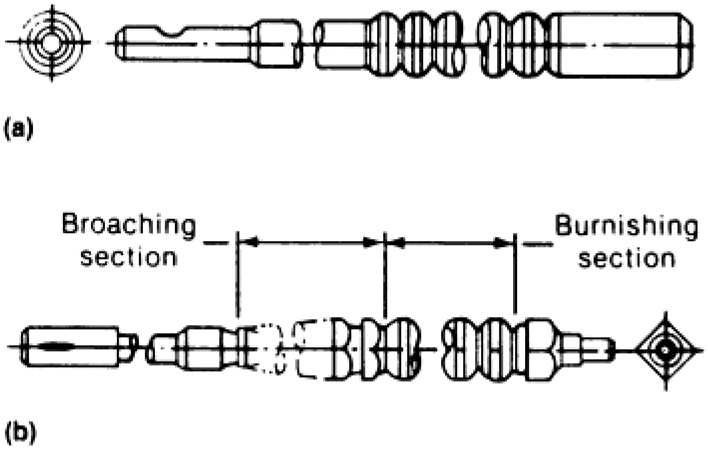

Fig. 3 Two types of broaches used for burnishing the walls of broached holes. (a) Broach for burnishing only. (b) Broach for cutting and burnishing. Source: Ref 10

Reference cited in this section

10. Broaching, *Machining,* Vol 16, 9th ed., *Metals Handbook,* ASM International, 1989, p 194-211

Finish Milling

Current practice is to use computer numerical control machining centers for milling, particularly finish milling. Milling is used primarily for machining surfaces and slots. Machining centers are divided into two types: vertical and horizontal. Both types are used for milling flat surfaces, contours, and slots. The workpiece is usually set on a portable pallet, and it is not unusual to find four to six pallets on a machining center. The spindle speed ranges from 40 to 6000 rpm with the possibility of using special spindles with speeds up to 8000 rpm. Spindle design has changed from the conventional add-on type to the current built-in type (Fig. 4). Machining centers are provided with automatic tool magazines (ATMs) capable of holding 20 to 30 tools. Special ATMs capable of holding 200 to 300 tools are available.

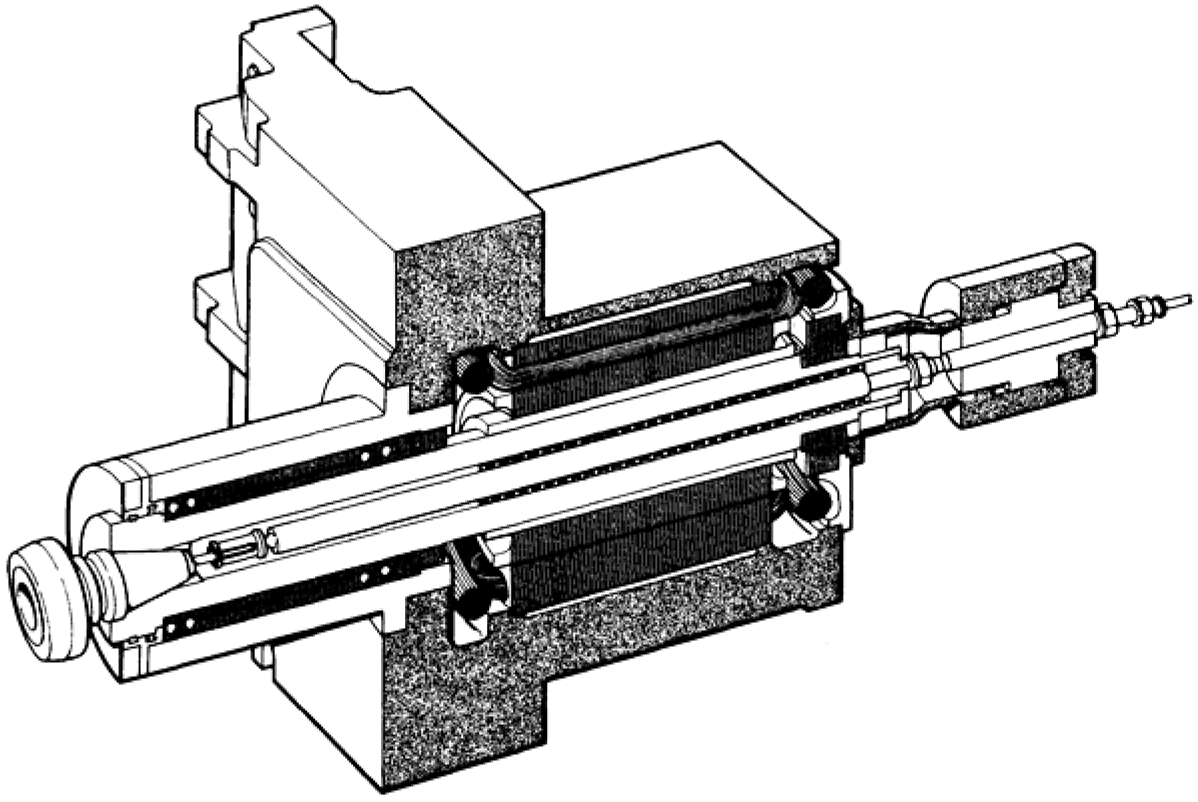

Fig. 4 Spindle head with built-in motor for high-speed (up to 12,000 rpm) finish milling

High-speed milling, which is usually associated with precision machining, involves the use of spindle speeds between 25,000 and 50,000 rpm, and in exceptional cases even as high as 100,000 rpm. A typical application on a horizontal machine is tool and die mold manufacture (Ref 12). High rake angles are used, typically 15° for carbon steels at 300 m/min (985 ft/min) and 25° for ductile materials such as copper and aluminum alloys at 500 m/min (1640 ft/min). Disposal of chips is very important, because they can envelope the tool and cause serious damage to the tool as well as the finished surface. Many machining centers therefore use a vacuum-type chip disposal system that collects the chips as soon as they are generated. However, to use this system, cutting tools must have chip breakers. Precision dies (made of high-carbon steel or chromium-molybdenum alloy steel) should be machined in the heat-treated condition (45 HRC), and in such cases CBN inserts can be used.

As with turning, ultraprecision milling is gaining ground, and a recent development is shown in Fig. 5(a). Single-crystal diamonds are used and mirror-like surfaces are obtained. With the development of diamond pseudo-end mills it is possible to manufacture sculptured surfaces such as toroids and paraboloids (Fig. 5b, c) with a typical feed and depth of cut of 2 and 75 μm, respectively, and with the spindle rotating at 23,000 rpm. Toroids and paraboloids can be generated by grinding (Ref 14), but small products are difficult.

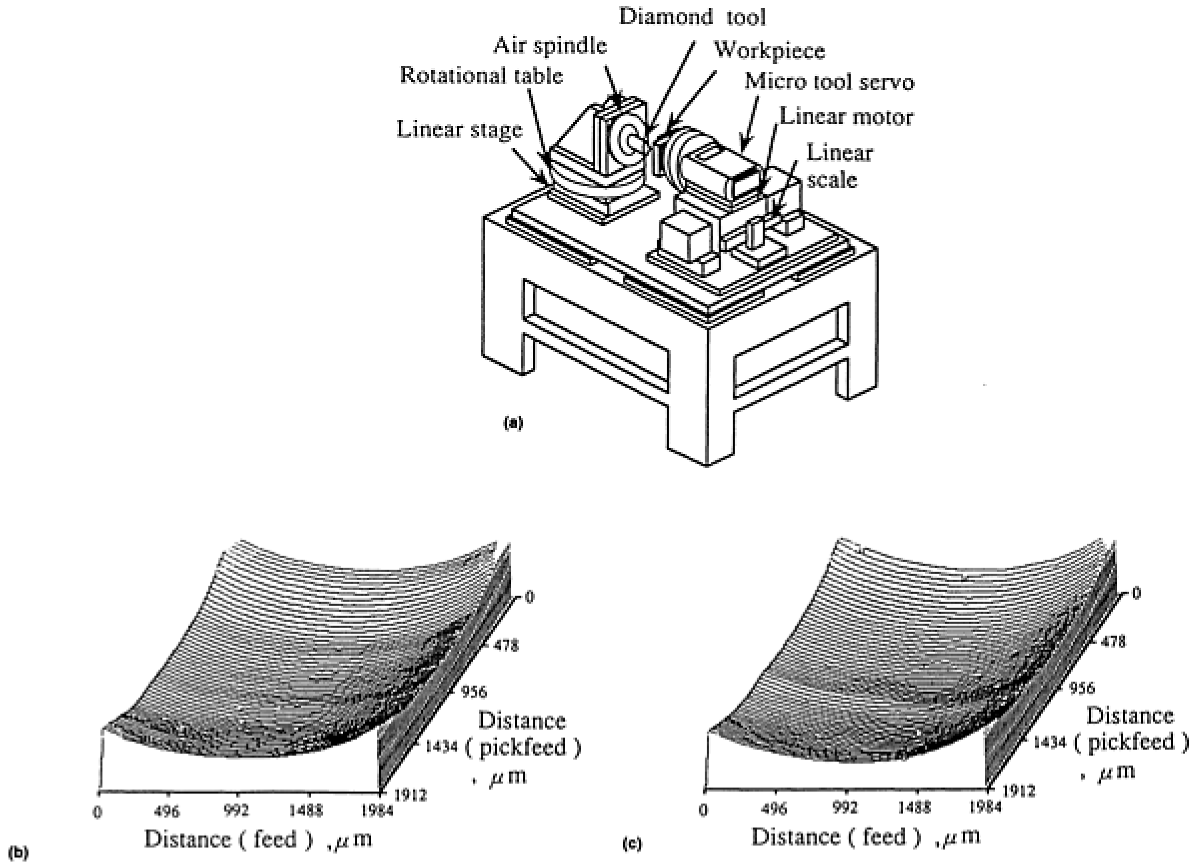

Fig. 5 Ultraprecision milling. (a) Ultraprecision machine for manufacturing sculptured surfaces. (b) Paraboloid surface. (c) Toroid surface. Source: Ref 13

References cited in this section

12. H. Schulz and T. Moriwaki, High Speed Machining, *Ann. CIRP,* Vol 41 (No. 2), p 637-643
13. Y. Takeuchi et al., Generation of Sculptured Surfaces by Means of an Ultraprecision Milling Machine, *Ann. CIRP,* Vol 42 (No. 1), 1993, p 611-614
14. Z.W. Zhong and V.C. Venkatesh, Generation of Parabolic and Toroidal Surfaces on Silicon and Silicon Based Compounds Using Diamond Cup Grinding Wheels, *Ann. CIRP,* Vol 43 (No. 1), 1994, p 323-326

Finish Drilling

Next to turning, drilling is the most widely used machining process, accounting for about 25% of all machining operations, and as much as 60% in some small and medium industries. Despite this wide use, conventional drilling remains a rough process that generally needs to be finished by boring or reaming. The tool materials used for drills are high-speed steels, carbides, CBN, and diamonds. High-speed steel in the form of twist drills comes in all sizes and is used for rough machining. Carbide drills come in three forms: solid carbide drills of diameters of 8 mm (0.3 in.) and less, drills with brazed tips, and drills with indexable inserts for diameters of 14 mm (0.6 in.) and above. Carbide drills need to be used at much higher speeds than high-speed steel drills but result in higher productivity and better surfaces, often not requiring a secondary reaming or boring operation. Getting high speeds with small drills necessitates very high spindle speeds, and such spindles require air bearings.

Drilling of holes in printed circuit boards is done with carbide drills. As in milling, machining centers are popular for drilling. Hole fabrication by ultraprecision drilling has not gained ground, primarily because the width of cut, which is equal to the hole diameter, is very high. Using PCDs does not help because they are not good enough for ultraprecision turning and milling, let alone drilling. PCDs *are* used, however, for finish drilling of aluminum and copper. Precision hole fabrication can be done by techniques such as grinding (for small diameters) and boring (for large diameters where single-

crystal diamonds can be used at low depths of cut and low feeds). Nontraditional machining techniques such as electrical discharge machining, electrochemical machining, and extrusion honing are other finishing techniques that are good for putting quality holes in difficult-to-machine materials.

The strategy for finish drilling is to modify twist drills to improve the hole quality, but not at the expense of productivity. A highly successful drill is the indexable drill, or endrill, where two indexable carbide inserts are used. The two inserts are positioned so as to get a negative (Fig. 6a) or a hybrid negative-positive (Fig. 6b) point angle. The negative point angle in drilling is equivalent to a negative side-cutting-edge angle in turning, and speeds of 70 to 120 m/min (230 to 395 ft/min) give excellent surface finish, cylindricity, and roundness. At speeds of 70 m/min (230 ft/min) a builtup edge is formed. Figure 7 shows a chip root obtained by using an explosive quick-stop device. Chip roots obtained in high-speed machining should show a secondary shear zone, and this has not been reported for indexable drilling (Ref 15).

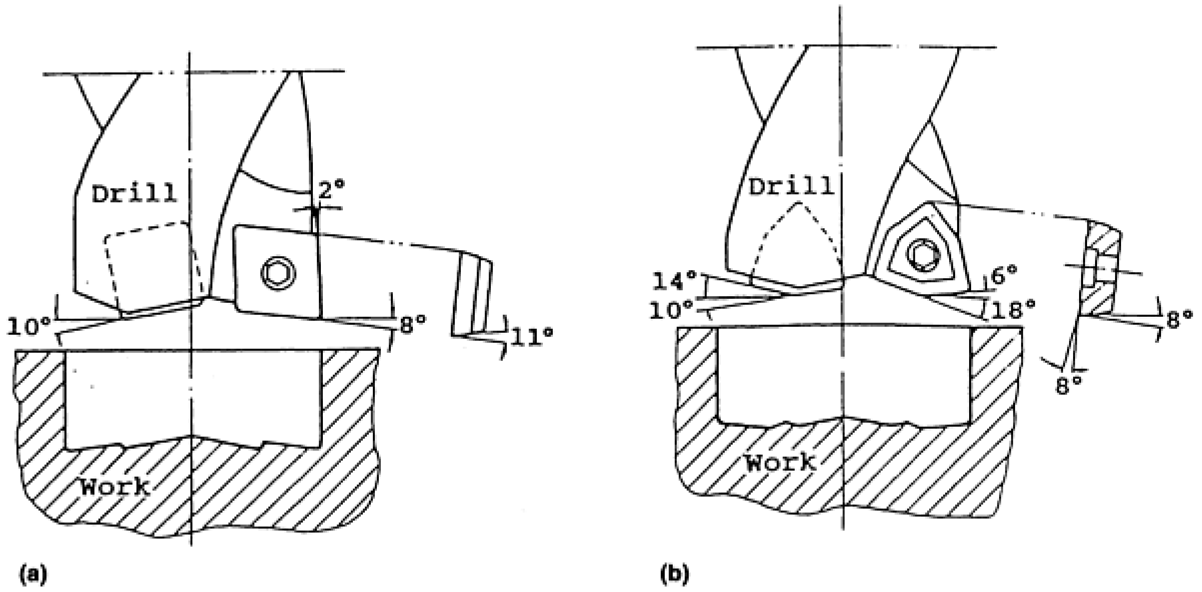

Fig. 6 Indexable drills using (a) square and rhomboid-shape inserts and (b) two trigon inserts to give (a) negative and (b) negative-positive point angles. Source: Ref 15

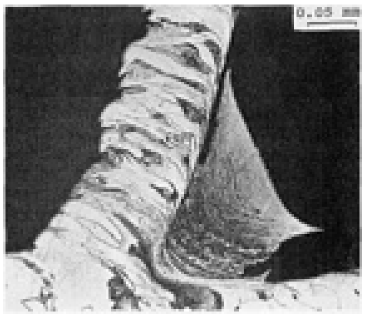

Fig. 7 A chip root obtained when machining 1018 steel with an indexable drill shows the presence of a builtup edge at a speed of 70 m/min (230 ft/min). Source: Ref 15

In a twist drill the two lips do the cutting while the chisel edge removes material by extrusion, which is less efficient than cutting and produces higher temperatures. This results in a lower removal rate and, hence, lower productivity. The chisel edge has a high negative rake angle equal to half the point angle (i.e., 59° in standard drills). By grinding a groove on both sides of the chisel edge (Fig. 8), the rake angle can be reduced from -59° to +5°, the thrust force can be reduced considerably, and extrusion action can be avoided. Surface roughness, roundness, and cylindricity can be improved by reducing vibration, which is often due to inefficient chip disposal. This can be achieved by providing nicks on the cutting edge of twist drills, as well as indexable drill inserts, to improve chip splitting and breaking (see Fig. 9).

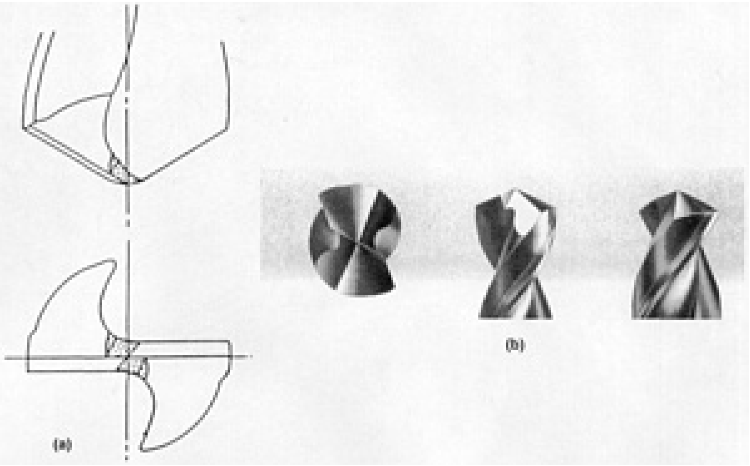

Fig. 8 Thrust force reduction achieved by eliminating the chisel edge by grinding grooves on either side. (a) Line diagram. (b) Three photographic views

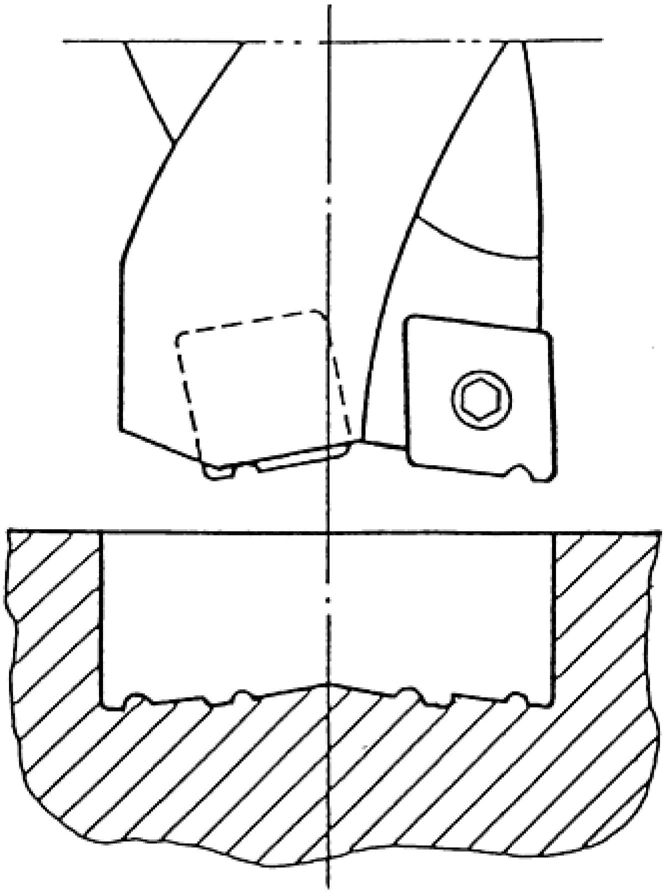

Fig. 9 Nicks or grooves on indexable inserts, used to reduce vibration by improving chip splitting and chip breaking. Source: Ref 15

Burr formation is undesirable, especially in fine finishing, and deburring can be a tedious and time-consuming operation. Burr height can be decreased by reducing the point angle from 118° to 90°, or by having a double cone with 118° and 90° for the two stages. A substantial decrease in burr height can be obtained by vibrating the drill in the feed direction at ultrasonic (Ref 17) or low (Ref 18) frequencies. In both cases, there is an optimum amplitude for each cutting condition.

References cited in this section

15. V.C. Venkatesh, D.Q. Zhou, W. Xue, and D.T. Quinto, A Study of Chip Surface Characterisitics during the Machining of Steel, *Ann. CIRP,* Vol 42 (No. 1), 1933, p 631-636
17. H. Takeyama and S. Kato, Burrless Drilling by Means of Ultrasonic Vibration, *Ann. CIRP,* Vol 40 (No. 1), 1991, p 83-86
18. H. Takeyama, S. Kato, S. Ishiwata, and H. Takeji, Study on Oscillating Drilling Aiming at Prevention of Burrs, *J. Jpn. Soc. Precis. Eng.,* Vol 59 (No. 10), 1993, p 137-142

Finish Reaming

Reaming is traditionally a finishing process for a rough hole produced by a twist drill. With the modified drills discussed earlier, high-grade reamers corresponding to ISO Grade 4 or 5, instead of the traditional 6, give fine finished holes. Recent developments by a Japanese firm include the broach reamer, which rotates, and the carbide mill reamer, which can be used in a machining center or preferably a jig borer (Fig. 10). Broach reamers are available in sizes from 3 to 100 mm and carbide mill reamers are available in sizes from 5 to 100 mm. Both reamers give R_a of 1 μm and cylindricity and roundness of <2 μm.

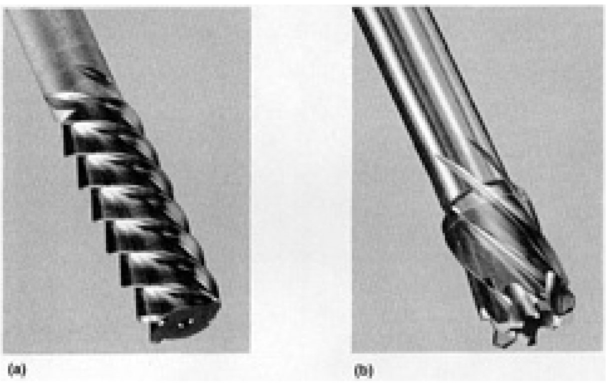

Fig. 10 Broach and carbide mill reamers. (a) Broach reamer, made of high-speed steel with a left-handed helix of 60° or more, that can cut at 20 m/min (65 ft/min) at a feed of 0.25 mm/rev (0.1 in./rev). (b) Carbide mill reamer that can cut at 30 m/min at a feed of 0.3 mm/rev (0.1 in./rev)

Introduction

ABRASIVE FINISHING includes many commercial processes, which can be generally classified as *rough grinding, precision grinding,* or *high-precision grinding.* The distinctions among these categories are based on the desired material removal rates and the acceptable tolerance or finish (Table 1). In rough grinding processes, material removal occurs at a rapid rate, with less emphasis on surface roughness/tolerances. In contrast, high-precision methods emphasize the attainment of fine surface finish and close tolerances at the expense of material removal rates. In precision grinding processes, removal rates are balanced with requirements of surface characteristics such as form, surface integrity, tolerances, and surface finish (roughness, waviness, roundness, etc.).

Table 1 Characteristics of abrasive finishing processes

Finishing processes	Cutting speed		Material removal rate		Tolerance		Finish	
	m/s	sfm	mm^3/mm/s	in.^{3}/in./min	mm	in.	µm	µin.
Rough grinding								
With grinding wheels	60-100	12,000-20,000	300-1000	30-100	±6-25	±0.250-1.0	2.5-25	100-1000
					±2.5	±0.100	2.5-25	100-1000
					±0.13	±0.005		
Belt grinding	15-25	3000-5000	6-3000	0.6-30	. . .	. . .	. . .	. . .
Precision grinding								
With grinding wheels								
Present	30-80	6000-16,000	0.1-50	0.01-5	±0.0025-0.125	±0.0001-0.005	0.75-1.25	30-50
Future	. . .	. . .	≤ 500	≤ 50	±0.25 µm	±10 µin.	0.0025	0.1
Belt grinding	15-37.5	3000-7500	. . .	. . .	. . .	. . .	. . .	. . .
High-precision abrasive finishing								
Lapping	<0.25	<50	. . .	. . .	<0.5 µm	<20 µin.	0.025-0.1	1-4
Honing	0.25-1	50-200	0.075	0.0075	0.5-1.25 µm	20-50 µin.	0.25-0.5	10-20
Polishing	Very slow	Very slow	(a)	(a)	. . .	. . .	. . .	. . .

(a) Surface finish altered; material removal rate is insignificant.

The basic idea of abrasive finishing is to use a large number of multipoint or random cutting edges for effective removal of material at smaller chip sizes than in the finishing methods that use cutting tools with defined edges. Machining at small chip sizes allows improved finish, closer tolerances, more localized control, and generation of more intricate surface features. Cutting tools with defined cutting edges are less feasible and less practical if small chip sizes are desired. An

effective way of delivering small cutting edges to the machining zone is to use abrasive grains incorporated into a bond or matrix material.

Recent Developments. Abrasive finishing processes have seen a spurt in new developments in the past 20 years or so, thanks to a number of technology drivers as well as user needs.

Tolerances. Improvements in product performance can often be related to improvements in abrasive finishing processes and their ability to achieve closer tolerances. For example, transmission efficiency is improved when gears roll against each other with less sliding. This is made possible by grinding the gear to closer tolerances. Efficiency of magnetic recording is improved when the magnetic recording heads are finished to closer tolerances and improved surface by improvements in grinding and lapping.

Consistency. When components are finished to greater consistency, inspection costs are reduced and the process becomes more amenable to control. As an example, in a centerless grinding process for a bearing component, the operation consisted of rough, semifinish, and finishing steps involving three operations, three machines, a large in-process inventory, and inspection between each operation. By consistent finishing with cubic boron nitride (CBN) grinding wheels, the process was reduced to two steps, rough and finish, with minimal in-process inspection.

Surface Finish. Constant demand for improvements in surface finish has resulted in new processes (e.g., superfinishing, flat honing, and microgrinding). These requirements span a wide range of materials, from metals to nonmetals and from ferrous alloys to ceramics.

Material Removal Rate. With the advent of new abrasives (CBN, seeded gel, etc.) and new processes (high-efficiency deep grinding, creep-feed grinding, microgrinding, etc.), the material removal rates achievable using abrasive finishing processes exceed the previously known capabilities.

Productivity. The technical benefits described above often translate into faster production rates, shorter cycle timing, improved yields, and so on. All of these gains lead to lower total cost per part or higher productivity. Advancements of this kind have been noted in aerospace, automotive, tool production, bearings, and computer component manufacturing operations that use abrasive finishing processes.

New Products. The range of new abrasive finishing products, introduced worldwide, includes novel shapes and configurations, a wider range of sizes, an expanded range of grit sizes, and new bond types. For instance, abrasives are now available in extremely fine particle sizes with uniform size and shape control, which were not commonly available only a few years ago.

Machine Tool Improvements. Developments such as multiaxis computer numerical control (CNC), higher horsepower, greater rigidity and accuracy, automatic wheel changes, and on-machine truing and balancing systems make it possible to achieve faster production, better quality, or both.

New Grinding Methods. *Mirror-finish grinding*uses extremely fine abrasive particles to achieve extremely fine reflective surfaces of precise geometry. These methods are used to finish precision molds and dies, such as those used for making contact lenses and other optical products. *Grinding from solid* combines the high-material-removal capability of modern abrasive finishing methods with the closer tolerances and forms that can be achieved using grinding processes. As an example, end mills of large sizes are now routinely ground from solid blank, eliminating premilling operations and expensive in-process inventory. Such methods are also advocated for grinding ceramics, which improves the yield and reliability of ceramic components while reducing total fabrication cost.

Processing of New Materials. Ceramics and other materials, such as high-silicon aluminum alloys, powder metals, and cements, are increasingly being finished using abrasive methods. As the abrasion resistance of the work material increases due to included second-phase material or hard particles, multipoint finishing methods are often preferable to single-point machining methods. With the advent of processes such as high-efficiency deep grinding, it is likely that some soft and easy-to-machine materials will be finished using abrasive finishing methods.

Abrasive finishing is used in industrial practice for a wide range of materials. Typical examples are shown in Table 2. This article provides a broad overview of the various categories of abrasive products and materials, abrasive finishing processes, and the mechanisms of delivering the abrasives to the grinding or machining zone.

Table 2 Relative usage of abrasive machining for various work material types

Work material	Relative use			
	Conventional abrasives		Superabrasives	Powders slurries, and compounds
	Bonded	Coated/ impregnated		
Plastics	Low	Low	Low	None
Composites	Low	High	High	Low
Metals	High	High	High	High
Steel	High	High	High	High
Glass	Low	High	High	High
Carbides	High	Low	High	High
Ceramics	Low	Low	High	High
Wood	Low	High	High	None
Stone	None	Low	High	Low
Minerals	None	None	High	None

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Abrasive Products

Abrasive delivered in a bond or matrix is often called the *abrasive product* or *abrasive tool.* The products can be grouped under three broad categories: coated/impregnated abrasives, bonded abrasives, and powders, slurries, and compounds (Fig. 1). Each of these product types can be used in rough, precision, or high-precision applications (Table 3).

Table 3 Abrasive products and their typical application categories

Abrasive product type	Abrasive finishing process category

product type	Rough	Precision	High-precision
Bonded abrasives	Snagging surfacing cutoff grinding	Grinding (surface, creep feed, form, thread, contour, cylindrical, disc, tool, and cutter)	Honing, superfinishing, flat honing, microgrinding
Coated abrasives	Belt grinding, sanding	Belt grinding (surface, form or profile, flat stock finishing, polishing)	Belt polishing
Impregnated abrasives	. . .	Polishing, deburring, buffing	. . .
Powder, slurries, compounds, and jets	Abrasive jet machining	Polishing, buffing, liquid buffing, ultrasonic machining	Lapping, polishing, buffing

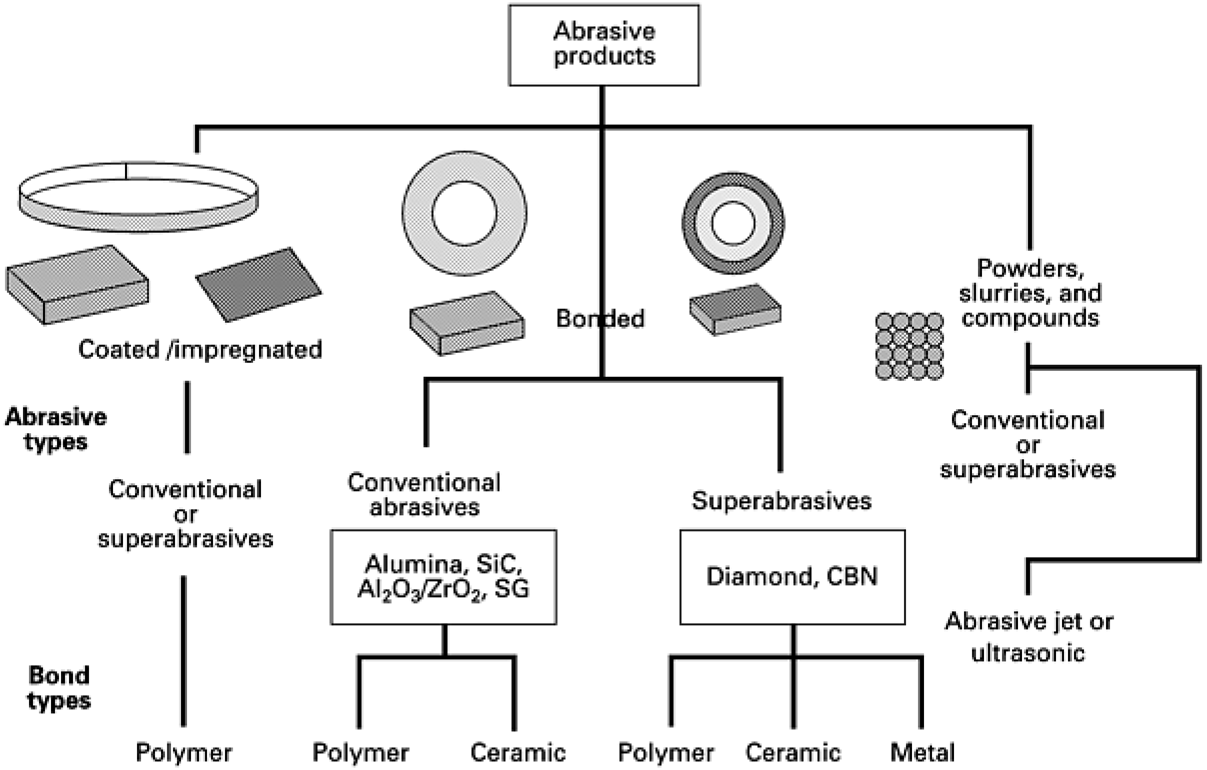


Fig. 1 Abrasive "machining" product categories

Bonded abrasives are so named because the abrasive is firmly retained in a matrix called the *bond.* They are available in discs or cylinders called *grinding wheels.* They are also available in segments of a cylinder, which are assembled into a wheel, and in rectangular blocks, nicknamed "stones," "sticks," or "hones," that are presented to the work material under various geometric configurations. The bond material can be made of phenolic resin, vitreous glass, or powder metal alloys, depending on the requirements. Every bonded abrasive product can be thought of as an engineered composite. This composite is usually of controlled pore size and structure, and its uniformity is critical for successful use of the abrasive product (Fig. 2). The size, shape, and configuration of bonded abrasives are constantly changing to meet growing needs. For example, grinding wheels are available in thicknesses from 0.02 to 500 mm (0.0008 to 20 in.). They are also available in a wide range of shapes.

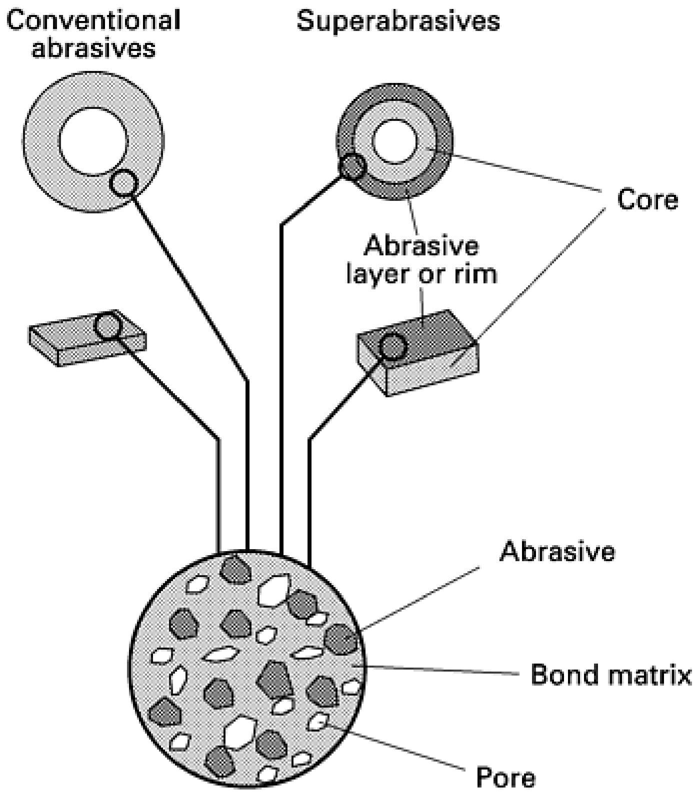


Fig. 2 Construction of typical bonded abrasive products

Coated / Impregnated Abrasives. *Coated abrasives* are single or multiple layers of abrasive products that adhere to a flexible sheet or belt. In *impregnated abrasives,* sold under various trade names, the abrasive is impregnated into flexible or woven material. Sometimes a layer of highly wear-resistant abrasives *(superabrasives)* are electroplated or brazed to a rigid steel core. Most coated and impregnated abrasives use a polymeric binder to retain the grains on the backing or the woven matrix. Most coated abrasives are available in flat sheets or belt loops of various lengths and widths.

Powders, slurries, and compounds are products in which the abrasive is delivered in a jet or in a liquid or paste configuration. When the abrasive is assisted by high-pressure water or air jet, the process is called *abrasive jet machining.* If the abrasive action is assisted by localized ultrasonic motion of a tool, it is called *ultrasonic machining.* Most abrasive powders, slurries, and compounds are delivered between the work and a wear-resistant plate called a *lapping plate,* flexible woven material called *polishing cloth,* or *buffing wheels.* (Lapping, polishing, and buffing are described in detail later in this article.) These products have extremely closely sized abrasive particles, often mixed in a liquid or carrier of controlled viscosity. Sometimes these abrasives remove the surface layer of work material through chemical action in addition to mechanical action.

Designations of Abrasive Products. A wide variety of products and their designations exist in industrial and consumer use. The common aspects of such designations are that:

- All abrasive products are identified by the abrasive type. The size of the abrasive used and its content are also frequently identified.
- In coated abrasives, the type of backing material (paper, cloth, etc.) and the features of the coating (open, closed, supersize, etc.) are also identified.
- In grinding wheels, the bond matrix used (resin, vitrified, metal, etc.) is designated along with its modifications, usually represented by a manufacturer code. The pore content is identified using the grade or hardness of the wheel.
- In the case of loose abrasives used in lapping or polishing, the particle size, shape, and distribution are critical and are identified in the specification. These products are also distinguished by the liquid

medium or carrier used and their flow properties, such as viscosity and temperature stability.

Abrasive Materials

Abrasive materials provide the cutting edges in abrasive finishing processes, so they are the essential element of any abrasive product. A variety of abrasives are used, selected for their hardness, thermal and chemical stability, and wear resistance. Figure 3 compares the hardnesses of abrasives to those of some common work materials. Figure 4 illustrates the range of abrasive sizes used and their applications.

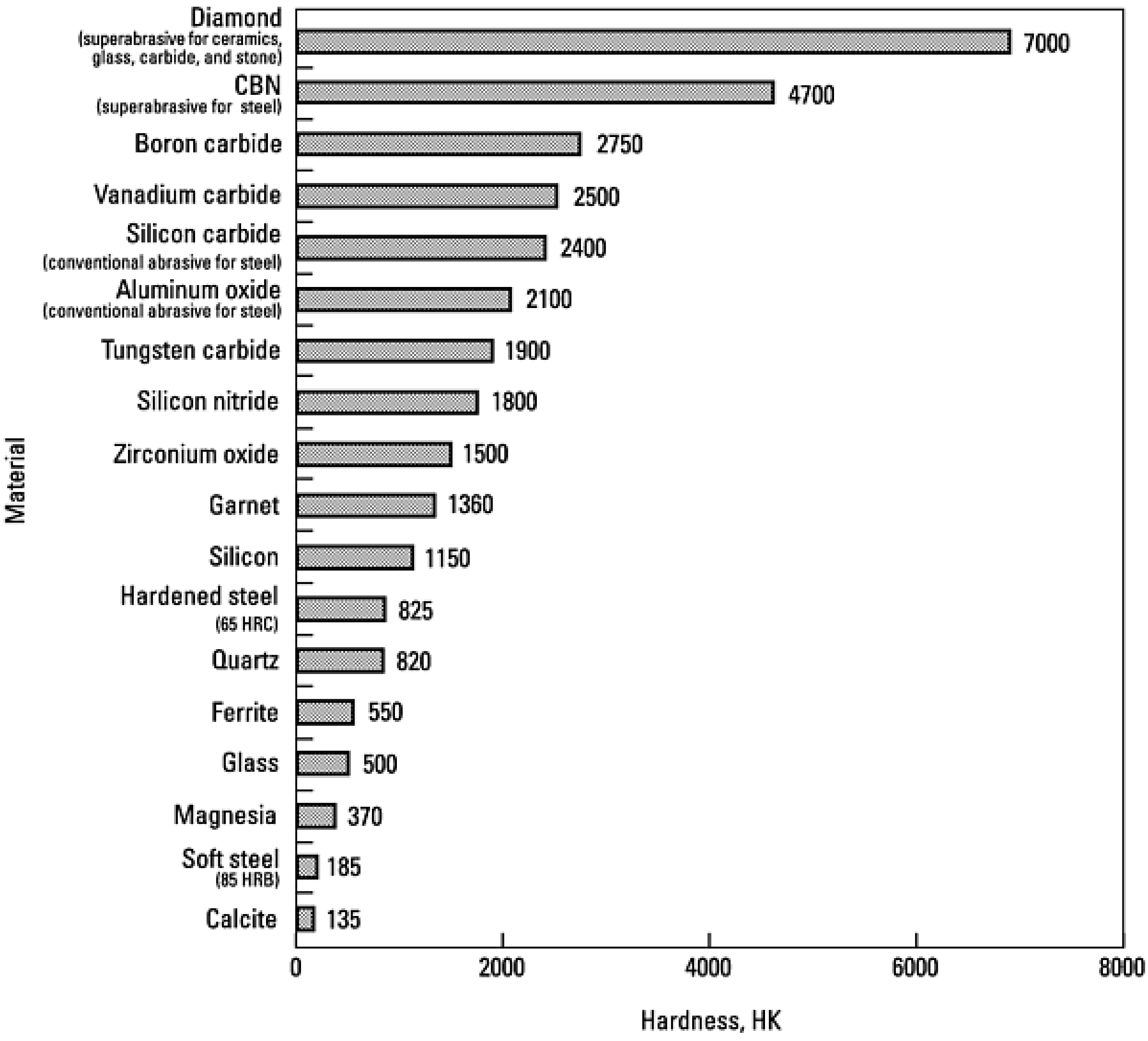


Fig. 3 Comparison of the hardnesses of work materials and the hardnesses of the abrasives used to machine them

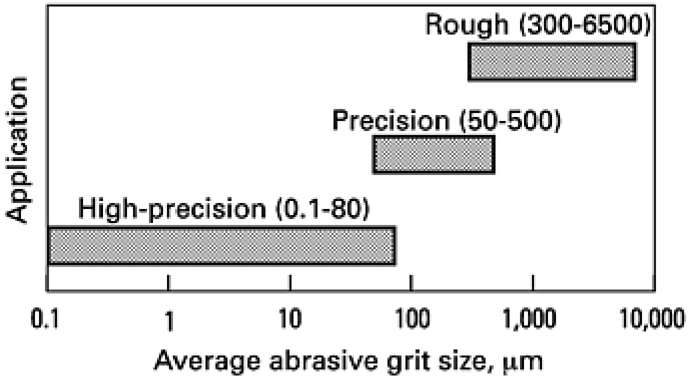


Fig. 4 Abrasive grain sizes vs. application type

The broad groupings of abrasives are identified in the following paragraphs, but in each category there are several versions that differ in shape, size, fracture strength, and so on. The reader is encouraged to obtain information about modifications from manufacturer literature and the references at the end of this article. This knowledge can be very useful in optimizing abrasive machining applications.

Conventional Abrasives. Emery and corundum are commonly used natural abrasives. Emery is a naturally occurring mixture containing between 57 and 75% aluminum oxide. The remainder is iron oxide and impurities. Corundum is a naturally occurring fused aluminum oxide that is tougher and harder than emery. Natural abrasives usually cost less than synthetic abrasives and are useful for polishing some softer metals. When applied to the harder metals, natural abrasives wear at a rapid rate, so they have been largely replaced by synthetic abrasives.

Synthetic Abrasives. Aluminum oxide and silicon carbide are the most widely used synthetic abrasives. They are harder, more uniform, longer lasting, and easier to control than natural abrasives. Because aluminum oxide grains are often very angular and have excellent bonding properties, they are particularly useful in finishing tougher metals, such as alloy steels, high-speed steels, and malleable and wrought iron.

Silicon carbide is harder and a better conductor of heat than aluminum oxide; it fractures easily, providing new cutting surfaces that extend the useful life of the abrasive. Silicon carbide is usually used in polishing low-strength metals, such as aluminum and copper. It is also applied in polishing hard, brittle materials, such as carbide tools, high-strength steels, and chilled and gray irons. Silicon carbide tends to decompose readily in the presence of iron and is not useful as an abrasive for grinding at high material removal rates involving ferrous work materials. However, it is used extensively in the grinding of titanium alloys.

Various types of alumina and silicon carbide are used as abrasives. The variations are derived from such factors as purity, crystal size, shape, and strength. Zirconia-alumina is a eutectic version with high impact strength and toughness, which are desirable characteristics for abrasives used in heavy or rough grinding conditions. A very pure form of aluminum oxide is produced using sol-gel techniques. In some cases, this microcrystalline alumina provides dramatic performance improvements compared to fused aluminum oxide.

Superabrasives. Diamond and CBN are the two superabrasive materials used in grinding applications. Diamond, available in both natural and synthetic forms, is the hardest known material. CBN, the second hardest material, is synthetic. Both of these superabrasive materials are synthesized at high pressures and temperatures in the presence of molten catalyst solvents.

Synthetic diamonds are available in a wide range of shapes and sizes. Weak, friable polycrystalline diamonds are generally used for grinding tough and brittle materials such as ceramics and carbides. Stronger abrasives find frequent application in the grinding of concrete, stone, and glass. The most popular form of CBN, used for grinding most steels and nonferrous high-strength alloys, is a monocrystalline variety. A tougher, polycrystalline form of CBN is also available.

Diamond and CBN are available with a coating of nickel metal. Metal-coated abrasives, predominantly used in resin-bonded wheels, increase grinding wheel life by a factor of 2 to 3. Diamond abrasives are also available with copper coatings, predominantly used in dry grinding applications.

Combinations of abrasive types (combinations of superabrasives with conventional abrasives, combinations of conventional abrasives, and combinations of superabrasives) are sometimes made to take advantage of the best properties of each.

Grinding

A wide variety of abrasive finishing processes termed *grinding* are practiced in the finishing of industrial components. They offer the following advantages (compared to machining processes that use defined cutting edges):

- The range of surface geometries generated (e.g., contours, profiles, etc.) is frequently more complex than is economically possible in single-point machining processes.
- Grinding wheels can be used for high stock removal (i.e., rough grinding). The same wheel is often modified in situ to achieve an extremely fine finish or close tolerance during finish grinding processes. In situ modifications of cutting tools are not possible or practical.
- Grinding wheels can be designed so that the abrasive, bond, and pore distribution are carefully controlled to meet unique requirements of surface generation efficiency and quality of the generated surface.
- The material removal rate per cutting edge is often controlled by abrasive grain size and content, and the total volume of material removed per unit of time can be modified by the design of the wheel geometry and the kinematics of the wheel/work motions. The separation often allows for control of surface features somewhat independently of production economics. This separation is not possible in the processes described in the article "Finishing Methods Using Defined Cutting Edges" in this Volume.

Typical grinding processes are shown in Fig. 5. Each of these applications can range from rough grinding to precision grinding to high-precision processes. Many of these operations in rough grinding are carried out using handheld grinders or manual effort. However, a large number of rough grinding processes and almost all precision grinding processes use automated equipment. They occasionally involve manual loading or unloading of parts and wheels. Large-volume production operations are often fully automated. Recent advancements in CNC grinding machines have extended the capability of conventional grinders by allowing for grinding of multiple surfaces in a single setup, using more than one wheel at a time as well as grinding multiple surfaces simultaneously.

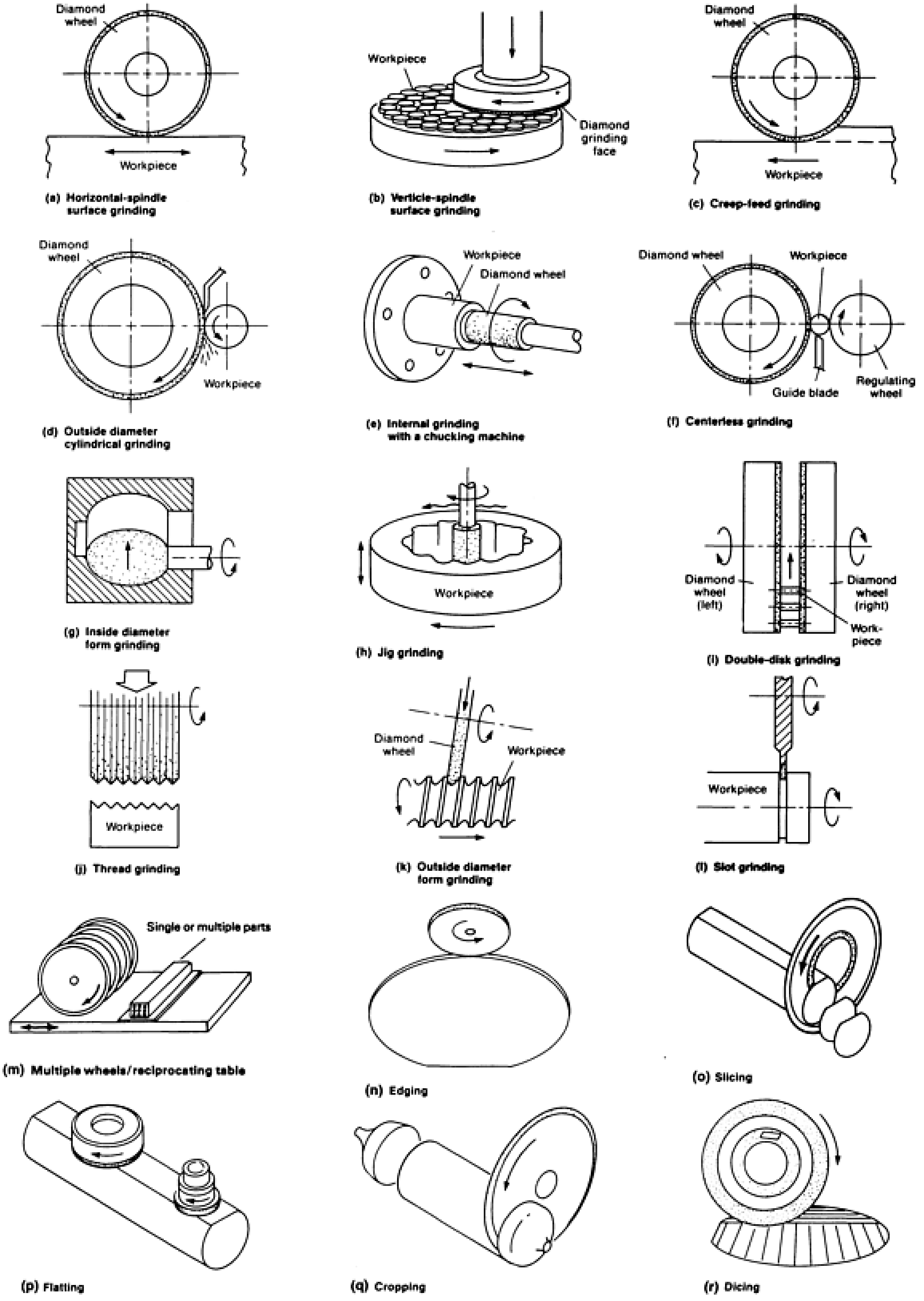


Fig. 5 Grinding processes

The grinding machine features that frequently determine the production rate and/or part quality are:

- Rigidity/stiffness

- Vibration level
- Coolant systems
- Precision movements and positioning accuracy
- On-machine dynamic balancing capability
- Truing and dressing systems
- Multiaxis CNC capability
- Spindle horsepower
- Speed range and variability
- Torque/speed capability of the motor
- Materials handling systems
- Work space and its accessibility
- Grinding cycle design or capability

Grinding Cycle Design. One of the key elements in the grinding process is the design of the grinding cycle. This involves a programmed application of the grinding wheel against the work material. It can be measured or monitored in terms of the position of the slide in which the wheel or part is mounted with respect to the time.

Initially the slide is moved rapidly, thus removing a large volume of work material rapidly. This is the rough grinding portion of the cycle, as illustrated in Fig. 6(a). This is usually followed by a short dwell, during which the motion of the slide is sometimes stopped to allow the elastic deflections produced during rough grinding to be eliminated. The need for this dwell and its duration are often determined by the stiffness of the wheel, the work material, the work fixture, or the machine tool.

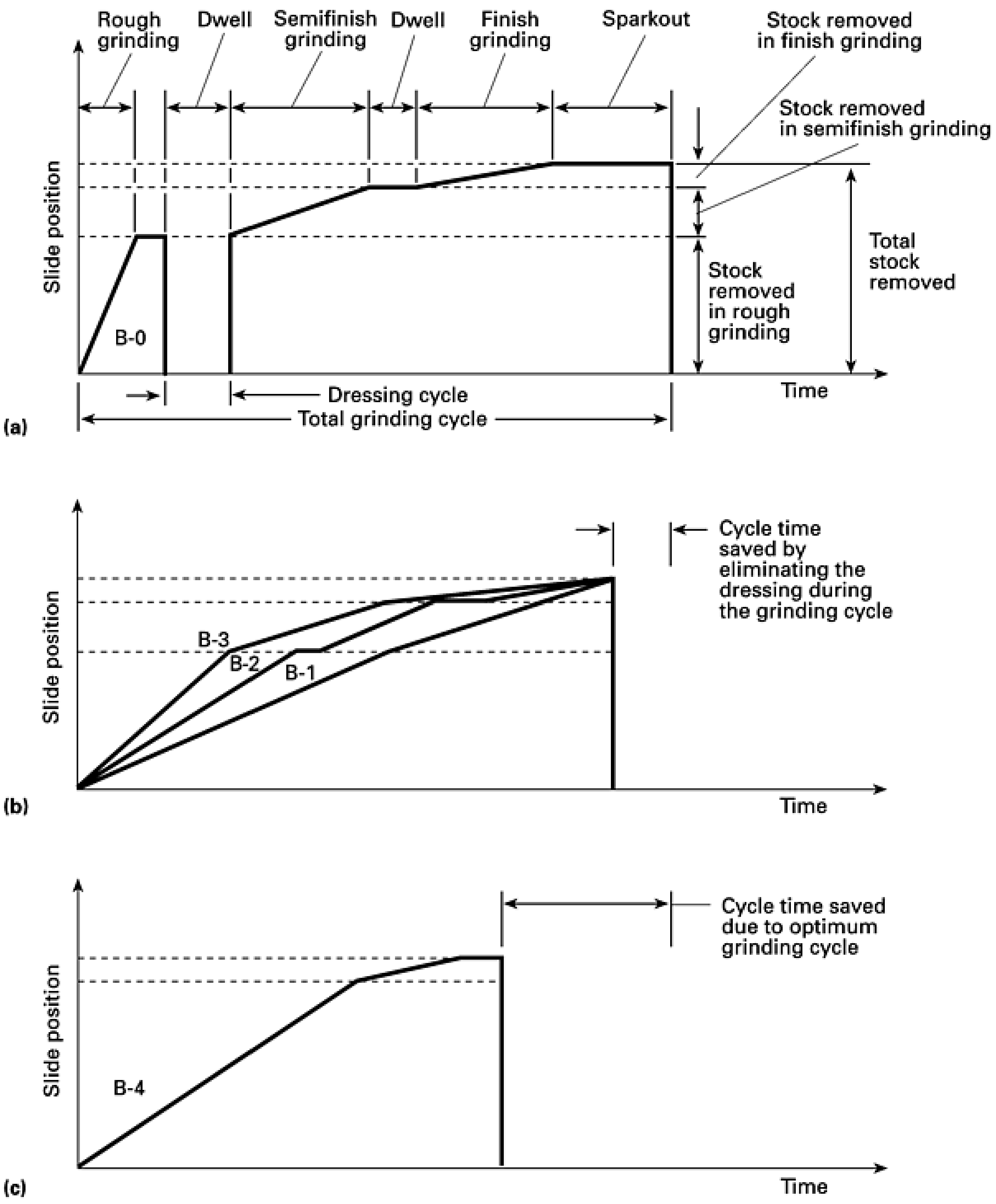


Fig. 6 Grinding cycle design. See text for details.

The rough grinding cycle has now affected the surface topography of the grinding wheel. This topography is modified by processes called *truing* and *dressing,* shown as "dressing cycle" in Fig. 6(a) and described in more detail later in this section. These processes are followed by a slower rate of grinding (judged by the smaller slope of the displacement/time curve), resulting in semifinish and finishing grinding cycles. The last portion of the cycle, akin to the dwell described earlier, is often called *sparkout.*

The suitable combination of rough, semifinish, and finishing grinding steps, with dwell, dress, and sparkout included as required, is called the *grinding cycle.* The design of the grinding cycle varies, depending on the machine tool characteristics and capabilities, grinding wheel characteristics and capabilities, work material properties and requirements, and operational conditions such as coolant applications, fixturing, and truing methods. Because of the range of variables

that can influence the grinding cycle design, the process is often perceived to be an art. However, it is far from an art and can be managed as an engineered system with defined causal relations, as described in the section "Systems Approach" in this article.

The potential to alter the wheel face using the dress cycle is unique to precision grinding processes using grinding wheels. With coated abrasive belts containing a single layer of abrasives, this is often not possible. In those processes, individual coated abrasive product grades are assigned to rough, semifinish, and finish steps.

The rough grinding portion of the cycle can be modified by changing the rate of slide motion (and hence material removal rate), as shown in Fig. 6(b). This figure shows three alternative rough grinding paths, B-1, B-2, and B-3. These in turn require alterations in the semifinish and finish grinding steps, as shown. One reason for using an alternative path may be to reduce the amount of dressing or the number of dressing cycles during a grinding process. Paths B-1, B-2, and B-3 in Fig. 6(b) are less aggressive rough grinding paths that could ensure that wheel topography is not significantly affected during rough grinding, compared to path B-0 in Fig. 6(a). Hence, all these alternative paths can be accomplished and the part can be ground to final tolerances without the need for dwell in some cases and without the need for dress cycle in all cases, as shown in Fig. 6(b).

If the abrasive grain in the grinding wheel is an efficient cutting tool, then the forces or deflection induced during rough grinding may be small. This, combined with the efficient cutting action, may permit further reductions in the semifinish and finish operations and often eliminate the need for sparkout (Fig. 6c). Such optimizing of the cycle reduces the cycle time and hence improves productivity. This is one of the frequent objectives in using premium abrasive wheels, such as CBN grinding wheels for steel grinding.

The total force or power consumed during the rough grinding cycle is generally high, because the associated material removal rate is largest during the rough cycle. Thus, the deflection of the part under the applied forces of the machine tool is generally the limitation during the rough grinding cycle. Sometimes the work material or the coolant system is not able to dissipate the heat generated and the power input must be decreased, thus requiring alterations to the rough grinding cycle.

During the later portion of the grinding cycle (i.e., semifinish, finish, or sparkout), as the size of the chip generated decreases, the forces and power consumed also decrease. However, the chip generation efficiency decreases as the chip size decreases. (This is based on the mechanics of chip formation, described in the article "Finishing Methods Using Defined Cutting Edges" in this Volume.) The result is a large increase in specific energy, or the energy input per unit volume of the material removed. To avoid surface damage, this specific energy needs to be minimized in the later portions of the grinding cycle. The duration of the sparkout portion of the cycle is usually a balance between improved part geometry due to recovery from elastic deflections and the potential for surface damage due to the sliding of the abrasive wheel against the work material.

Truing and Dressing of Grinding Wheels. The tolerances and surface finishes produced on workpiece surfaces and the forces developed during grinding depend to a great extent on the manner in which the grinding wheel was prepared for operation. Preparation of the grinding wheel generally involves two operations: truing and dressing.

Truing refers to the process of generating a geometrically correct wheel surface in order to grind with minimal or no chatter. Successful use of grinding wheels requires that the wheel is concentric and free of lobes (Fig. 7). Conventional abrasives are most commonly trued by feeding a single-point or multipoint diamond dressing tool across the rotating wheel surface. Superabrasive wheels are trued with a vitrified silicon carbide truing wheel mounted on a brake-controlled truing device. Some of the other truing devices used are diamond truing rolls and cutters driven by hydraulic motors and diamond crush rollers.

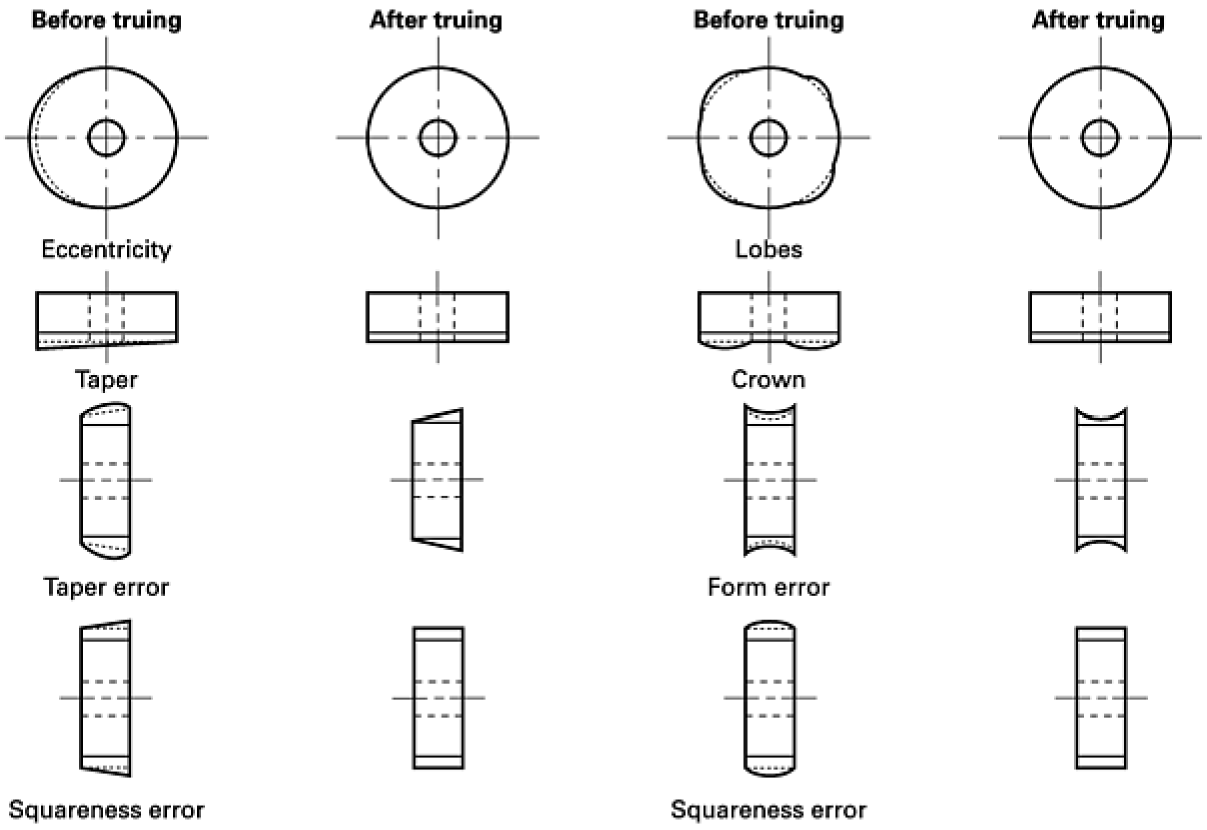


Fig. 7 Typical examples of conditions that require truing

Dressing is the process of eroding the bond matrix in the wheel surface after a truing operation or after grinding in order to expose the abrasive grains for efficient grinding. After truing, the wheel surface is generally very smooth; the bond adjacent to the grits has to be eroded in order to expose the grits. Occasionally, the chips fill up the pores and clog the wheel during grinding, resulting in an inefficient cutting action. The wheels then have to be dressed in order to remove the chips from the wheel surface. Dressing is usually accomplished by pressing or sliding an abrasive stick against the wheel surface. Recently, in-process dressing of metal bond diamond wheels using electrodischarge machining has been introduced. Electrolytic in-process dressing is another emerging technology for dressing fine abrasive metal bond diamond wheels. Abrasive slurries are also occasionally used for dressing operations.

Wheel Shapes. Grinding wheels are used in a variety of operations, as shown in Fig. 5. The different geometric configurations require that suitable grinding wheels also be available, so grinding wheels are made in several different shapes, including cylinders, cups, cones, and plugs (Fig. 8). In general, conventional abrasive wheels can be readily "machined" to the desired shape, but this is generally not true with superabrasive wheels, which are therefore available in a wider variety of shapes. Superabrasives are almost always made to near-net shape as required prior to their use. (See the article "Superabrasives" in Volume 16 of the *ASM Handbook.*)

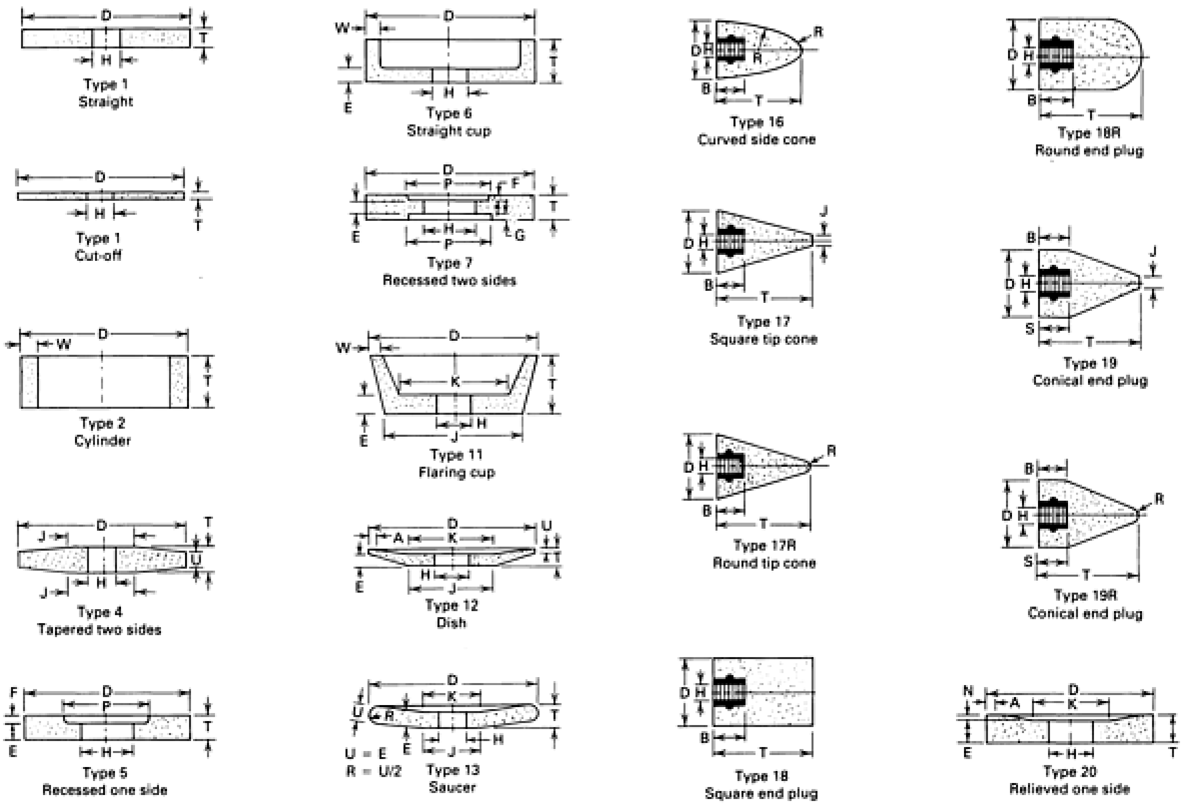


Fig. 8 Standard wheel configurations for conventional grinding wheels

Types of Bonds for Grinding Wheels. In order to effectively grind a large range of materials, a variety of bonding systems are available to hold the abrasives in the wheel. The most common bonding materials are resin (phenolic), ceramic (glass), and metal (bronze). Other bond types, such as shellac, oxychloride, rubber, and silicate are available but are not commonly used. The superabrasive wheels are also available in a metal-single-layer (MSL) specification that consists of a single layer of abrasives held together with the help of a metallic braze. Other superabrasive products, called *plated wheels* or *E-process wheels,* have a single layer of abrasives electroplated to the preform. Table 4 lists the characteristics of the four bond types available for grinding wheels.

Table 4 Characteristics of bond types used in abrasive products

Resin bonds
Readily available
Easy to true and dress
Moderate freeness of cut
Applicable for a range of operations
First selection for learning the use of superabrasive wheels

Generally used with coated abrasive product and rough grinding or operations with high material removal rates
Vitrified bonds
Free-cutting
Easy to true
Do not need dressing (if selected and trued properly)
Controlled porosity to enable coolant flow to the grinding zone and chip removal
Intricate forms can be crush formed on the wheels
Suitable for creep-feed or deep grinding, inside-diameter grinding, or high-conformity grinding
Potential for longer wheel life than resin bond
Excellent under oil as coolant
Metal bonds
(Available with superabrasives only)
Very durable
Excellent for thin-slot,groove,cutoff,simple form,or slot grinding
High stiffness
Good form holding
Good thermal conductivity
Potential for high-speed operation
Generally require high grinding forces and power
Difficult to true and dress

Layered products
Single abrasive layer plated on a premachined steel preform
Extremely free-cutting
High unit-width metal removal rates
Form wheels easily produced
Form accuracy dependent on preform and plating accuracy
Abrasive density is easily controlled
Generally not truable
Generally produce poorer surface finish than bonded abrasive wheels

Vitrified bonds made of clay, feldspar, and a glass frit are the most commonly used bonds for conventional abrasives and are becoming popular for use with superabrasives. They are rigid, free cutting, and have very good form retention. In addition, the porosity in these bonds can be controlled for more chip clearance and better coolant application at the grinding zone. These bonds do not have high impact resistance, however, and they are not used in heavy-pressure operations such as foundry snagging or steel conditioning.

Resin bonds are made of thermosetting polymers, usually phenol formaldehyde or epoxy resins. These bonds are resilient, have good impact resistance, and are very free cutting. Their rigidity can be varied by adding fillers such as glass fibers. Resin bonds are used in most rough grinding operations, such as snagging, weld grinding, and cutoff. Resin bonds are extremely popular for use with superabrasives and find extensive use in tool and cutter grinding, grinding of ceramics, carbide drill fluting, and glass beveling. The resilience of these bonds results in reduced chippage of brittle workpiece materials. Extremely fine-grit abrasives retained in flexible polyurethane bond material are commercially available and are used in extremely fine finishing processes.

Metal bonds are commonly used with superabrasives and are made from sintered bronze produced by powder metallurgy methods. Cast iron and aluminum bonds have been recently introduced. These bonds are very durable, have excellent form-holding characteristics, and have high stiffness. They require rigid machines, however, in order to withstand the high forces generated. Metal bonds are very popular in geological drilling, in asphalt and concrete cutting, and for cutoff wheels in precision electronic applications. Strong blocky diamonds are generally used as abrasives in metal bonds.

For more information on grinding wheels, see "Grinding Equipment and Processes" in Volume 16 of the *ASM Handbook*

Quantitative Aspects of Grinding Processes. When the work material is subjected to a grinding process, the interactions can be represented in terms such as equivalent diameter, chip size, specific energy, and grinding force. These parameters are described later in this section. A key parameter is the material removal rate (MRR), the volume of material removed in a unit of time. It is expressed as:

$$\text{MRR} = \text{Work speed } (v_w) \times \text{depth of cut } (d) \times \text{width of cut } (b_w)$$

When grinding takes place uniformly along the entire width of the wheel, the MRR can be normalized using the equation

$$\text{Unit width MRR}' = \text{MRR/width of cut}$$
$$(\text{in.}^3/\text{min/in.})$$

Equivalent Diameter. Figure 9 is a schematic representation of the concept of equivalent diameter. Grinding processes of various configurations can be normalized for ease of comparison using the following equations:

- *Outside diameter grinding:* $D_e = D_w \times D_s/(D_w + D_s)$
- *Inside diameter grinding:* $D_e = D_w \times D_s/(D_w - D_s)$
- *Surface grinding:* $D_e = D_s$

where D_e is equivalent diameter, D_w is the work diameter, and D_s is the wheel diameter. Large equivalent diameter represents longer arc of contact between the wheel and the work material. Hence, as D_e increases, the sliding interactions between wheel and the work material become dominant. This is usually observed as increased grinding power or force for the same grinding condition. In practice, this situation is overcome by using a "softer" grinding wheel as the D_e is increased.

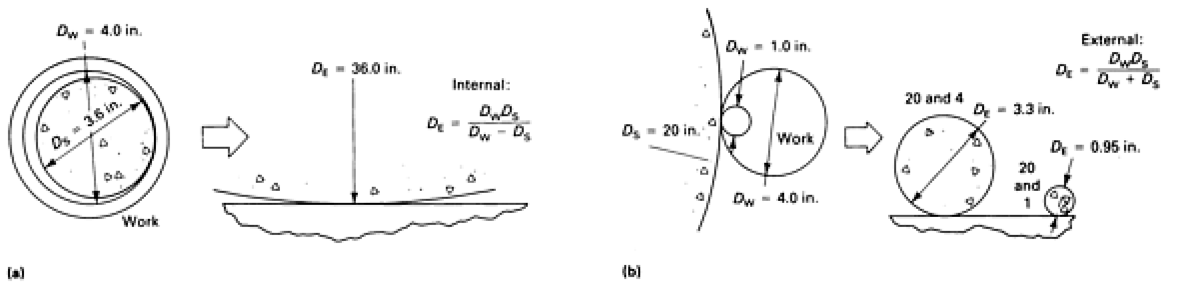


Fig. 9 Use of equivalent diameter to relate (a) internal and (b) external cylindrical grinding to surface grinding

There are unique situations, such as grinding a cam lobe profile, where D_e changes constantly from a small value, during outside diameter grinding of the nose or the base circle, to a large value, during surface grinding of the opening and closing ramps. The grinding wheel and the grinding system should be capable of accommodating such variations within one operation. Disc grinding or grinding of flat surfaces with cup wheels is another unique situation because the D_e can be perceived to be infinity. In such situations every attempt must be made to eliminate the frictional interactions. This is usually accomplished by using coolant slots in the grinding wheels, interruptions to the wheel face, and improved coolant applications.

Chip Size. The size of the chip produced by the abrasive grain during a grinding process (h) can be estimated as:

$$h = (v_w/v_s)^{1/2} \times (d/D_e)^{1/4} \times (KC)^{-1/2}$$

where v_s is wheel speed, K = 1 to 20, and C is the number of grains per square inch of grinding wheel surface. C is larger for fine abrasive grains and smaller for large abrasive grains. Like D_e, chip thickness can be used to compare grinding operations. In some cases, the larger the chip thickness, the higher the "cutting efficiency" as measured by a decrease in specific energy. However, as chip thickness increases, the force per cutting edge may increase, thus degrading the surface finish.

Grinding force is the force exerted between the grinding wheel and the work material. These forces can be normal to the work surface (F_n), tangential to the wheel (F_t), and occasionally in the transverse direction (F_z).

Specific energy is the ratio of grinding power to the material removal rate. It is a measure of the energy input per unit volume of material removed.

G-ratio is the ratio of the volume of work removed per unit volume of abrasive product consumed. It is a measure of the life or durability of abrasive product for a given application. In many applications, the wheel is trued or dressed frequently or even continuously. In those situations, the *G*-ratio may need to reflect the abrasive consumed during these nongrinding operations.

Grinding system performance index (GSPI), or "grindability," is one measure of the ease or difficulty in grinding. It is defined as:

$$\text{GSPI} = G\text{-ratio/specific energy}$$

Higher values of GSPI imply lower specific energy, greater performance economy (larger *G*-ratio), or both. More commonly, *G*-ratio is equated with grindability, although it is an incomplete description of grinding results.

Effect of Material Removal Rates on Force and Power. Figures 10(a) and (b) show the variation of normal force and power with material removal rate in a typical grinding operation. In general, the force and power increase with an increase in material removal rate, and a minimum force is required to initiate cutting. This minimum value of force or power is termed the *threshold force* or *threshold power*. Thus:

$$\text{Total power} = \text{Cutting power} + \text{threshold power}$$

which when divided by the MRR results in the relation:

$$\text{Specific energy} = \text{Specific power} + \text{threshold power/MRR}$$

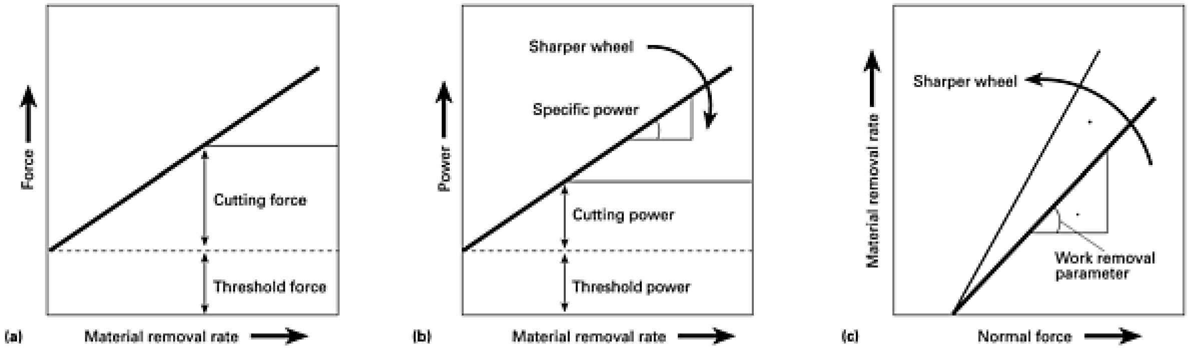


Fig. 10 (a, b) Effect of material removal rate on force and power. (c) Work removal parameter

Specific power is the slope of the power-versus-MRR curve (Fig. 10b) and is another important parameter used to analyze grinding results. It represents the cutting component of the specific energy and in physical units could be considered the specific cutting energy. The threshold power can be approximated as the power component required to overcome friction and material deformation effects. If these frictional effects are absent, specific energy is equivalent to specific power (or, more precisely, to specific cutting energy).

Figure 10(c) is a plot relating the material removal rate to the normal force. Such data can be obtained on a grinding machine using force-measuring equipment and can be effectively used to differentiate between the "sharpness" or cutting efficiency of grinding wheels. The slope of the MRR-versus-F_n curve is called the *work removal parameter* (*WRP*). A steep slope indicates a sharp wheel and low force, and a shallow slope indicates a dull wheel and high force. Like the power relation, force is modeled as follows:

$$\text{Total force} = \text{Cutting force} + \text{threshold force}$$

which when divided by the MRR results in the relation:

$$\text{Total force/MRR} = (\text{WRP})^{-1} + \text{threshold force/MRR}$$

where $(\text{WRP})^{-1}$ is the ratio of cutting force and MRR.

High-Precision, Fixed-Abrasive Finishing

A variety of high-precision processes have been in use, and new processes are constantly being developed to achieve extremely close geometric tolerances or to improve surface finish. The objective of all high-precision processes is to achieve geometrically precise components or surfaces of controlled texture or surface finish (Fig. 11). Table 5 compares the processes described in this section. A parallel set of processes using loose abrasives, called *lapping, buffing,* and *polishing,* are reviewed in later sections of this article.

Table 5 Comparison of high-precision finishing processes

Process features	**Process category**			
	Honing	**Superfinishing**	**Flat honing**	**Microgrinding**
Bonded abrasive tool used	Yes	Yes	Yes	Yes
Cutting speeds	<500 sfm	<500 sfm	<500 sfm	500 to 12,000 sfm
Oscillation of abrasive tool	Yes	Yes	No	No
Amplitude of oscillation of abrasive tool	Large	Small (about 1 to 6 mm)	. . .	. . .
Abrasive product size relative to the work size	Small to large	About equal	Large	Varies widely
Frequency of oscillation	Small (100-200 strokes/min)	Large (300-4000 strokes/min)	. . .	. . .
Abrasive tool motion	Linear or reciprocation	Angular, linear, or reciprocation	Rotation	Rotation
Work material motion during the abrading process	Fixed	Circumferential rotations	Epicyclic	Large range of motions and velocities are involved
Work surface	Generally straight cylindrical internal	External or internal surfaces, not limited to	Generally flat and parallel surfaces. Occasionally	Large range of surfaces and

configuration	surfaces	straight surfaces	cylindrical or sphere	contours
Amount of stock removed	Rough 0.010 to 0.015 in.	0.0001 to 0.0005 in.	Rough 0.010 to 0.015 in.	Similar to honing and superfinishing
	Finish 0.002 to 0.006 in.		Finish 0.002 to 0.006 in.	
Surface texture controlled	Yes	Yes (to a lesser degree than honing)	Maybe	Maybe
Abrasive tool bond type	Vitrified (also metal bond for superabrasives)	Vitrified	Vitrified (also metal bond for superabrasives)	Resin, metal or vitrified using conventional abrasives or superabrasives

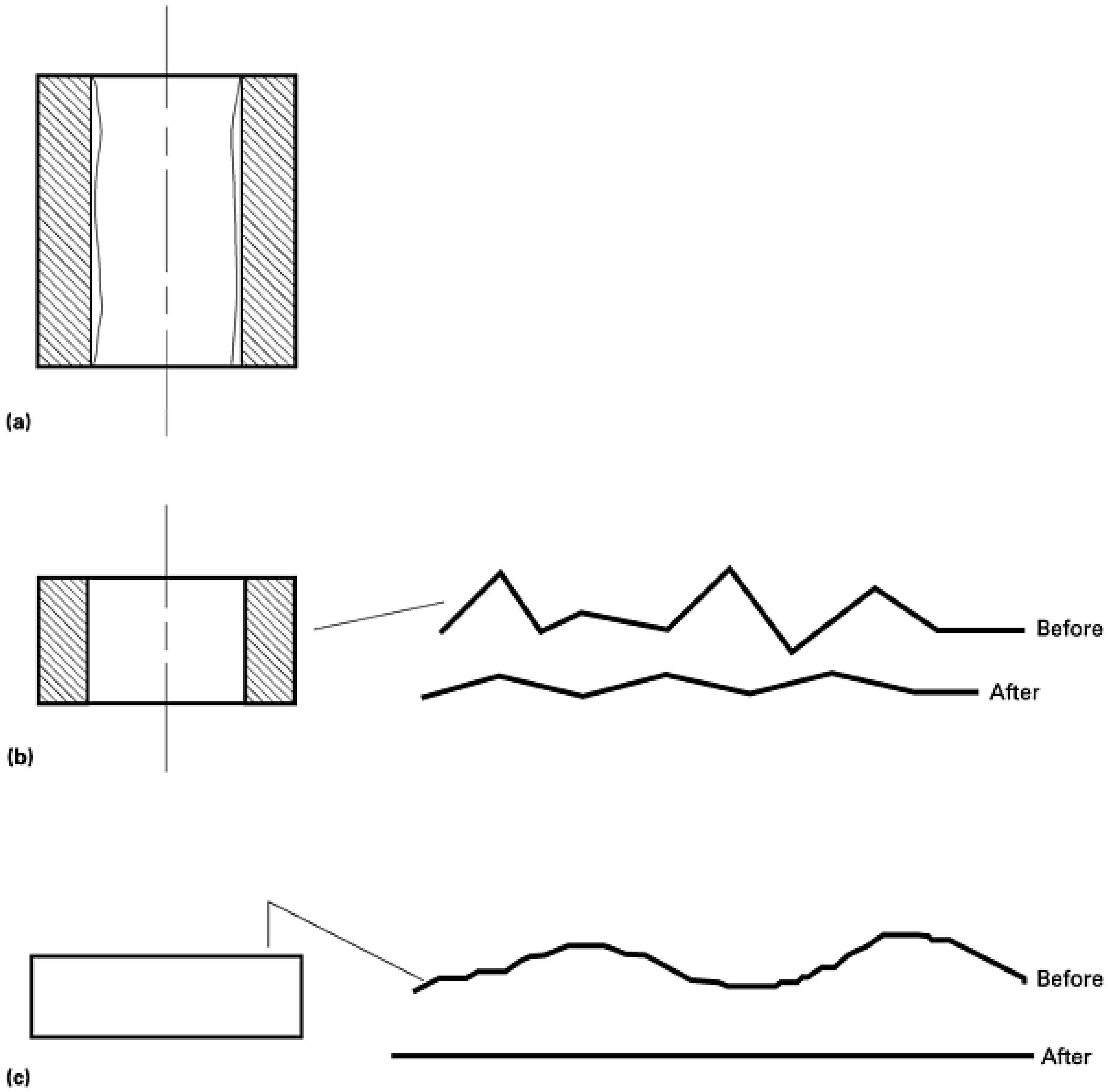


Fig. 11 Applications of high-precision processes using bonded abrasives. (a) Honing is most commonly used to correct the internal geometry of a bore hole. (b) Superfinishing is most commonly used to improve external

surface finish. (c) Flat honing is most commonly used to improve flatness and the parallelism between surfaces.

Honing is a low-velocity abrading process that uses bonded abrasive sticks to remove stock from metallic and nonmetallic surfaces. As one of the last operations performed on the surface of a part, honing generates functional characteristics specified for a surface, such as geometric accuracy, dimensional accuracy, and surface features (roughness, lay pattern, and integrity). It also reduces or corrects geometric errors resulting from previous operations.

The most common application of honing is on internal cylindrical surfaces (Fig. 12a). However, honing is also used to generate functional characteristics on external cylindrical surfaces, flat surfaces, truncated spherical surfaces, and toroidal surfaces (both internal and external). A characteristic common to all these shapes is that they can be generated by a simple combination of motions.

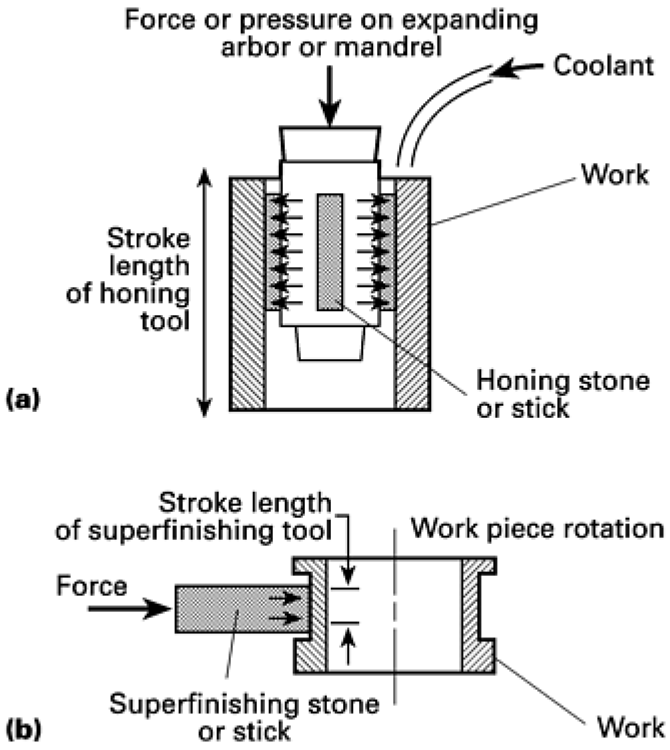


Fig. 12 (a) Schematic representation of honing. (b) Schematic representation of superfinishing

Superfinishing is a low-velocity abrading process very similar to honing. However, unlike honing, superfinishing processes focus primarily on the improvement of surface finish and much less on correction of geometric errors (Fig. 12b). As a result, the pressures and amplitude of oscillation applied during superfinishing are extremely small. This process is also referred to as *microhoning, microsurfacing,* and *microstoning.*

Flat honing is a low-velocity abrading process, similar to honing except that a large flat honing surface is used to simultaneously finish a large number of flat parts (Fig. 13). The predecessor to the flat honing process was *hyper lap,* in which the lapping plate was simply replaced by an abrasive product such as a grinding wheel. Modern flat honing machines "float" the abrasive product such that it can be applied under controlled pressure against the work surface. It is also critical to ensure that the flat honing tool wears uniformly and accepts uneven work surfaces that require correction during the honing process. These processes also true and dress the flat hone in a manner very similar to a grinding process. With suitable adaptation, flat honing equipment can be used for finishing cylindrical surfaces such as pins or rollers, as well as spherical surfaces such as balls.

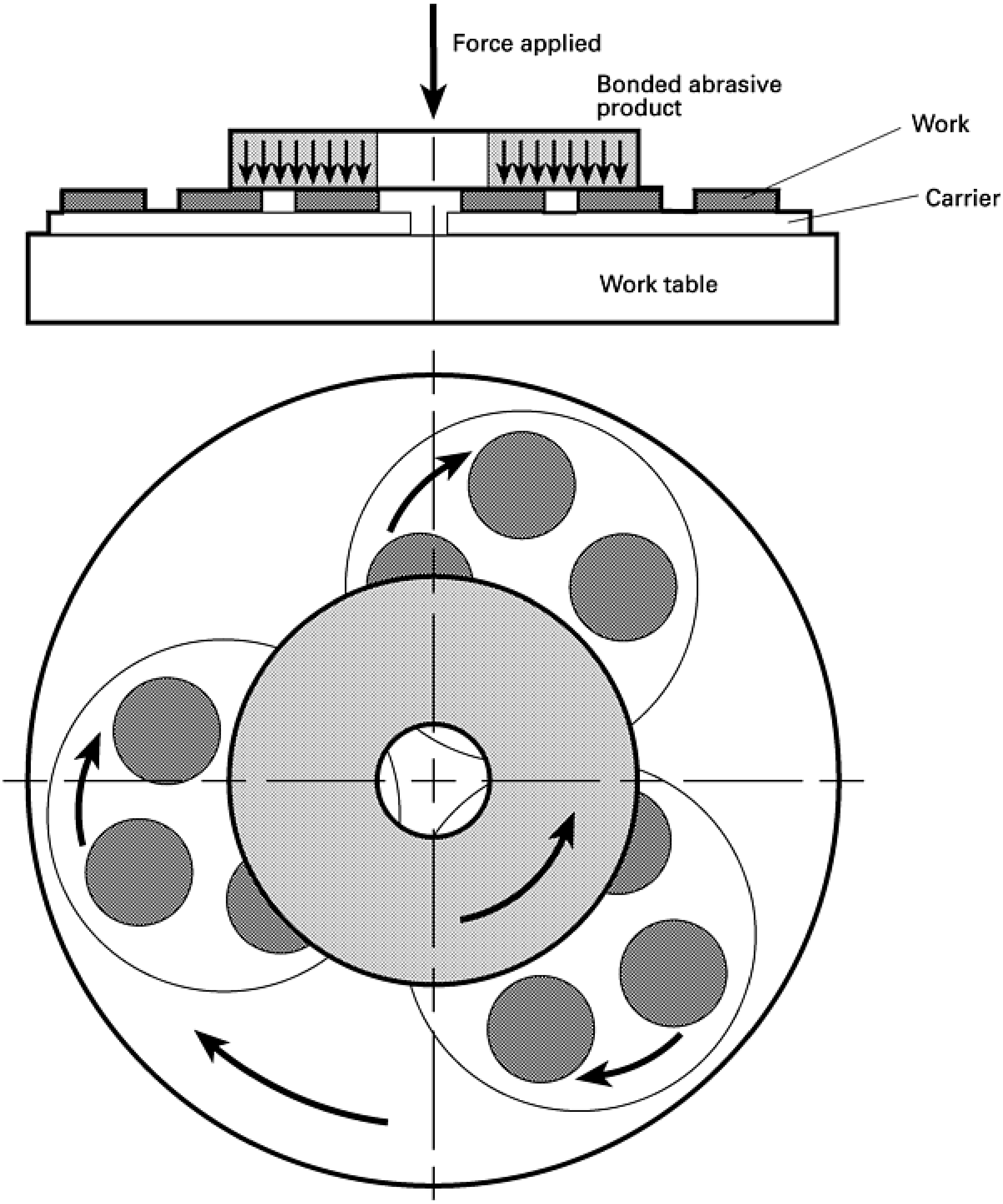


Fig. 13 Schematic representation of flat honing

Flat honing requires abrasive wheel(s) that will produce the required surface finish and accuracy of flatness and parallelism. To be efficient, the wheel(s) must continue to cut, load after load, without requiring frequent truing. The accuracy obtained depends on the flatness of the wheel surfaces. If the faces wear, then they must wear away evenly in order to keep the wheel surfaces flat.

At the time of this writing, the use of diamond or CBN wheels for flat honing is relatively new. Research is presently being done to flat hone hard ceramic materials with metal bond, fine-grit diamond wheels. The anticipated benefits of diamond wheel honing over conventional grinding are cost effectiveness, less surface damage, better accuracy and finishes, less chipping, and easier fixturing.

The coolant normally used in the flat honing process wets the small particles generated during the machining process and carries them away. In addition, it cools the workpiece and provides lubrication. Mineral oil or mineral seal oil are conventional fluids that meet these requirements and still have low enough odor and high enough flash point to be feasible and safe. Water-based coolants have specific applications, and some workpieces composed of carbon and other ceramics are often processed using water.

Microgrinding is akin to the precision grinding processes described above, except that extremely fine abrasives are used (50 μm and finer). The cutting velocities in microgrinding range from very low (500 sfm) to as large as those used for grinding (6000 to 12,000 sfm). This process is also called *fine grinding* or *microfinishing grinding.*

The Future. Each of these high-precision processes is an emerging technology, and many advancements can be expected, driven by functional or performance improvements of industrial components and their systems. For example:

- Honing and microgrinding are used to achieve closer-fitting cylinders and pistons that reduce leakage past the piston and improve performance efficiency in hydraulic cylinders and automotive engines.
- Flat honing and microgrinding improve the quality of flat and parallel surfaces that are used to align, join, or seal other surfaces.
- Microgrinding can be used to modify surfaces ground to a certain feature to improve the bearing area, which in turn improves load-bearing capacity (in the case of bearings) or signal processing capability (in the case of the magnetic heads used in computers).

Abrasive Belt Grinding and Polishing

Endless cloth belts precoated with abrasive are widely used in grinding and polishing operations. In comparison to grinding with bonded wheels, they offer the following advantages:

- Ability to finish large areas simultaneously
- Elimination of the need for costly wheel setup operations such as balancing, truing, and dressing
- Less heat generation in polishing because of the larger surface area of belts
- Ease of setup and ease of changing the abrasive belts
- Flexible or compliant abrasive tooling, not easily prone to chatter
- Smaller inventory of polishing accessories

Typical configurations of abrasive belt applications are shown in Fig. 14, 15, 16, and 17. In general, the abrasive belt is held between a drive roll and a contact roller. The belt tension determines its torque-carrying ability and hence the power delivered to the grinding zone. The work is usually applied against the belt under controlled force or pressure. Occasionally the work may be fed at a constant rate against the abrasive belt. The belt is replaced when it loses or sheds the abrasives or when the rate of material removal is decreased.

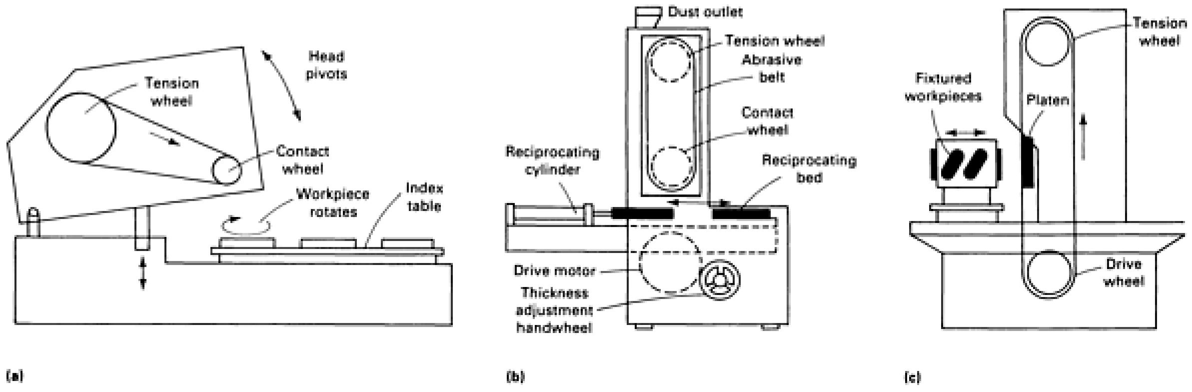


Fig. 14 Schematics illustrating the primary components of coated abrasive precision grinding machines. (a)

Rotary-table type. (b) Reciprocating (bed) table type. (c) Vertical-platen type (with hydraulic feed table)

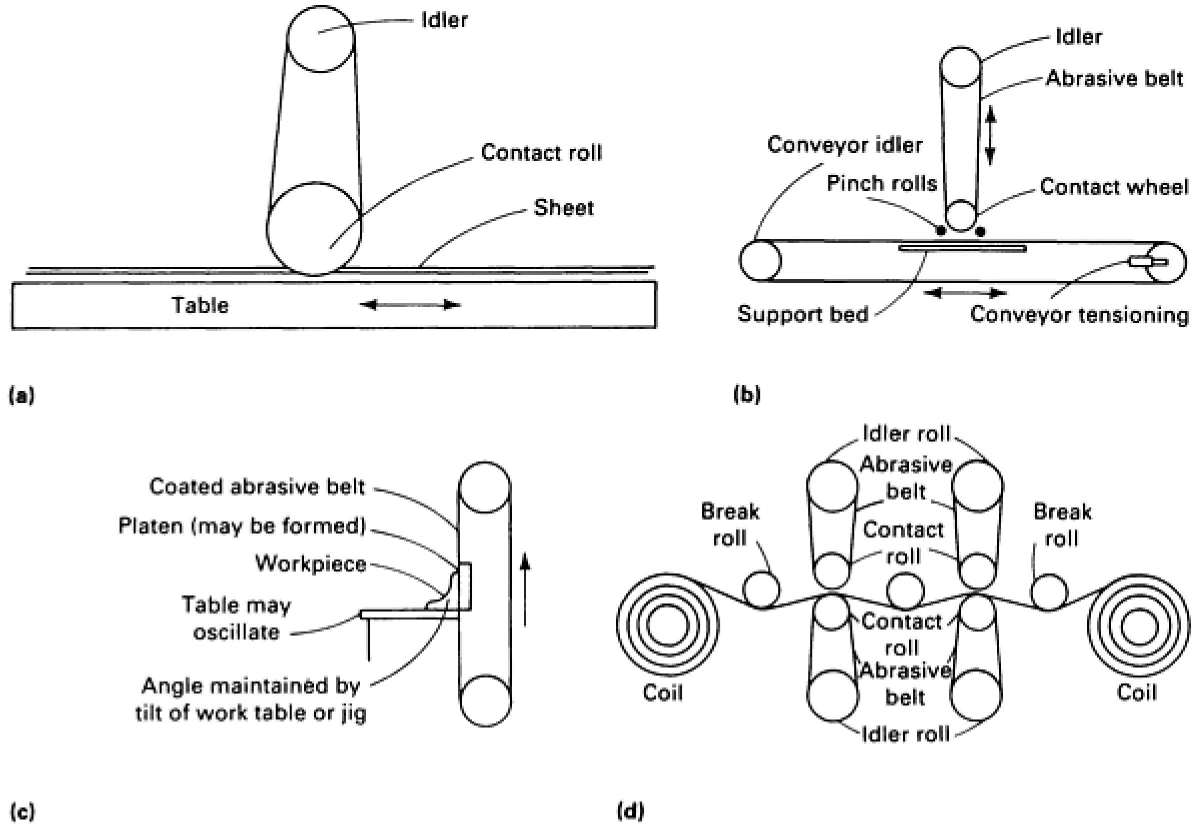


Fig. 15 Schematics illustrating the primary components of coated abrasive precision grinding operations. (a) Sheet dimensioning. (b) Conveyor grinding. (c) Vertical-platen sanding. (d) Coil

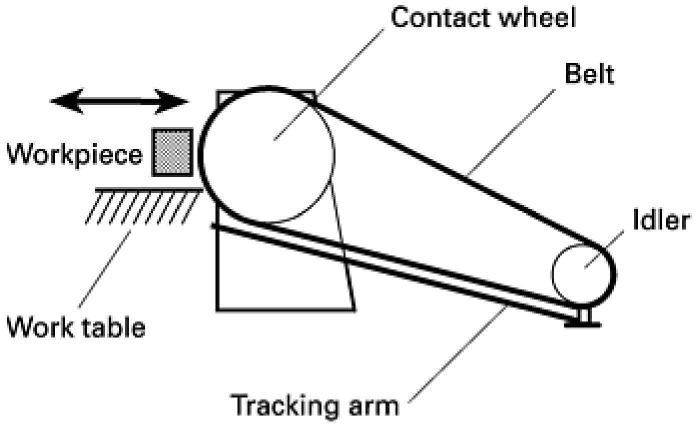


Fig. 16 Schematic of backstand grinder having coated abrasive belts for use in off-hand rough grinding operations

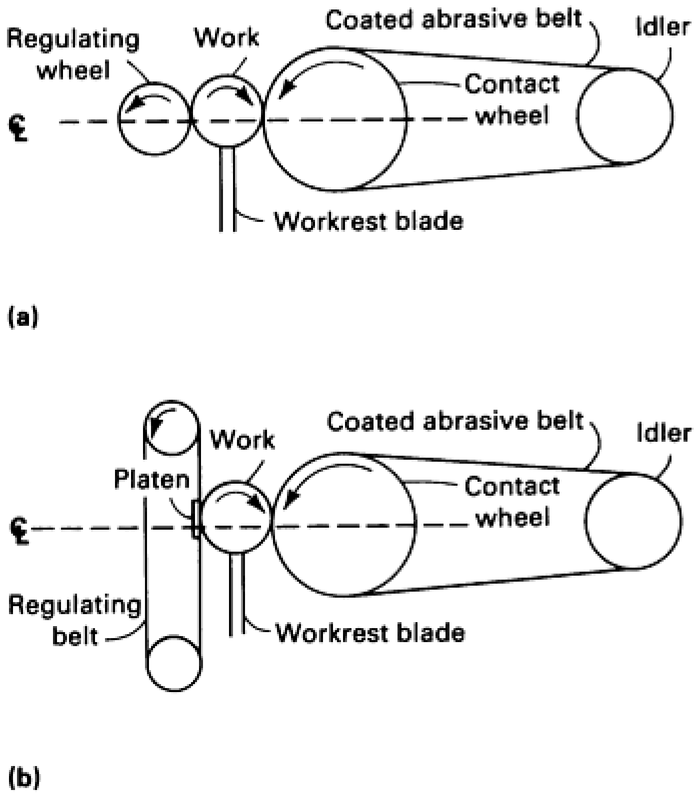


Fig. 17 Schematic of two different coated abrasive centerless grinding setups. (a) Abrasive belt centerless grinder with regulating wheel. (b) Abrasive belt centerless grinder with regulating belt

As in grinding wheel applications, the abrasive belt applications can be manual or make use of mechanical drives. In manual applications, the operator can vary the contact area during use to maximize the material removal rate and minimize the force or effort required. Mechanical means are adapted for large-volume production processes, usually involving components of constant geometry.

Coated abrasives are a composite of three components: backing, adhesive, and abrasive. In general, the backing for a belt is either paper or cloth. Different weights of paper and types of cloth are used, depending on requirements for strength, flexibility, and water resistance. The adhesive is usually resin or glue and is used to bond the abrasive to the backing. It is applied in two coats, with the first layer ("make coat") anchoring the abrasive in place on the backing. The second layer ("size coat") is applied over the abrasive to further strengthen its bond to the backing.

The abrasives most commonly used on coated abrasive belts are aluminum oxide and silicon carbide. Coated products containing CBN or diamond abrasives are beginning to be developed, with unique application for finishing steel components and glass or ceramics, respectively. The abrasive is applied to the backing by electrostatic deposition, then passed through an electric field where an electrostatic force propels it into the resin, while the orientation of each abrasive grain on the backing is controlled. This results in a sharp coated abrasive product containing many exposed, well-oriented cutting points.

An efficient belt grinding operation uses the coarsest grade that produces an acceptable finish. Depending on the objective of an operation, more than one abrasive grade may be needed. When both stock removal and finish are required, a sequence of abrasive grades is used. The coarsest grade is determined by the amount of stock removed and by the type of material. It should be the finest possible grade that still removes stock at an acceptable rate so that no excessively coarse scratches are produced. The finishing grade is determined by final finish requirements. If a number of grit sizes of intermediate grades are skipped, some deep scratches will remain that decrease buffability. In general, more grades can be skipped in the coarser grades and when finishing a softer material. Parts with small contact areas allow more grades to be skipped and require fewer finishing grades because of increased buffability. Table 6 shows the abrasive grades used for a given operation and the approximate number of grades that can be skipped.

Table 6 Abrasion grades for various operations

Operation	Grade range	Condition
Stripping	12-20	Removal of old finishes, rust, and other materials that tend to load belt
Heavy stock removal	24-30-36-40	Used for rapid stock removal and large depths of cut. Skip 1 to 3 grades.
Medium stock removal	50-60-80	Average stock removal and progression from rougher finishes. Skip 2 grades.
Light stock removal	100-120-150	Used in operations requiring minor dimensional changes. Skip 1 or 2 grades.
Finishing	180-220-240	Negligible stock removal. Produces the desired appearance or surface for plating. Skip 0 or 1 grade.
Polishing	(280-320)-(360-400)-(500-600)	Preparation for mirror or near-mirror finishes

In many operations, the surface finish specifications are determined by scratch depth, which is affected by factors such as abrasive grade and type, lubricant, material to be finished, and finishing conditions (e.g., contact wheel and abrasive speed). Figure 18 shows the typical range of surface finishes that can be obtained with a given abrasive grade. Finishes outside this range are used for some applications, so the graph should be used only as a general guideline.

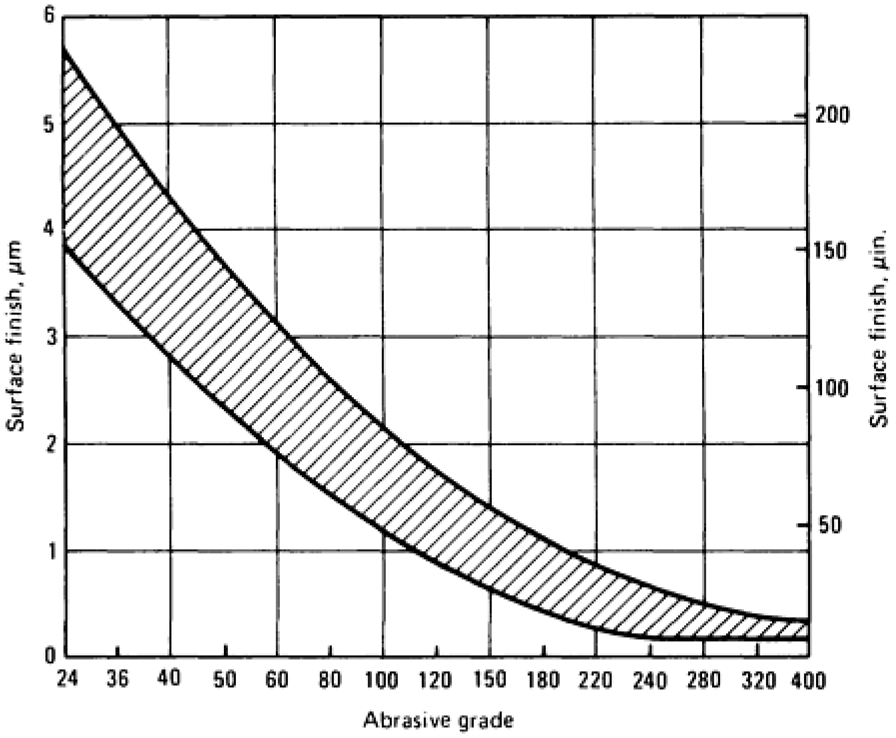


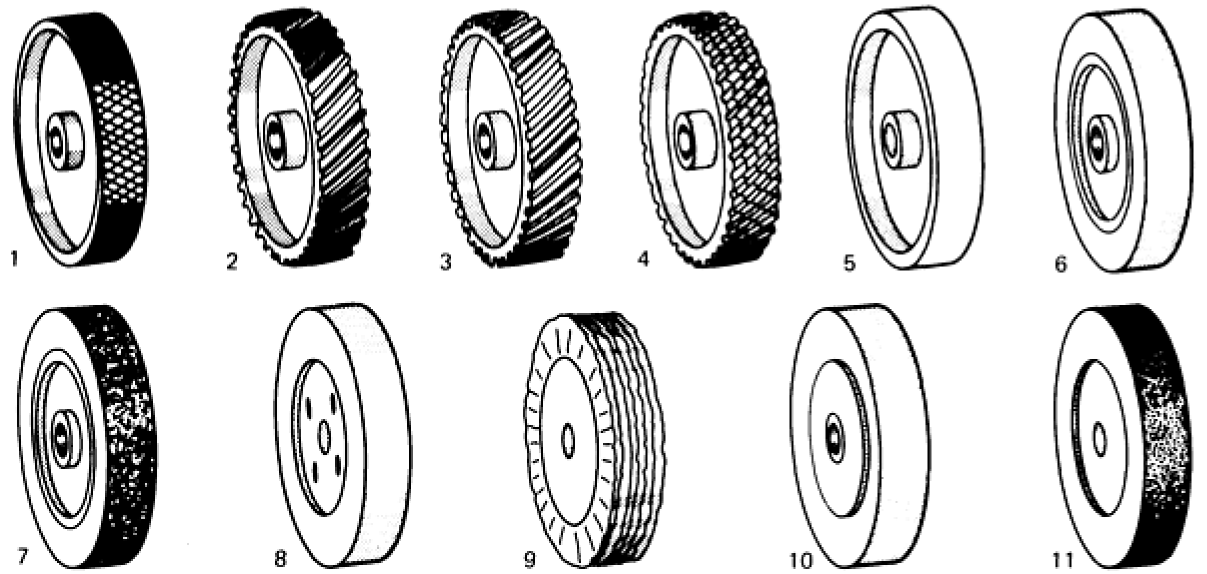
Fig. 18 Surface finishes obtained with varying grades of abrasive belts

Contact wheels over which the abrasive belt rides provide pressure of the belt against the workpiece. Depending on its hardness, the contact wheel can provide either high unit pressure, hard wheel, or low unit pressure, soft wheel. Selection of contact wheel directly affects the rate of stock removal, the ability to blend in polishing, the surface finish obtained, and the cost of the polishing operations.

Although it is possible to operate a contact wheel satisfactorily at speeds from 10 to 50 m/s (2000 to 10,000 sfm), normal operation speeds usually range from 18 to 38 m/s (3500 to 7500 sfm). Table 7 illustrates and describes the principal types of contact wheels and indicates their applicability to various grinding or polishing operations.

Table 7 Characteristics and uses of abrasive belt contact wheels

Wheel	Type	Material	Hardness	Purpose	Characteristics
1	Knurled or spiral grooved[(a)]	Steel	Rockwell C 52 to 55	Heavy grinding	Provides most aggressive action
2	Cog tooth[(b)]	Rubber	70 to 90 durometer	Grinding[(c)]	Fast-cutting, allows long belt life
3	Standard serrated[(d)]	Rubber	30 to 50 durometer[(e)]	Grinding[(f)]	Leaves rough-to-medium surface, excellent life
4	X-shaped serrations[(g)]	Rubber	30 to 60 durometer	Grinding, polishing[(h)]	Flexibility allows entry to contours
5	Plain face	Rubber	20 to 40 durometer[(i)]	Grinding, polishing[(j)]	Allows controlled penetration of abrasive grain
6	Flexible	Compressed canvas	[(k)]	Grinding, polishing[(l)]	Tough and durable
7	Flexible	Rubber-coated canvas	Medium	Contour polishing	Contours well, yet gives substantial stock removal
8	Flexible	Solid section canvas	Soft, medium, hard	Polishing[(m)]	A low-cost wheel with uniform face density
9	Flexible	Buff section canvas[(n)]	Soft	Contour polishing	For fine polishing and finishing, low-cost
10	Pneumatic drum	Inflated rubber	[(o)]	Grinding, polishing	Gives uniform finishes, adjusts to contours
11	Plastic foam	Polyurethane	Extremely soft	Fine polishing	Most flexible, for extreme contours



(a) No. 14 standard face; 4-pitch 2 by 2 mm ($\frac{1}{16}$ by $\frac{1}{16}$ in.).

(b) Land, 5 mm ($\frac{3}{16}$ in.); groove, 14 mm($\frac{9}{16}$ in.); depth, 1.5 mm ($\frac{1}{16}$ in.); cushion, 19 mm($\frac{3}{4}$ in.).

(c) For cutting down projections, such as weld beads, gates, risers, and sprues.

(d) Land, 10 mm ($\frac{3}{8}$ in.); groove, 10 mm($\frac{3}{8}$ in.); depth, 10 mm ($\frac{3}{8}$ in.);cushion, 22 mm($\frac{7}{8}$ in.).

(e) Wheel also may be of dual density, with hard rubber; 60 durometer, at hub, softer rubber, 20 to 40 durometer, at working surface.

(f) For smoothing or blending cutdown projections or surface defects.

(g) Land, 5 mm ($\frac{1}{16}$ in.); groove, 14 mm($\frac{1}{16}$ in.); depth, 8 mm ($\frac{5}{16}$ in.); slit, 13 mm ($\frac{1}{2}$ in.) spaced; cushion, 22 mm($\frac{7}{8}$ in.).

(h) For light stock removal and medium polishing; preferred to standard serrated wheel for softer nonferrous materials.

(i) Softer wheels give better finishes.

(j) For flat surfaces.

(k) Nine densities (very hard to very soft). Hard wheels can remove metal, but more slowly than wheel 2; softer wheels can polish to fine smoothness.

(l) Good for medium-range grinding and polishing. See footnote [k]

(m) Handles all types of polishing, giving uniform results without leaving abrasive pattern on work; adjusts to contours or can be preformed for contours.

(n) Can be widened or narrowed by addition or removal of sections.

(o) Hardness controlled by air pressure

Abrasive belt machines perform grinding, polishing, and deburring operations on bar, strip, coils, blanks, stampings, forgings, die castings, and sand castings. Parts made of metal, plastic, ceramic, wood, or rubber can be handled on this equipment. Any flat surface that requires finishing, sizing, deburring, and descaling can be processed. Parts can be fed against abrasive belt polishing heads by conveyor belts or feed rolls. Conveyor belts can be made from oil-resistant rubber, sponge rubber, or abrasive-coated cloth. Hold-down fingers and cleats are used to hold nonferrous materials for grinding or polishing operations and prevent slippage. Feed rolls are made of steel or rubber-covered steel.

Abrasive belts can be tensioned by mechanical or pneumatic means, and manual or automatic tracking devices are available. Automatic tracking devices are generally used for belts 300 mm (12 in.) or more in width. Manual or automatic adjustments for grinding pressure can be used to suit specific applications. Tandem arrangements of any of the machines mentioned can be made using as many polishing units as are necessary to produce the required successive grit finish in one pass through the machine. Conveyor belt machines can be furnished with an automatic turnover arrangement to polish or deburr both sides of parts. Abrasive belt heads or flap wheels can be mounted on the bottom side of the pass line to permit two-sided simultaneous polishing operations. Flat-surface polishing machines can be equipped for wet or dry finishing. A means for the application of oil spray, oil mist, or other wet polishing media may be provided.

A few of the applications for wide-sheet polishing mills include:

- Extrusion sizing, grinding, and deburring
- Prepolishing of stock before forming
- Polishing sheets to a high-quality satin finish
- Obtaining engineered finishes on stainless steel
- Upgrading finish of commercial cold-rolled stock
- Sizing operations on all types of sheet and coil stock

Sheet-polishing heads can be used as individual units or assembled in tandem arrays. Applications of these heads include prepolishing of carbon steel sheet for plating applications, conditioning of stainless steel coil stock, and polishing of sheet and plate to standard finishes. A broad (2 m, or 7 ft) wheel, angled to the sheet to be buffed, can achieve high degrees of microfinish and reflectivity by allowing the sheet to be transferred by the head or heads in a continuous mode or by having sheets placed individually on a reciprocating conveyor. The heads can be mounted at the top and bottom of the sheet in a pinch roll configuration. With some degree of oscillation, buffing streaks are avoided and uniform fine finish is achieved on both ferrous and nonferrous materials for finishing prior to the sheet's being blanked, stamped, or used full-dimensionally for other purposes.

Applications of Belts. Originally, the use of coated abrasive belts was limited to the finishing of flat surfaces, using straight-face contact wheels. Now that resin bonding of abrasives is practical, it is possible to produce belts with greater flexibility and improved joints. In addition, improvements in polishing machinery have made it possible use of coated abrasive belts for contour polishing operations. The selection of tough, flexible polyester backings also contributes to the ability of coated abrasives to contour polish. Extremely fine-grit abrasive belts are used for lapping and polishing applications. Use of superabrasive belts for ceramics finishing is also an emerging technology.

Polishing and Buffing

Polishing and buffing improve edge and surface conditions of a product for decorative or functional purposes. These techniques are abrading operations, although some plastic working of surfaces may occur, particularly in buffing. Buffing is the use of abrasives or abrasive compounds that adhere loosely to a flexible backing, such as a wheel. Polishing is the use of abrasives that are firmly attached to a flexible backing, such as a wheel or belt.

Polishing operations usually follow grinding and precede buffing. In general, polishing permits more aggressive abrading action than buffing. It has greater capability to modify the shape of a component and has greater definition of scratches. Buffing achieves finer finishes, has greater flexibility, and follows the contours of components.

Polishing and buffing processes are used on most metals and many nonmetals for refining edges and surfaces of castings, forgings, machined and stamped components, and molded and fabricated parts. Traditionally, these processes have been considered a means of developing attractive, decorative surfaces and generating suitable preplate and prepaint surfaces.

Polishing is used to remove or smooth grinding lines, scratches, pits, mold marks, parting lines, tool marks, stretcher strains, and surface defects that adversely affect the appearance or function of a part. Polishing is performed with either a wheel or belt to which an abrasive is bonded. The process causes some plastic working of the surface as metal is removed. The resulting polished surface usually has a finish of 0.4 μm (16 μin.) or less.

Polishing wheels are disks made of materials such as cloth and leather, sewed and/or glued together. The periphery is coated with alternating layers of adhesive and abrasive grain to the desired thickness. The type of material and construction determines the hardness and flexibility of the wheel. Muslin, canvas, leather, sheepskin, felt, and various weaves of cotton are among the materials used. Canvas is usually glued and pressed together, which makes it the hardest of these materials. The solid felt wheel is also hard, but its hardness depends on the density of the felt. Leather and sheepskin can be glued and pressed, machine sewn, or hand sewn to give the flexibility desired. Differences in types of leathers also determine the final effect. A leather strip can be glued to the periphery of a cloth or wooden wheel to combine the hardness of the underlying wheel with the flexibility of the leather.

The two main types of adhesives used are hide glue and silicate cements. Hide glue is the more resilient, but it melts under heavy pressure, must be soaked and made up daily, requires controlled heating between 60 and 65 °C (140 and 150 °F), and must be formulated to the size of the abrasive. Despite these disadvantages, hide glue is popular because it gives the softness, flexibility, or cushion required for certain applications. Silicate cement does not usually melt under heavy pressures when high heats are developed, and it can be used as received from the manufacturer; no heating is required. Silicate cements are formulated to give a range of effects.

The technique and care required to make the polishing or setup wheel can be eliminated by using polishing belts, but in certain applications, polishing wheels cannot be replaced. An obscure or confined area, such as an automobile wheel that is to be plated, is readily polished with a polishing wheel. The cutlery industry and the jewelry industry use polishing wheels and bobs for special effects, in some areas that are difficult to reach, and where the polished finish must be confined to certain areas.

During polishing with setup wheels, efficiency, the quality or results obtained, and cost are most significantly affected by the following operating variables:

- Type and density of the polishing wheel
- Preparation of the wheel before application of adhesive
- Wheel-curing (drying) procedures
- Wheel balancing
- Wheel abuse due to improper use
- Wheel speeds
- Type and grit size of abrasive

Limitations of polishing generally are associated either with part size and shape or with the ability of the process to attain a specific surface finish. A part with hooked edges or sharp projections can cut or snag the polishing belt or wheel. Limitations in terms of surface finishes obtainable are related primarily to the abrasive grit sizes available.

It is relatively simple to polish a part that is small enough to be manually manipulated against a stationary wheel, but it is exceedingly difficult to achieve a uniform finish over a large surface with a traveling wheel. As parts become too small to be manipulated manually, they must be held in jigs and fixtures. At this point, part configuration also becomes a controlling factor, because the complexity of the shape of a part frequently dictates the complexity of the jigs and fixtures required. A simple geometric shape, such as a ball, can be readily polished to a high finish in sizes down to 0.25 mm (0.010 in.) diameter by locating it in a circular groove of appropriate size and allowing it to move in contact with a firm wheel. Very small cylindrical parts can be polished in a similar manner. However, as part configuration becomes more complex, the polishing of small parts becomes increasingly difficult unless a mass finishing method can be used.

Large surfaces can be uniformly finished by affixing the part to a moving conveyor and having a polishing wheel exert even pressure against this component as it is drawn past the polishing head. Pneumatic controls allow automatic polishing equipment to be extremely exact in repeating finish generation or work to be accomplished.

Buffing produces smooth, reflective surfaces. It is the rearrangement and refinement of component scratch and has the ability to level surfaces where the scratch is visible only under high magnification. Buffing is accomplished by bringing a workpiece into direct contact with a revolving cloth or buffing wheel that is charged with a suitable compound. Depending on the type of wheel and compound, substantial stock can be removed, radii can be generated consistently, and smooth, bright, and lustrous surfaces can be produced with precision.

Hard buffing is used to cut down or smooth the surface of a material that may or may not have been polished previously. Buffs used for hard buffing are usually made of cloth with a high thread count (e.g., 86/80). The density of the thread count varies with the requirements of the job. Because hard buffing entails both a cutting action and a plowing action, an aggressive compound is generally used.

Color buffing refines a surface to a very low finish and produces a lustrous, scratch-free condition. Any marks or scratches left on a surface after hard buffing can be removed by color buffing. Color buffs are always softer than buffs used for hard buffing and are made of cloths with a lower thread count (e.g., 64/68). Color buffing compounds must produce a high finish and permit the buffing wheel to shed or throw off the small particles of metal and compound that build up during buffing. If a compound does not provide this shedding action, the buildup of particles forms a solid cutting head, requiring the buff to be raked or cleaned frequently.

Contact Buffing. Most conventional modern automatic buffing equipment is set up for contact buffing. A machine imitates the movement of a manual buffing operation, and densely packed wheels are used, rotating at shaft speeds that are usually higher than 1200 rpm. Because the wheel is very hard when rotating at high speeds, the area covered is relatively small. To increase the versatility of finishing equipment and to maintain more precise control, hydraulic drives for conveyors and for the buffing and polishing heads are readily available. Hydraulic drives facilitate precise control of speed, which can be readily changed when there is a change in the product to be finished. Other developments include high-speed and straight-line indexing conveyors, programmed controls, and three-dimensional fixture manipulation.

Mush buffing is a technique in which a broad wheel is used to cover much larger areas than is possible in contact buffing. Shafts can be up to 3.6 m (12 ft) long, with buffs mounted along the shafts, usually separated with 13 to 75 mm ($\frac{1}{2}$ to 3 in.) of space between each of the buff sections. The wheel itself flexes and envelops the contours of the components being finished. Parts travel across the face of the wheel without precise manipulation of the fixtures. In general, simple rotation or oscillation is all that is required to ensure a uniform finish on component faces. Shaft speeds for mush buffing are almost always much slower than for contact buffing. The slower speed of rotation keeps the working temperature of the buff sections lower, resulting in longer buff life. Productivity is generally considerably higher than with conventional methods. Uniformity and quality of finish are enhanced by the increased flexibility of the slower-speed buffs.

Refinement of the mush buffing process led to the development of modular construction of buffing equipment. Modular conveyors may be assembled from standard carriages mounted on a rigid framework. Modular design of equipment increases both short-term and long-term versatility. The suspended mush buffing heads can be placed inside or outside the conveyor and can be relocated for quick application changes. Hence, a single machine can finish a range of components simultaneously and can then be set up to handle a completely different range of parts, just by changing the positions of heads and component fixtures. When requirements change or production increases, the shape or size of the conveyor can be modified, and more heads of the same or a different type can be added.

Surface Finishes after Buffing. Following are descriptions of the typical surface quality achieved after various buffing operations:

- *Scratch brush finish* shows a combination of coarse lines with a slight underlying luster. This finish was used only on nonferrous metals and has been superseded in practically all cases by greaseless compound. Prior to the development of greaseless compound, the scratch brush finish was produced by a brass wire or nickel-silver wire wheel revolving over a tray. A mixture of water and bran meal was applied liberally over the work being finished and over the wheel. The bran meal provided a slight lubrication.
- *Butler finish* is composed of soft, fine parallel lines produced by a lubricated greaseless compound. This finish is generally found in the silver industry and is classified as dull butler, butler, or bright butler, according to the degree of brilliance achieved.
- *Satin finish* is the equivalent of scratch brush finish. It is a more economical finish to produce and has considerable luster. It is now widely accepted as an excellent finish for consumer products.
- *Colonial finish* is achieved by relieving an oxidized surface, emphasizing the lack of luster adjacent to the relieved area. The finished highlights are satin finished and create an attractive decorative effect against the oxidized background. Articles with raised or embossed designs are often given a colonial finish.
- *Matte finish* is produced by using a sand blast or acid dip, creating on the metal a frosted and nonreflective surface completely free of parallel lines. On metals such as aluminum, the greaseless compound method can produce a comparable finish by eliminating the lubricant and operating at high speeds.
- *Sanded finish* is applicable to wood and plastics and is produced in the same way as a satin finish would be produced on metal. In many cases, this method is used in place of belt sanders for finishing ornamental wood earrings, wood heels, and other irregularly shaped articles.

Nylon wheels are flexible, resilient, and made of abrasive-impregnated nonwoven nylon or another synthetic fiber. Abrasive is dispersed evenly throughout these materials, so that wheel performance remains substantially constant despite wheel wear. In many cases these wheels can be shaped to conform to curved, irregular surfaces. They are water resistant and range from 25 to 2000 mm (1 to 80 in.) in width and from 25 to 400 mm (1 to 16 in.) in diameter. A wide variety of densities and grit sizes are available. Nylon wheels may be used wet or dry or with grinding lubricants, such as waxes, oils, or greases.

These wheels are especially useful for imposing uniform scratch patterns or satin finishes on nonferrous metals, plastics, and wood. They are recommended for various types of blending, as well as for the removal of light surface stains, scale, rust, or old coatings. They are not suitable for the removal of large amounts of stock, deep defects, or surface irregularities, but they are effective in removing burrs and radiusing sharp edges. They operate with speeds ranging from 3 to 33 m/s (500 to 6500 sfm), depending on the specific wheel and application.

When nylon wheels are used to finish flat sheet stock, wheel oscillation is recommended to attain a uniform finish, free of streaks. An oscillation of about 200 cycles/min with 10 mm ($\frac{3}{8}$ in.) amplitude gives good results in a variety of applications. Greater amplitudes, up to 50 mm (2 in.), can be used on steel or other hard metals, but on softer metals, amplitudes greater that 13 mm ($\frac{1}{2}$ in.) are likely to create "snake marks."

Flap Wheels. There are basically two types of metal hub flap wheels: reloadable and throwaway. Either style can be used with coated abrasive materials for polishing and with various types of materials for buffing.

The basic construction of a flap wheel incorporates a metal hub that contains coated abrasive packs or buffing packs. Located around the outer perimeter of the wheel are a specific number of keyhole-shaped slots, and flap wheel packs are inserted into these slots. In polishing and buffing operations, the metal hub conveys the material to the workpiece, presenting a longer-lasting, stronger, and better-balanced tool that imparts a uniform finish from the time the wheel is put on until the packs are completely worn. This is accomplished by continually allowing new grain or buffing fabric to be exposed to the workpiece as the flap wheel packs wear.

Some features of modern flap wheels include contouring the face, slashing the packs, reversing the lead sheet, preoiling the packs, and combining the coated abrasive sheets with materials that cushion the cut. Although flap wheels are ideally used in automatic operations, they are quite effective in manual or off-hand polishing operations.

Abrasive Slurries and Compounds

Most compounds consist of an abrasive that is immersed in a binder carrier. The abrasive serves as the principal cutting medium; the binder provides lubrication, prevents overheating of the work, and firmly cements the abrasive to the wheel face or lapping plates. Binders must not chemically etch, corrode, or mar the metal surface. Abrasive slurries are similar to compounds, except that the percentage volume of the carrier fluid is large, providing fluid flow properties to the slurry.

Abrasive grains generally used with all finishing compounds include:

- Tripoli and/or silica for finishing of most nonferrous materials and plastics
- Fused aluminum oxide for finishing of ferrous products
- Calcined alumina for finishing of ferrous and nonferrous materials
- Red rouge for high coloring or finishing of brass products
- Green chromium oxide flours for high coloring or finishing of nonferrous materials and stainless steel, and for finishing of plastic products
- Silicon carbide or diamond for finishing of ceramics and hard materials such as carbides

All of these materials are used with fatty acids and wetting agents in liquid form and are made to suit all of the cleaning processes that are necessary prior to any plating or anodizing operation.

The action of any individual compound can be altered by increasing or decreasing the particle size of the abrasive or varying the amount and types of lubricant used in the binder. If a more intense cutting action is required of a given compound, the particle size of the same abrasive or the quantity of binder may be increased. Modern compounds use water-soluble binders. The lubricant used in the binder generally has a mineral, animal, or vegetable base.

Types of Compounds. The names of many buffing compounds are derived from the abrasives used in their formulas. The designations of other compounds reflect the type of metal on which they are most commonly used or the function they perform. Several of the more widely used buffing compounds are described in the following paragraphs.

Tripoli compound contains a form of silica, of which there is approximately 75% free or crystalline silica. It has the ability to cut sharply at first and then break down in size, resulting in a finer cut and a higher coloring action. It is used extensively for buffing nonferrous metals, particularly copper, zinc, aluminum, and brass.

Bobbing compounds usually contain some form of coarse silica, such as flint or quartz. These abrasives are considerably harder and sharper than tripoli compounds, and they are used for heavy cutting down and the removal of pits from extruded or cast aluminum and silver alloys.

Cut or cutdown compounds usually contain tripoli for buffing nonferrous metals and fused aluminum oxide abrasives for buffing carbon or stainless steel.

Cut and color compounds combine fast cutdown and coloring operations, sacrificing maximum cutting properties of cutdown buffing and the extra brilliance of separate color buffing. Abrasive mixtures are selected to suit the particular metal being buffed and the desired levels of cut and color.

Color or coloring compounds produce maximum brilliance and freedom from scratch on the buffed piece through the use of a very fine, soft abrasive. Choice of buff hardness, buffing compound, peripheral speed, rate of speed, contact pressure, and buffing time vary with the type of pieces being colored and the degree of luster required by the customer. Very fine, soft, white silica powder, very fine alumina powder with highly lubricated binders, or red rouge is usually used in compositions for coloring precious metals such as silver or gold. Fine alumina with lubricated binders and a minimum of buffing pressure is usually the choice for pewter, thermoplastic and thermosetting plastics, and magnesium and aluminum and their alloys. Fine calcined alumina, chromic oxide abrasives, and lime substitutes are combined with clean

working binders to color nickel, chromium, and zinc. Fine fused or calcined alumina, or combinations of the two, are the abrasives generally used to color carbon and stainless steel.

Stainless steel buffing compounds generally contain fused or unfused aluminum oxide powder or a mixture of both. These abrasives are available in a wide range of particle sizes, hardnesses, and oil-absorbing qualities. The cutting and coloring action obtained depends on the type of aluminum oxide used and the amount of grease binder in the formulation.

Steel buffing compounds generally contain a mixture of fused and unfused aluminum oxides. They provide a sharp cutting action as well as a lustrous finish.

Chromium buffing compounds consist of fine unfused alumina. These abrasives are also used as secondary coloring compounds on stainless steel. They were developed to color buff chromium-plated parts that had been stained or frosted in the electroplating process.

Rouge compounds are prepared from almost pure red iron oxide powder and are intended for finishing the noble metals. Another form is made with green chromium oxide powder for buffing hard ferrous metals to produce an extremely high finish without stock removal.

Emery paste is a grease or tallow stick impregnated with emery. Although it can be used on setup polishing wheels during the breaking-in period, it is used most extensively on tampico brush wheels for producing a light satin or brush finish.

Greaseless compounds are a special variety of compounds that are entirely free of grease binders. The abrasive is blended with water and gelatin glue, then packaged in airtight containers. It should not be exposed to the air for an extended period of time as it becomes dry and too hard for efficient wheel transfer. When greaseless compounds are applied to cloth buffing wheels, a flexible, dry cutting abrasive head is formed. By varying the type of abrasive, a variety of finishes can be obtained, ranging from an almost bright luster to an almost totally nonreflective finish. Applied to loose buffs, greaseless compounds are effective in producing satin finishes or performing light polishing operations. Their cutting action is increased when they are applied to sewed cloth buffs or felt wheels. Because greaseless compounds are completely free of tallows, oils, or waxes, workpieces are left clean and dry and require no subsequent cleaning. The storage temperature of the product should be between 4 and 21 °C (40 and 70 °F) because it is perishable.

Liquid compounds or slurries contain abrasives that are suspended in a liquid binder carrier. The abrasives are identical to those used in solid bar compounds. Liquid compounds are applied to the buff or the work surface by means of gravity feed, spraying, brushing, or dipping. Liquid compounds are preferred for large-volume production on semiautomatic or automatic buffing equipment. Their advantages are that:

- They reduce direct labor costs, because less time is involved in applying or replacing compounds.
- They reduce waste of buffing compound, because they can be applied in small quantities with manual or automatic controls and leave no unusable waste.
- They provide a wider range of cutting and coloring characteristics because they can be formulated from a wider range of grease binders.
- They extend buff life by wetting and penetrating the buff to a greater depth, by maintaining an optimum amount of buffing compound on the surface of the buff at all times, and by permitting a cooler buff operating temperature.
- They saponify and emulsify faster than bar compounds and therefore are less likely to back-transfer on the workpiece or to set up solidly in crevices or recesses. Thus, they are easier to remove in subsequent cleaning operations.
- They are formulated precisely to meet the requirements of a specific application. Unlike bar compounds, they are not limited by the need to form a bar that is physically strong enough to survive application shock

Lapping

Lapping is the process of finishing work materials by applying a loose abrasive slurry between a work material and a closely fitting surface, called a *lapping plate.* When loose abrasive is used to machine the work material, it may slide, roll, become embedded, or do all three, depending on the shape of the abrasive grain and the composition of the backup surface.

Rolling Abrasives. Lapping takes place when abrasive grain entrained in a liquid vehicle, often known as *slurry,* is guided across the surface to be lapped and is backed up by a lapping plate. Because the abrasive grains used for lapping have sharp, irregular shapes and each grain is backed up by a lapping plate, when a relative motion is induced and pressure is applied, the sharp edges of the grains are forced into the workpiece material to be lapped and either make an indentation or cause the material to chip away microscopic particles. Even though the abrasive grains are irregular in size and shape, they are used in large quantities, so the cutting action takes place continuously over the entire surface of a workpiece. With regard to the movement of the abrasive grains, special importance has to be assigned to the liquid vehicle.

Sliding Abrasives. The initial conditions for lapping with sliding abrasives are similar to those for lapping with rolling abrasives. However, because the abrasive grains are flat or platelike in configuration, they simulate tiny scrapers. The exact movement of the abrasive grains has not been established; however, the platelike abrasive grains are believed to stack on top of each other, somewhat like tipped-over dominoes, providing many cutting edges to machine away the surface being lapped. The direction of cut is constantly shifted by the constantly changing direction of movement of the workpieces against the backup lapping plates, so that all edges of the abrasive grains are used.

With both rolling and sliding abrasive processes, the abrasive grit mixed with water vehicle is carefully metered and fed automatically to the work area to enable a uniform cutting action.

Charged Plate Abrasives. An early form of lapping, still used for some applications, utilizes embedding of abrasive in the lapping plate or tool. The abrasive grains that are doing most of the work become embedded and act as microscopic scraping tools. These abrasive grains eventually dull or break and are replaced by fresh grains, which are added periodically by hand or from an abrasive paste that works up from slots in the lap plate. The large abrasive grains that become embedded provide the most aggressive lapping action when a relative motion takes place between the workpiece and the lapping plate. As these larger grains are worn down or break down, the smaller grains start to embed and work. The cutting action of a charged plate abrasive is actually a combination of rolling, sliding, and embedding abrasive processes.

Most lapping plates used for this kind of processing have grooves in a waffle pattern and use a paste form of the lapping compound. The paste can be used as-purchased, or it can be mixed with an oil to the consistency of a heavy cream. The grooves hold the lapping compound, which works its way out to keep the lap plate lubricated and provide a recharging effect on the lapping surface. This type of lapping is more labor intensive than the two systems described above and requires the operator to manually apply the proper amount of compound. The cutting action changes as the abrasive grains are used up, thus requiring more operator attention.

Lap Plate Materials. The most commonly used material for making laps is cast iron, which has a special close-grain microstructure that has no porosity or other defects to affect the lapping action. Cast iron is very versatile and can be used for rolling abrasive, sliding abrasive, and embedding abrasive applications and for polishing with hard abrasives. The close-grain iron has the unique ability to grip the abrasive grains and make them roll or shave effectively (as in the case of the platelike aluminum oxide), giving them a foothold to work against the workpiece efficiently.

Another material sometimes used for the lapping plate (wheel) for one-wheel, single-sided flat lapping machines is made of a steel alloy hardened to 60 HRC. This plate is reported by the manufacturer to resist embedding of the rolling abrasive grains for the purpose of obtaining a deeper indentation of each working abrasive grain into the workpiece. A high pressure is applied to the workpiece, and a generous amount of abrasive slurry is fed to the lapping area to prevent the workpieces from making extremely close contact with the lapping plate.

Other materials, used less frequently, include nodular iron, aluminum, and nonmetallics such as granite.

Lapping Vehicle Fluids. Water-based vehicles are commonly used for lapping. Oil is also a good vehicle, but it is often objectionable because of its tendency to penetrate into the pores of some materials. In addition, oil is expensive to purchase, and its disposal is difficult and expensive because it is now classified as a hazardous waste.

The purpose of any vehicle is to carry the abrasive grains and position them to work most efficiently. The vehicle also lubricates the surfaces and carries away the abraded material removed from the workpieces. To prevent rust to the machine components, inhibitors are often added to water-based vehicles. Depending on the equipment, the vehicle is sometimes also depended on to carry away heat generated by the lapping process.

Suspension agents are occasionally added in order to prevent settling of the abrasive. These agents do not necessarily improve the actual lapping action. A variety of methods can be used to keep the abrasive in suspension with minimal negative effect at the area where the machining takes place.

Lapping Process. When lapping takes place on one side of the work material against a lapping plate, it is called *single-sided lapping.* If the work is held between two parallel lapping plates and the abrasive finishes both sides of the work simultaneously, the process is called *double-sided lapping.* Sometimes cylindrical components such as piston pins are finished between two parallel laps. Double-sided flat lapping offers the following advantages:

- Two sides of a workpiece can be machined in the time required to machine one side.
- A large number of workpieces can be produced simultaneously.
- Nonmagnetic material can be held, from plastic to diamond.
- It is the best available method to obtain close tolerances for flatness, parallelism, and size.
- Removing stock from both sides of a workpiece simultaneously helps to relieve the internal stress of the workpiece, thus making it easier to achieve flatness.
- The simple workholder design, with no need to clamp or rigidly hold the workpiece, eliminates stresses in the workpiece and thus improves tolerances for flatness, parallelism, and size.
- Accuracy with double-sided lapping is achieved by using flat lap faces and a freefloating top wheel. No critical machine alignment, precision high-speed spindle bearing, or accurately machined sliding ways are involved.
- The workpiece is exposed to minimal stress and surface damage, because lapping generates no heat.
- The cut rate is uniform and repeatable. No dulling of the abrasive takes place, because fresh sharp abrasive particles are fed to the lapping area continuously during the processing cycle.
- Operating costs are often lower because of less handling, higher efficiency, and the feasibility of combining machining operations.

Ultrasonic Machining

In ultrasonic machining, electrical energy is converted into mechanical motion. The linear motion is typically only 0.025 mm (0.001 in.), but at a rate of 20 kHz. The low-amplitude vibration is acoustically transmitted to a toolholder and specially designed tool. When combined with an abrasive slurry, the workpiece material is microscopically ground away, and the machined area becomes a mirror or counterpart of the vibrating tool. Ultrasonic machining is nonthermal, nonchemical, and nonelectrical. Therefore, no change takes place in the metallurgical, chemical, or microstructural properties of the workpiece. Although it can cut any material, ultrasonic machining is most effective on materials harder than 40 HRC.

The ultrasonic motion is produced by the combination of an electronic generator coupled to a transducer package (magnetostrictive or piezoelectric). The generator converts typical line voltage into the voltage and frequency required to energize the transducer coupled to the generator. The transducer is connected to a transmitting connecting body. The physical size is designed to resonate naturally at the same frequency as the electric current. A threaded stud is used on the end of the connecting body to connect the toolholder. Figure 19 shows an ultrasonic transducer and toolholder assembly.

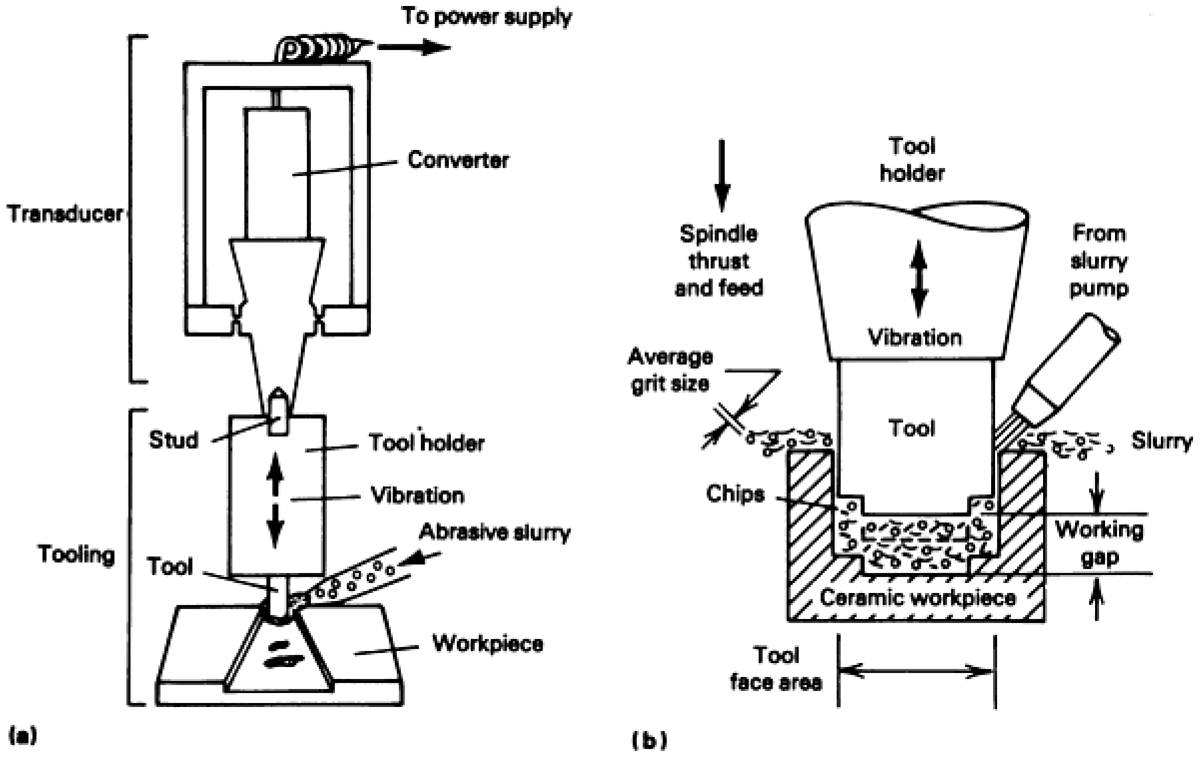


Fig. 19 Schematic showing primary components of a typical ultrasonic machining installation. (a) Transducer assembly coupled to tooling assembly of unit. (b) Closeup view of tooling assembly being used to machine a ceramic

Ultrasonic machining is frequently used to provide faster deliveries and to lower tooling costs for the machining of ceramics. When changes are required during the early design stages, alternatives can be made quickly and economically through the application of impact grinding.

Frequently, ultrasonic machining provides the only method that is capable of machining oddly shaped cuts or shapes in hard, brittle material. Sharper radii and tighter tolerances are also process advantages in some applications. Because of its nonthermal characteristics, ultrasonic machining produces virtually stress-free machined surfaces. An ultrasonic assist added to a rotating tool enhances material removal rates, finish capabilities, and overall drilling efficiency. Rotary ultrasonic machining uses a diamond-plated drill and is water cooled because the diamond-impregnated abrasive provides the cutting edge.

Rotary ultrasonic machining can be used for milling, drilling, threading, and grinding applications. However, its use is limited to round tool configurations.

Abrasive Jet Machining

Conventional abrasive jet machining is the use of abrasive-gas jets to propel particles against a surface and remove the material from that surface via particle impact and shear. Typically, abrasives in quantities up to 0.05 kg/min (0.1 lb/min) are propelled through a nozzle at inlet pressures ranging from 170 to 860 kPa (25 to 125 psi) in a gas (nitrogen or air) medium. Outlet velocities are generally supersonic, and the volume of material removed varies as particle velocity is raised to a power between 2 and 3. Sand blasting and deburring are the two most common applications for abrasive jet machining. Material removal rates can be enhanced by increasing the inlet pressure (experiments up to 12 MPa, or 1.8 ksi, have been carried out) and by optimizing nozzle design. However, difficulties in controlling shock-laden jet structure and particle distribution within the jet make this process impractical for precision machining. An extremely high noise level (>85 dB) is another problem.

Abrasive Waterjet Cutting. High-velocity water can be used to entrain and accelerate abrasive particles. Unlike gas jets, waterjets can be confined to a small diameter without spreading, and they can accelerate particles to desired

velocities in a relatively short distance. In addition, relatively high abrasive mass flow rates (1.4 to 1.8 kg/min, or 3 to 4 lb/min) can be easily accommodated. The result is an extremely high-energy jet that can easily cut through a solid steel plate more than 102 mm (4 in.) thick.

In *abrasive slurry jets*, a thin slurry mixture of abrasive and water is directly pumped to a high pressure and then passed through a nozzle to form the jet. A slurry jet is more efficient because energy losses due to mixing and particle collision are much reduced. In addition, high abrasive loading can be readily achieved. However, other problems easily outweigh these advantages. Pump and component life is greatly reduced, and uniform mixing of the slurry is a problem. A continuous-batch, lower-pressure (20 to 105 MPa, or 3 to 15 ksi) system has recently been introduced that is designed primarily for portable applications.

Abrasive flow machining is a novel technique in which copious amounts of an abrasive compound (whose viscosity is between that of a compound and that of a slurry) is applied between the work material and a closely fitting mandrel. The abrasive "fluid" removes and sizes the work material as it is "extended" on the surface being finished. Some of the applications of abrasive flow machining are finishing of dies and molds, finishing of jet engine components, and cutting or trimming of sheet metals.

System Concepts

The key results of successful abrasive finishing or machining are improvements in:

- Surface quality
- Retained strength
- Tolerances/finish
- Production rate
- Cost per part
- Product performance

These results are affected by four categories of factors. Following is a list of these factors and some of the variables that influence them:

Machine tool factors

- *Design:* rigidity, precision, dynamic stability
- *Features:* controls, power/speed, slide movements/axes, truing and dressing equipment
- *Coolant:* type, pressure, flow, filtration system

Work material factors

- *Properties:* mechanical, thermal, chemical, abrasion resistance, microstructure
- *Geometry:* wheel-part conformity, access to coolant, shape/form required
- *Part quality:* geometry, tolerances, consistency

Wheel selection factors

- *Abrasive:* type, properties, particle size, distribution, content/concentration
- *Bond:* type, hardness/grade, stiffness, porosity, thermal conduction
- *Wheel design:* shape/size, core material, form or profile

Operational factors

- *Fixtures*

- *Wheel balancing*
- *Truing, dressing, and conditioning:* techniques, devices, parameters
- *Grinding cycle design*
- *Coolant application*
- *Inspection methods*

Regardless of the choice of variables in the four input categories, for every abrasive machining process it is possible to visualize four interactions between the abrasive product and the work material (Fig. 20):

- Abrasive/work interaction
- Chip/bond interaction
- Chip/work interaction
- Bond/work interaction

Of these, the abrasive/work interaction is the most critical, analogous in many respects to machining processes with cutting tools (Fig. 21). The interactions between the abrasive product and the work material may be categorized as *cutting* (material removal process), *plowing* (material displacement process), and *sliding* (surface modification process) (Fig. 20). Every abrasive machining process is an effort to balance cutting (surface generation) and plowing/sliding (which controls the characteristics of the generated surface).

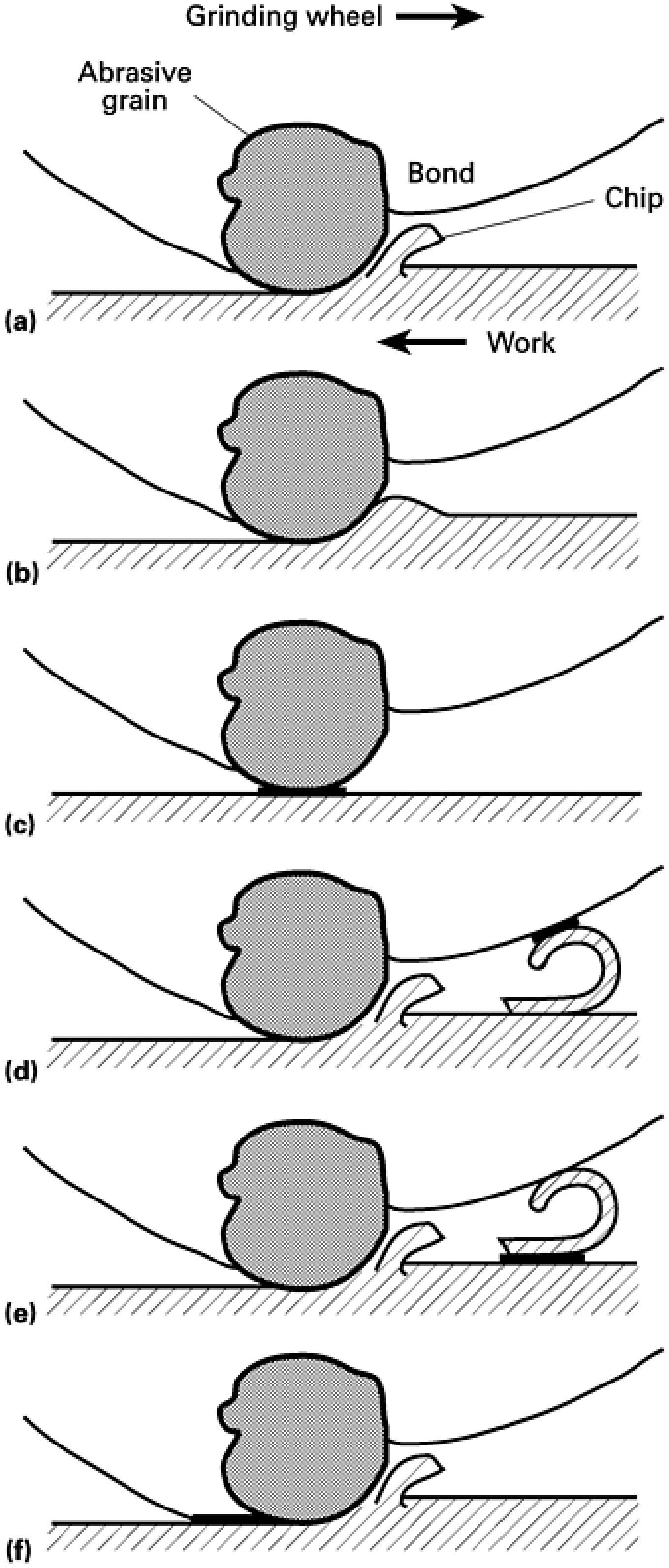


Fig. 20 Interactions in the grinding zone. (a) Abrasive/work cutting (material removal process). (b) Abrasive/work plowing (material displacement process). (c) Abrasive/work sliding (surface modification process). (d) Chip/bond sliding. (e) Chip/work sliding. (f) Bond/work sliding. See text for details.

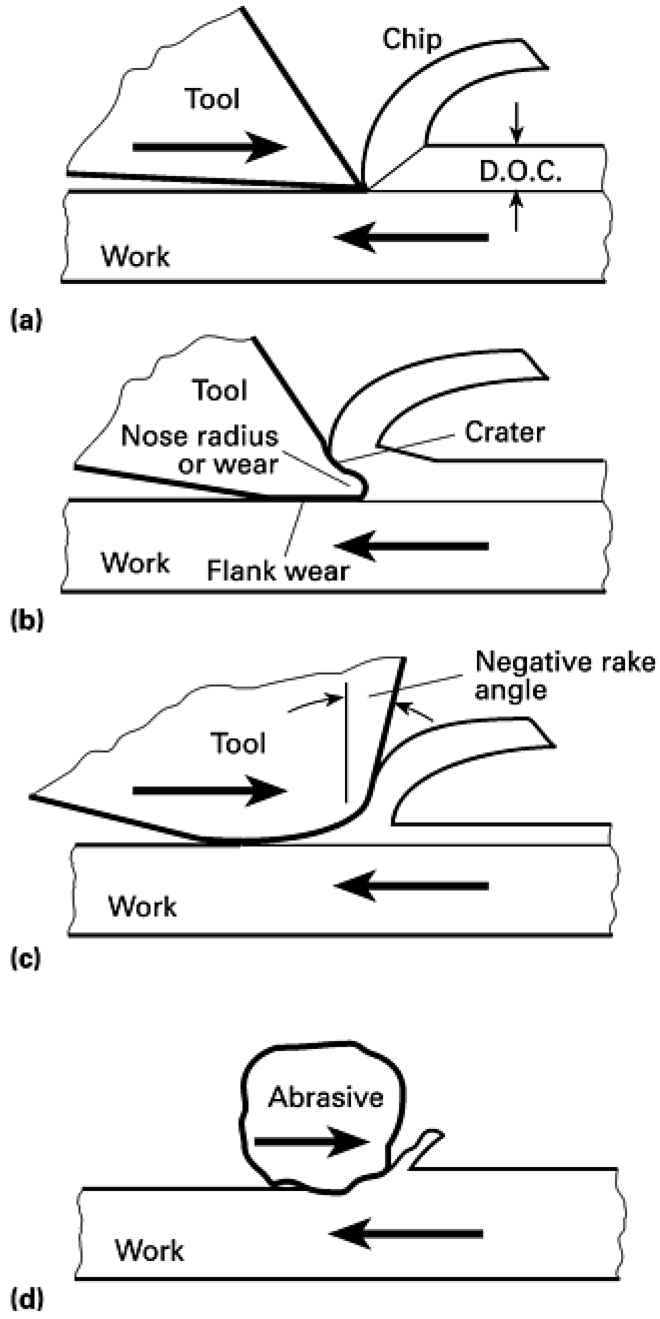


Fig. 21 Schematics of cutting and abrasive "machining" processes. (a) Ideal process. (b) Practical process. (c) Modified processes (diamond turning). (d) Abrasive process

Thus, every abrasive machining process can be thought of as an input/output process with defined microscopic interactions of cutting and tribological aspects of plowing and sliding. These interactions can be measured or monitored using macroscopic process variables such as force, power, and temperature. These result in certain technical outputs, and based on the rules of manufacturing economics, these in turn result in economic or system output. Figure 22 is a representation of the *systems approach* and illustrates the use of the principles of machining and tribology to manage and/or improve abrasive machining processes. Details of the systems approach can be obtained from the references to this article.

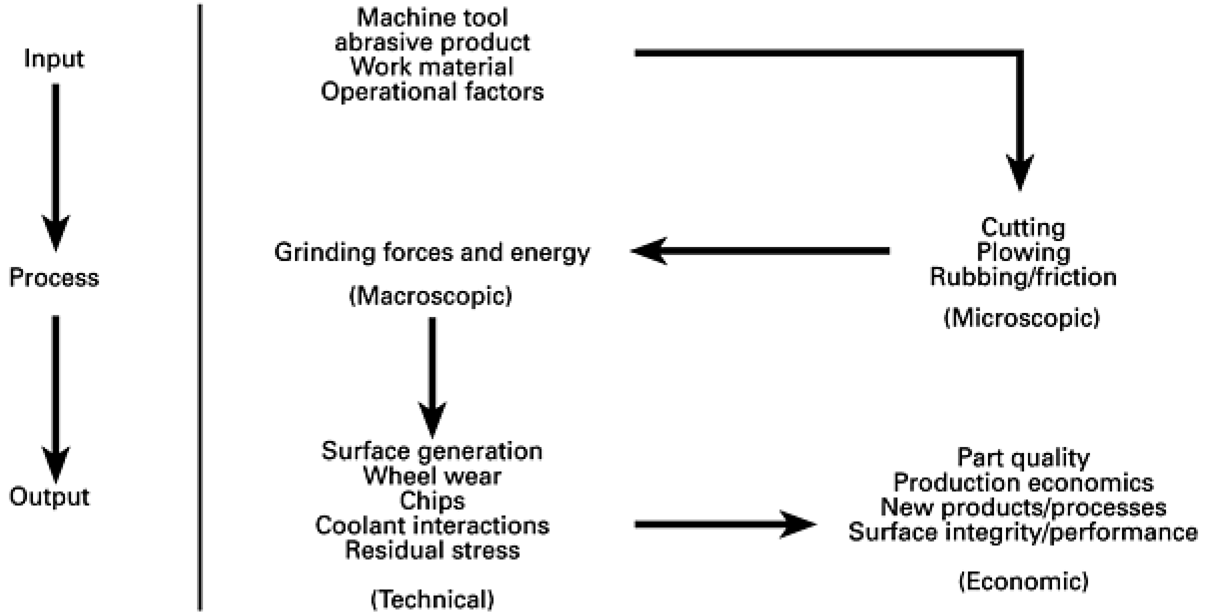


Fig. 22 A systems approach for abrasive finishing processes

The four interfaces in the grinding zone,listed above, may be elaborated as shown in Fig. 20. The presence of coolant or other liquids influences the nature of these sliding interactions. From this point of view, every abrasive finishing process becomes a situation of maximizing the cutting action of the abrasive (Fig. 20a) and minimizing all the sliding or tribological interactions (Fig. 20b to f):

- Minimizing abrasive/work plowing (Fig. 20b) implies proper choice of abrasive/work combination, appropriate size or shape of abrasives, and suitable chip thickness.
- Abrasive/work sliding (Fig. 20c) is minimized when the abrasive used is self-sharpening and wear flats are not generated in the abrasive during setup or truing.
- Chip/bond sliding (Fig. 20d) is minimized by suitable selection of bond/work combinations. Changing coolant, porosity in the bond, or lubricants in the bond matrix are other means of reducing this interaction.
- Minimizing chip/bond sliding has the complementary effect of simultaneously reducing chip/work sliding (Fig. 20e). From the principles of tribology, the sliding interaction between like materials has the highest coefficient of friction; hence, a poor combination must be avoided at all costs. In practice, this simple principle is often missed or ignored, resulting in high grinding forces, extensive abrasive product wear, or poor work surface quality.
- Bond/work sliding (Fig. 20f) is generally minimal when porous abrasive products are used or when vitrified or resin bond is used. However, they are very pronounced when metal bond abrasive products are used. This interaction becomes critical when fine abrasive grits are used or during finish grinding processes, when the abrasive exposure is deliberately small and the bond matrix is very close to the work surface.

The cutting action can be maximized using the principles of machining described in the article "Finishing Methods Using Defined Cutting Edges" in this Volume.

Managing sliding or tribological components while maximizing the cutting component determines whether finishing is rough, precision, or high-precision. For instance, rough finishing processes minimize the tribological components as much as possible. Precision finishing processes minimize the tribology during the rough grinding portion of the cycle and selectively use them during the semifinish and finish grinding portions of the cycle to achieve the desired surface finish or similar surface features. High-precision processes, such as lapping and polishing, depend entirely on the tribological components to achieve the desired results of surface finish, surface texture, luster, and so on.

The results of both cutting and tribological interactions are surface generation, surface deformation, or mechanical-to-thermal energy conversion. Maximizing the cutting component and minimizing tribological interactions are often associated with minimum use of forces or energy. Coolants dissipate the thermal energy to minimize the heat dissipation through the work material, if it affects the integrity of the parent material.

All of the above observations are true for a wide range of abrasive machining processes, independent of the work material type. Hence, the science of grinding may be expressed as simultaneous manipulation of four categories of inputs (i.e., machine tool factors, work material factors, wheel selection factors, and operational factors) to maximize the tribological components with the minimum force and at the minimum expenditure of energy. The balance between cutting and tribological components may depend on both technical and economic considerations. When all four categories of inputs are varied simultaneously, the benefits achieved are quantum improvements. If only one category is manipulated, the results generally are small or incremental in nature. When the microscopic interactions are not understood or considered, abrasive finishing processes are reduced to empirical and statistically managed operations, with extreme cost and quality penalties.

Nonabrasive Finishing Methods

K.P. Rajurkar, Jerzy Kozak, and Arindam Chatterjee, Nontraditional Manufacturing Research Center, University of Nebraska-Lincoln

Introduction

NONABRASIVE FINISHING METHODS are processes in which the surface generation occurs with a very little or insignificant amount of mechanical interaction between the processing tool and the workpiece surfaces. These processes are classified in general as the nontraditional or unconventional machining processes. In these processes, chemical, electrical, or thermal actions, or a combination, are used for metal removal. Nontraditional processes include electrochemical machining (ECM), electrodischarge machining (EDM), and laser beam machining (LBM). The inherent nature of ECM and EDM makes them ideal for stock removal as well as finishing operations. The same is not true of LBM at the present time. Therefore, this article provides a brief review of ECM and EDM and their role in finishing operations. More detailed discussions of equipment and process characteristics appear in *Machining,* Volume 16 of the *ASM Handbook.*

Electrochemical Machining

ECM consists basically of the electrochemical dissolution of the surface metal of a workpiece by conversion of metal to its ions by means of an electric current. The whole process is accomplished in an electrolytic cell by applying a positive (anodic) potential to the workpiece and a negative (cathodic) potential to the tool used to shape the workpiece. ECM can be used for shaping, finishing for improving the quality of the surface, deburring, and radiusing. One kind of ECM is electropolishing. Figure 1 shows the various schematics for machining different geometries using ECM.

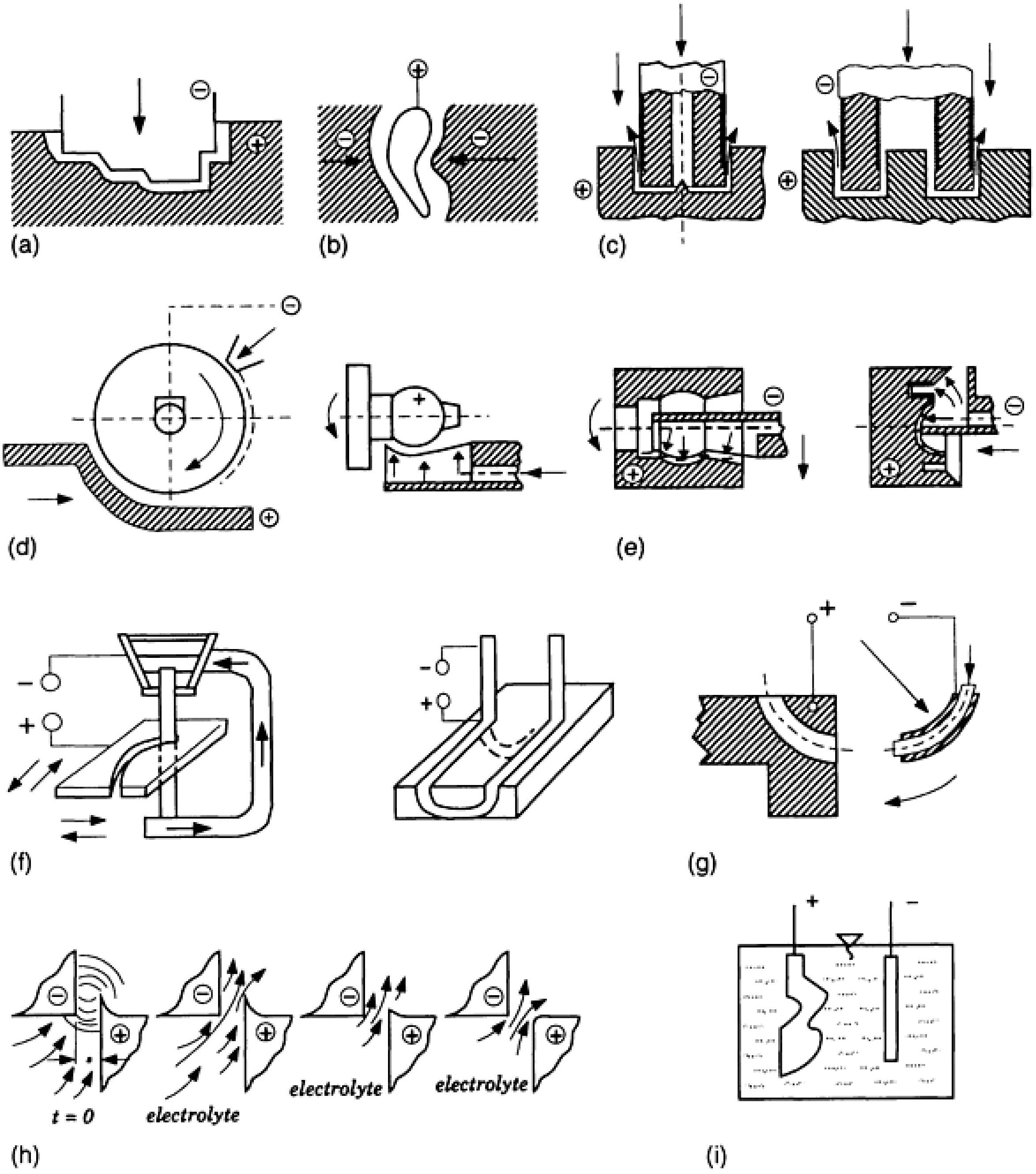


Fig. 1 Schematics of electrochemical machining (ECM) operations. (a) Die sinking. (b) Shaping of blades. (c) Drilling. (d) Milling. (e) Turning. (f) Wire ECM. (g) Drilling of curvilinear holes. (h) Deburring and radiusing. (i) Electropolishing

The rate of material removal in ECM is governed by Faraday's law, since it is a function of current. The primary variables that affect the current density and the material removal rate are:

- Voltage
- Feed rate
- Electrolyte conductivity
- Electrolyte composition
- Electrolyte flow
- Workpiece material

The voltage across the gap influences the current and the material removal rate and is controlled in most ECM operations. However, for a constant voltage, the current also depends on the electrical resistance of the cutting gap. Resistance is much more difficult to control because it depends on the conductivity of the electrolyte and the distance across the gap.

The feed rate, or penetration rate, is also controlled in most ECM operations. At a constant voltage, the gap is inversely proportional to the feed rate. The distance across the frontal gap is a function of feed rate because, as the cathode is fed into the workpiece at a higher rate, the gap closes, causing resistance to drop. As resistance drops, amperage increases; therefore, machining rate also increases until an equilibrium is reached. At slower feed rates, the material removal rate decreases as the gap increases because the cathode is not keeping up with the workpiece surface. As the gap increases, the resistance rises and amperage drops. Frontal gaps are usually between 0.1 to 0.8 mm (0.005 to 0.030 in.), and side gaps, in the case of drilling, are about 0.5 to 1.3 mm (0.020 to 0.050 in.).

The feed rate also varies directly with the current. For example, a hole machined at 2.5 mm/min (0.100 in./min) at 10 V and 1000 A would require 2000 A if the feed were increased to 5.0 mm/min (0.200 in./min). This would also require a potential of about 20 V and would increase power consumption ($V \cdot I$) from 10 to 40 kW.

The feed rate also depends on the application. Typical feed rates for different ECM operations on Inconel 718 are:

Operation	Feed rate	
	mm/min	in./min
Round holes (blind)	2.2	0.085
Simple cavities	2.2	0.085
19×10^3 mm^2 (30 $in.^2$) faces	1.3	0.050

Accurate estimates of feed rates usually require pilot testing in the desired ECM configuration.

Electrolyte conductivity also affects resistance across the gap. Increasing the concentration of an electrolyte causes conductivity to rise, which causes a decrease in resistance. Temperature increases of the electrolyte also increase conductivity. Therefore, electrolyte concentration and temperature must be controlled.

Electrolyte composition directly influences conductivity, material removal rates, and surface characteristics. The parameters used for a given application may not yield the same ECM results if a different type of electrolyte is used. The normal development of an operation usually begins with the selection of the correct electrolyte. The other parameters and the cathode are then adjusted to obtain the desired result.

Electrolyte flow rate is also a factor in ECM process control. The temperature increase of the electrolyte passing through the gap is dependent on the flow rate. In addition, the rate at which hydrogen bubbles are carried away is thought to influence conductivity. Pressure control is the method of controlling flow rate (especially when a centrifugal pump is used). The flow rate also affects the level of turbulence of the electrolyte as it passes through the gap, and this influences the surface finish. The flow rate must also be great enough to remove machining byproducts (sludge).

The workpiece material also affects the material removal rates. Theoretical removal rates for various metals are listed in Table 1. These removal rates are derived from Faraday's Second Law, which states that 1 Faraday (96,494 coulombs or ampere seconds) will liberate 1 g equivalent weight of a substance, or its atomic weight divided by the valence. For example, the gram equivalent weight of iron is the atomic weight divided by the valence of the dissolved iron, or 56 divided by 2 equals 28. Thus, 28 g of iron will dissolve during the passage of each Faraday of electricity. Table 1 lists the theoretical metal removal rates at 1000 A of current flow.

Table 1 Theoretical removal rates in electrochemical machining

Metal	Valence	Density		Removal rate (1000 A current, 100% efficiency[a])			
				Mass		Volume	
		g/cm^3	$lb/in.^3$	kg/h	lb/h	$mm^3 \times 10^3/min$	$in.^3/min$
Aluminum	3	2.7	0.098	0.34	0.74	2.1	0.13
Beryllium	2	1.9	0.067	0.17	0.37	1.5	0.09
Copper	1	9.0	0.324	2.37	5.22	4.4	0.27
	2	9.0	0.324	1.18	2.61	2.1	0.13
Iron	2	7.9	0.284	1.04	2.30	2.3	0.14
	3	7.9	0.284	0.69	1.53	1.5	0.09
Magnesium	2	1.7	0.063	0.45	1.00	4.4	0.27
Molybdenum	3	10.2	0.369	1.19	2.63	2.0	0.12
	4	10.2	0.369	0.89	1.97	1.5	0.09
	6	10.2	0.369	0.60	1.32	1.0	0.06
Nickel	2	8.9	0.322	1.09	2.41	2.1	0.13
	3	8.9	0.322	0.73	1.61	1.3	0.08
Niobium	3	8.6	0.310	1.16	2.55	2.3	0.14
	4	8.6	0.310	0.87	1.92	1.6	0.10
	5	8.6	0.310	0.69	1.53	1.3	0.08

Tantalum	5	16.6	0.600	1.35	2.98	1.3	0.08
Titanium	3	4.5	0.163	0.59	1.31	2.1	0.13
	4	4.5	0.163	0.45	0.99	1.6	0.10
Tungsten	6	19.3	0.697	1.14	2.52	1.0	0.06
	8	19.3	0.697	0.86	1.89	0.8	0.05
Commercial alloys							
4340	. . .	. . .	. . .	. . .	. . .	2.18	0.133
17-4 PH	. . .	. . .	. . .	. . .	. . .	2.02	0.123
A-286	. . .	. . .	. . .	. . .	. . .	1.92	0.117
M-252	. . .	. . .	. . .	. . .	. . .	1.80	0.110
René 41	. . .	. . .	. . .	. . .	. . .	1.77	0.108
U-500	. . .	. . .	. . .	. . .	. . .	1.80	0.110
U-700	. . .	. . .	. . .	. . .	. . .	1.77	0.108
L-605	. . .	. . .	. . .	. . .	. . .	1.75	0.107

(a) It is not always possible to predict the valence at which some metals will dissolve nor how much current will flow through the gap. Also, practical factors, such as the shape of the electrode, can limit current flow.

Removal rates for a given current are, of course, less than the theoretical limit, and variations in temperature, metallurgy, and electrochemical reactivity of the electrolyte affect the metal removal rate. The most accurate method of determining removal rates is by empirical testing.

The electrical current in a particular application is determined by the current density and the area of the gap between the anode (wheel) and the cathode (workpiece). Current density most often depends on the material being processed, although it is also affected by gap distance and voltage. To obtain maximum removal rates, the area should be as large as possible so that it will draw greater current.

ECM Equipment

Figure 2 shows a schematic representation of the ECM system for finishing of a die or other complex shapes. The major components include the workpiece, cathode tool, electrolyte, power supply, and electrolyte circulating and purification system. A low voltage (8 to 30 V) is normally applied across the electrodes. A small gap (0.2 to 1 mm) is maintained

between them, producing a current density of the order of 10 to 100 A/cm^2 (Ref 1, 2, 3). The electrolyte is forced through the small gap between the cathode tool and the anodic workpiece with velocities of 5 to 30 m/s (15 to 100 ft/s). The electrolyte movement flushes away the debris removed from the workpiece.

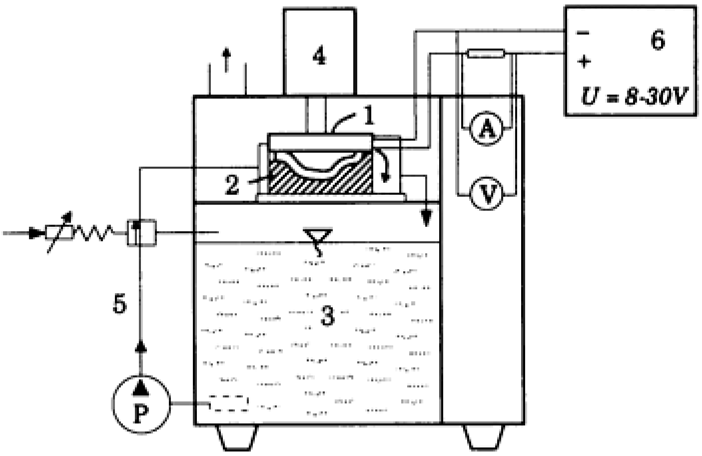


Fig. 2 Electrochemical machining equipment schematic. 1, tool electrode; 2, finishing workpiece; 3, tank of electrolyte; 4, clamping system; 5, electrolyte supply system; 6, power supply

A typical ECM machine consists of a table for mounting the workpiece and a platen mounted on a ram or quill for mounting the tool. The workpiece is mounted on the table and connected to the positive side of the power supply. The tool is mounted on the platen with electrical connection to the negative side of the power supply. The part to be machined is held on a fixed table and the tool is held on a ram that moves either horizontally or vertically onto the workpiece. During the finishing operations while ECM sinking, the tool is either stationary or is fed in the direction of the workpiece. During deburring and machining of contours, however, the tool usually does not move relative to the workpiece.

The corrosive nature of the electrolyte requires that any portion of the machine or tooling that comes in contact with it must be made of a corrosion-resistant material. Workholding fixtures for ECM are usually made from stainless steel, copper, or copper alloys.

Water-cooled power supplies are used on ECM equipment to convert alternating current (ac) electrical power to the direct current (dc) voltages required. ECM machines are available that can deliver currents from 50 to 10,000 amperes, with a voltage range of 4 to 30 V. Sufficient current must be available to maintain a current density of 10 to 500 A/cm^2 at the workpiece (Ref 1, 3).

References cited in this section

1. G.E. Benedict, *Nontraditional Manufacturing Processes,* Marcel Dekker, 1987
2. J.A. McGeough, *Principles of Electrochemical Machining,* Chapman and Hall, London, 1974
3. C. Wick and R.F. Veilleux, Ed., *Materials Finishing, and Coating,* Vol 3, *Tool and Manufacturing Engineers Handbook,* Society of Manufacturing Engineers, 1985, p 15.24-16.126

ECM Process Capabilities

There are numerous parameters that influence the ECM process in terms of machining rate, surface finish, and other end product physical characteristics. In particular, the metal removal rate and the surface finish depend on current density, machining gap, feed rate, electrolyte composition, temperature, and flow rate or pressure of the electrolyte. The design of an ECM system for a specific application should take into account the range of values for these parameters.

The only requirement of the workpiece material for ECM is that it should be electrically conductive. Because the physical properties (rather than the chemical properties) of the material determine the machining rate, alloys that contain more than

one phase of the same material usually present no problem for ECM. However, alloys with inclusions of different materials may be difficult to machine by ECM , or the surface may be unacceptable because of the preferential erosion of one of the materials (e.g., some high-silicon aluminum alloys) (Ref 4). One of the benefits of ECM is the higher machining rates (0.2 to 10 mm/min) for difficult-to-machine materials such as heat-resistant alloys and titanium alloys. Table 1 lists some theoretical removal rates.

Surface Integrity. In addition to high machining rates, ECM produces smooth, damage-free surfaces. The surface finish produced by ECM depends on the workpiece metal or alloy, the electrolyte, and the operating conditions. In general, ECM of nickel-base, cobalt-base, and stainless steel alloys produces smoother surfaces (0.1 to 0.4 μm R_a) than the surfaces obtained with iron-base alloys and steels (0.6 to 1.5 μm R_a), where R_a is the surface roughness in terms of arithmetic average. Most of the ECM in industry, at present, is carried out with NaCl electrolyte because NaCl is inexpensive and gives surface finishes in the ranges mentioned above. However, $NaNO_3$ and KNO_3, which are more expensive electrolytes, are found to give smoother surfaces for many metals, including iron, copper, nickel, aluminum, and cobalt. Table 2 lists various electrolytes for common work metals.

Table 2 Electrolytes for the electrochemical machining of various metals

Work metal	Electrolyte		Removal rate, $mm^3 \times 10^3$/min ($in.^3$/min) per 1000 A
	Major constituent	Concentration (max), kg/L (lb/gal) of H_2O	
Steel; iron-, nickel-, and cobalt-base alloys	NaCl or KCl	0.30 ($2\frac{1}{2}$)	2.1 (0.13)
	$NaNO_3$	0.60 (5)	2.1 (0.13)
Steel; hardened tool steel	$NaClO_3$	0.78 ($6\frac{1}{2}$)	2.0 (0.12)
Gray iron	NaCl	0.30 ($2\frac{1}{2}$)	2.0 (0.12)[a][b]
	$NaNO_3$	0.60 (5)	2.0 (0.12)[a][b]
White cast iron	$NaNO_3$	0.60 (5)	1.6 (0.10)[c]
Aluminum and aluminum alloys[d]	$NaNO_3$	0.60 (5)	2.1 (0.13)
	NaCl or KCl	0.30 ($2\frac{1}{2}$)	2.1 (0.13)
Titanium alloys	NaCl or KCl[e]	0.12 (1)	1.6 (0.10)
Tungsten	NaOH[f]	0.18 ($1\frac{1}{2}$)[g]	1.0 (0.06)

Molybdenum	NaOH[h]	0.18 ($1\frac{1}{2}$)	1.0 (0.06)
	NaCl or KCl	0.30 ($2\frac{1}{2}$)	1.0 (0.06)
Copper and copper alloys[d]	NaCl or KCl	0.30 ($2\frac{1}{2}$)	4.4 (0.27)
	$NaNO_3$	0.60 (5)	3.3 (0.20)
Zirconium	NaCl or KCl	0.30 ($2\frac{1}{2}$)	2.1 (0.13)

(a) Feed rates limited by graphite particle size.

(b) Maximum; can vary widely.

(c) Rough surface finish.

(d) $NaNO_3$ electrolyte provides better surface finish.

(e) Voltage must be greater than 11.

(f) NaOH used up in process and must be replenished.

(g) Minimum of 0.09 kg/L ($\frac{3}{4}$ lb/gal).

(h) pH of electrolyte decreases with use; maintain pH by adding NaOH or KOH.

The main parameter affecting surface roughness of the workpieces is the current density (Fig. 3). Increasing the grain size of a material has also been found to increase the surface roughness, as shown in Fig. 4 (Ref 5). Under normal operating conditions, ECM produces stress-free, burr-free surfaces with no burning or thermal damage to workpiece surfaces or other detrimental effects on materials. ECM-produced surfaces frequently have better wear, friction, and corrosion-resistant characteristics than surfaces obtained with mechanical finishing. ECM also eliminates the need for subsequent operations such as polishing (Ref 4).

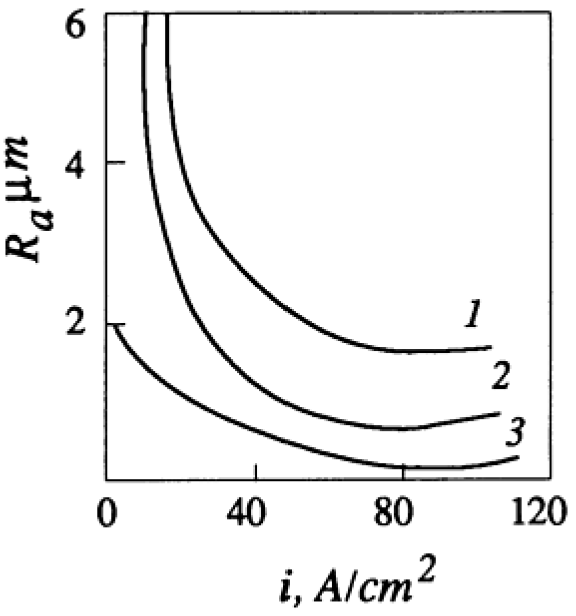


Fig. 3 The effect of electrochemical machining current density (*i*) on surface roughness (R_a) of three steels. 1, steel with Mo; 2, steel with Mo + W; 3, steel with Ni + Nb. Electrolyte: 150 g/L NaCl + H_2O

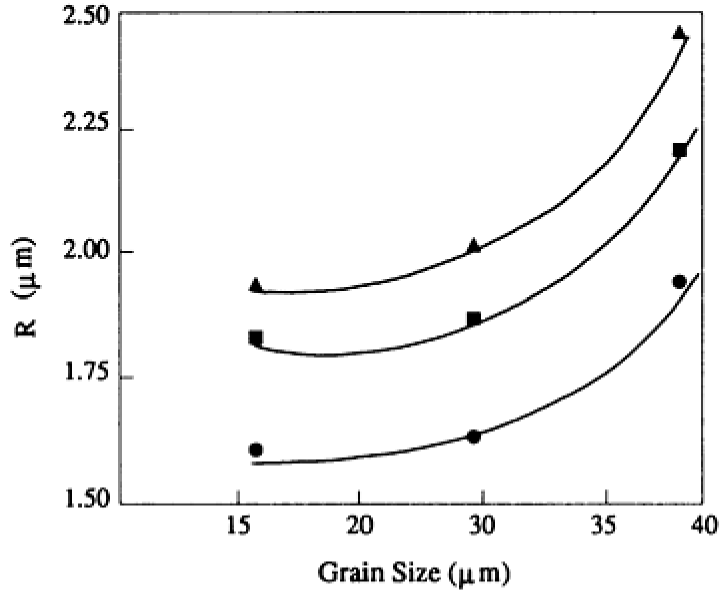


Fig. 4 Surface roughness (R_a) as a function of grain size (at 15 volts). Feed rate: (•), 2.54 mm/min; (■), 1.72 mm/min; (▲), 0.86 mm/min

However, the accuracy of the machining obtained by ECM is not very high, as ECM may not be able to produce clear cuts or sharp corners. The tolerances achieved by ECM are in the range of 0.02 to 0.2 mm. The positioning accuracy of ECM tools now reaches ±0.01 mm. ECM also requires special corrosion protection systems and waste (sludge) disposal techniques.

Electrochemical deburring (ECD) is used exclusively to deburr or radius workpieces (Fig. 5). ECD equipment is constructed with either single or multiple workstations. Some machines are designed with multiple workstations served from a single power supply. ECD equipment is extremely simple, with the electrolyte pump being the only moving part. The principle of ECD is to use a stationary tool, thus eliminating the need for feed mechanisms and control.

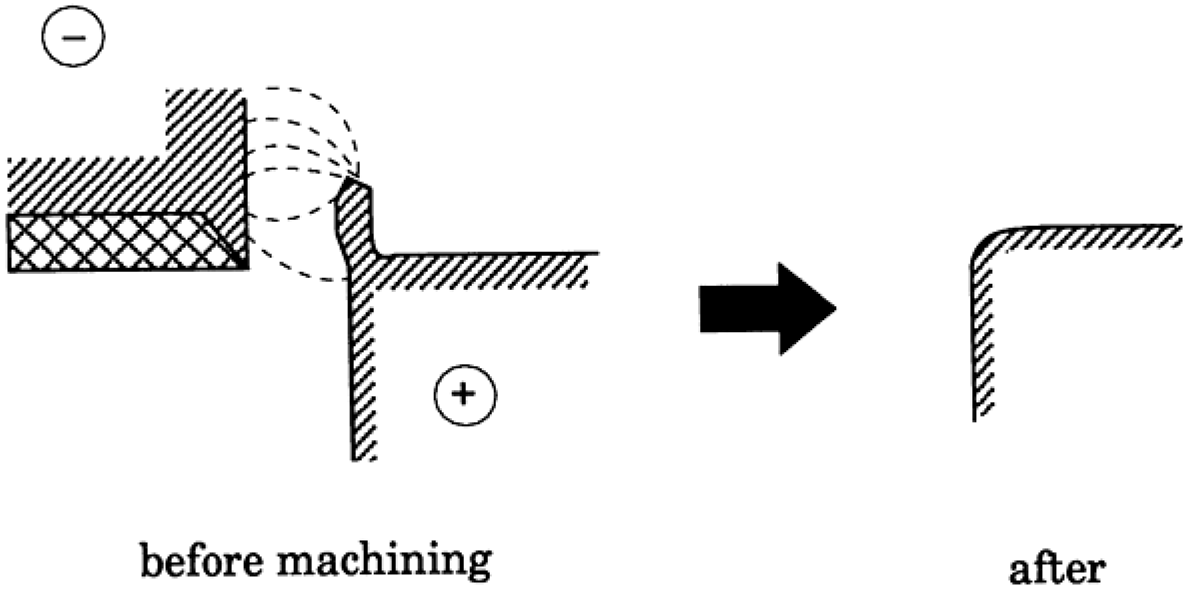


Fig. 5 Schematic of deburring and radiusing process

ECD systems have current ratings from 100 to 2000 A at a dc voltage of 7 to 25 V. Typical outputs are 100 to 1000 A and 0 to 30 V. The high power requirements result in heating of the equipment and thus it requires cooling. The units are normally air- or water-cooled. Depending on the thickness of the material and the current density, there are various methods of supplying the electric current. With thick materials, the current can be supplied directly to the workpiece by means of sliding contacts or pressure contacts. With thin material, the current can be conducted through a conductor beneath it, such as platinum. If higher current densities are required, a system can be used in which the workpiece floats with respect to the electrodes and the current is supplied through the electrolyte.

In an ECD system, the electrolyte pressure ranges from 0.15 to 0.5 MPa (15 to 70 psi), at a flow rate of 3 to 15 L/min (0.8 to 4 gal/min) for each 100 A. The electrolyte used is usually a neutral pH salt solution, such as sodium nitrate or sodium chloride.

The gap between the tool and the burr ranges from 0.2 to 1.2 mm (0.008 to 0.05 in.). ECD systems can handle workpieces manually as well as on completely automated transfer lines. ECD tools are usually made from brass, copper, or stainless steel and are insulated on all surfaces except the surface adjacent to the burr. The insulations range from acrylic and polyvinyl chloride to Delrin and epoxy coatings.

Applications and Limitations. Examples of tooling for ECD are shown in Fig. 6 and 7. ECD is used in industries ranging from consumer appliances and automobiles to biomedical and aerospace products. ECD is used to deburr a variety of parts including gears, gear plates, and fuel injector nozzles.

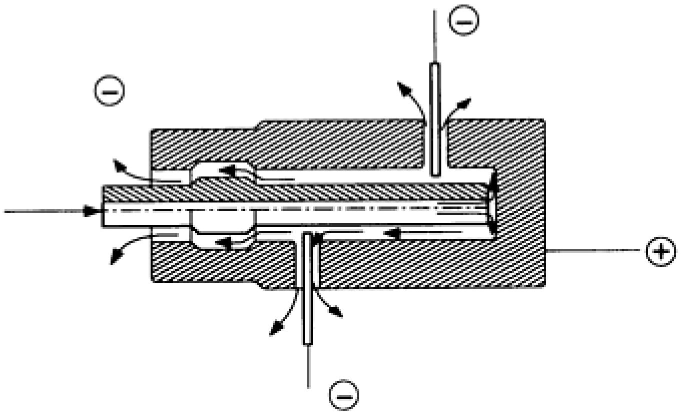


Fig. 6 Schematic of electrochemical machining: smoothing, deburring, and radiusing of piston pin. Machining parameters: *U* (in Fig. 2) = 17 V; electrolyte pressure, 0.3 MPa; electrolyte, 15% NaCl; time of machining, 75 s; maximum current per piece, 180 A

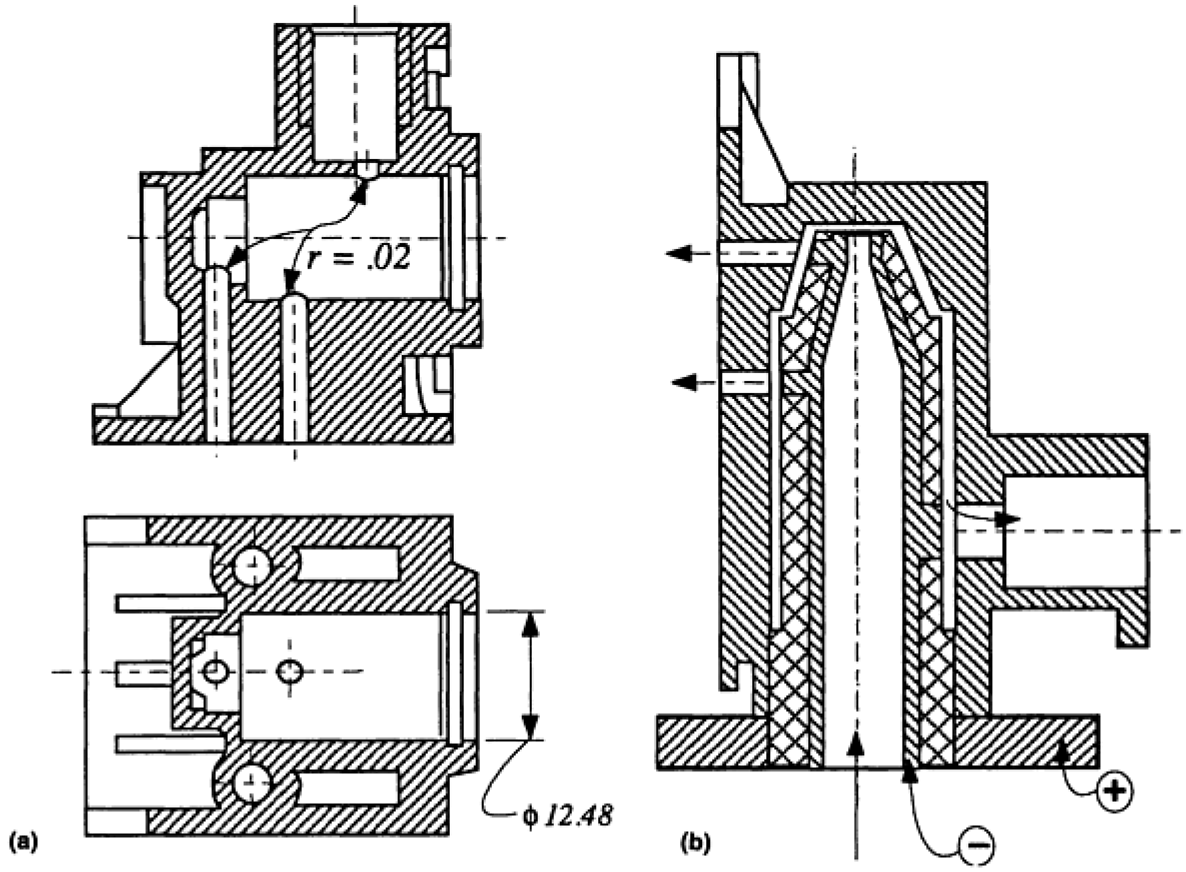


Fig. 7 Tooling for electrochemical machining deburring. (a) Valve casing. (b) A fragmentary schematic of the production jig. Machining parameters: 15% water solution of $NaNO_3$; *U* (in Fig. 2) = 15 V; machining time, 8 s; electrolyte pressure, 1 MPa; maximum current per piece, 20 A

Limitations. One of the major limitations of the ECM and ECD processes is their inability to machine electrically nonconductive materials. Usually, sharp corners or clear cuts cannot be obtained by ECM. The complexity of the shape to be machined, the workpiece material, and the electrolyte put a limit on the dimensional accuracy and the surface finish that can be achieved by ECM. Etching of the constituents, grain-boundary attack, and pitting due to electrochemical action may have drastic effects on the mechanical properties of the material, particularly the fatigue strength.

Recent Advances in ECM as a Surface Finishing Process. As mentioned earlier, different anodic reactions take place at high current densities during ECM, depending on the metal-electrolyte combination and operating conditions. Electropolishing is another finishing process (discussed in the next section) that involves anodic reactions. The rate of these reactions depends to a great extent on the ability of the system to remove the reaction products as soon as they are formed. All of these factors influence the machining performance (i.e., the dissolution rate, shape control, and the surface finish of the workpiece). An understanding of the kinetics and stoichiometry of anodic reactions and their dependence on mass transport conditions is therefore essential in order to optimize relevant ECM and electropolishing parameters. The high rate of anodic dissolution of metals that is applicable to ECM and electropolishing has been reviewed recently (Ref 6). Electrochemical and hydrodynamic parameters influence the nature of the anodic reactions and their rates. These in turn influence the performance of metal shaping and finishing operations. Surface finish during high-rate anodic dissolution depends on the mass transport conditions at the anode. At potentials below the limiting current range, rough surfaces are obtained as a result of crystallographic etching and grain boundary attack. The limiting current, which appears at higher potentials, is mass transport controlled. This corresponds to the formation of a salt layer at the anode that suppresses the influence of the metallurgical phenomena on the dissolution process (Ref 6). Dissolution at or above the limiting current therefore yields smooth surfaces (0.12 to 0.2 μm R_a). Pulsed dissolution is considered most suitable for electrochemical micromachining of thin films and foils when low dissolution rates are desirable for better control over the machining process (Ref 7).

In another recent development, "maskless" and "throughmask" electrochemical micromachining (EMM) techniques have been developed for the processing of thin films and foils of materials that are difficult to machine by other methods (Ref 7). In these processes at higher potentials, a layer of salt forms at the anode. The presence of this salt film also influences the current dissolution, hence the uniformity of metal dissolution and the shape profiles during throughmask EMM.

A new finishing method has been developed using an electrochemical finishing machine (Ref 8). This method enables the operator to set the timing of a switchover to pulses having a high current density, to provide an optimum working condition and thereby improve working efficiency. This method permits the removal of an oxide layer generated on a three-dimensional surface of an object, so that a highly accurate surface can be obtained in a short period of time.

Recently, ECM with an ac source was used for machining of some special alloys such as tungsten carbide. The pulse train used for the ac was asymmetric. This type of ECM is also known as alternate polarity ECM. Alternate polarity ECM has been found to be good for obtaining a uniform dissolution of tungsten carbide and for suppressing the dissolution of the tool electrode (Ref 9). A smooth surface (3.5 to 8 μm R_{max}) without any heat-affected layer or cracks was obtained by this method, where R_{max} is the maximum peak-to-valley roughness height.

The quality of surfaces produced by ECM has been investigated recently, based on how changing process variables affects the resulting plasticity index, which is an indication of surface capacity to bear plastic deformation during service of electrochemically machined surfaces (Ref 10).

Another variation of the ECM process is the use of pulsed current during ECM. This is known as pulse electrochemical machining (PECM). The electrochemical principles of PECM are identical to those of ECM with continuous current. In the PECM process, discrete machining pulses are applied, and the system is allowed to relax between these pulses. It is this alternating pulse on-time and off-time that fundamentally distinguishes PECM from continuous current ECM. Recent studies have shown that PECM results in higher anodic dissolution localization, smaller gap sizes, higher peak current densities and better surface finish (0.16 to 0.63 μm R_a) (Ref 11). Experimental results with pulse EMM indicate that good surface finish can be obtained even at low average current densities. In PECM, shorter pulse on-times (0.2 to 4 ms) are preferable for achieving better surface finishes.

References cited in this section

4. K.P. Rajurkar, C.W. Walton, and T.A. Kottwitz, "State of the Art Assessment of the Electrochemical Machining Process," Final Report, National Center for Manufacturing Sciences, 1989
5. K.P. Rajurkar and C.L. Schnacker, Some Aspects of ECM Performance and Control, *Ann. CIRP,* Vol 37/1, 1988, p 183-186
6. M. Datta, Anodic Dissolution of Metals at High Rates, *J. Res. Dev.,* Vol 37 (No. 2), 1993, p 207-226
7. M. Datta, *Electrochemical Microfabrication,* M. Datta, K. Sheppard, and D. Snyder, Ed., The Electrochemical Society, Pennington, NJ, 1992, p 61

8. Y. Kuwabara, T. Asaoka, S. Yoshioka, and H. Sugiyama, "Finishing Method Employing Electro-Chemical Machining, and an Electro-Chemical Finishing Machine," U.S. patent 4,956,060, 1990
9. T. Masuzawa and M. Kimura, Electrochemical Surface Finishing of Tungsten-Carbide Alloy, *CIRP Ann.,* Vol 40 (No. 1), 1991, p 199-202
10. M. Abdel-Rahman and H.M. Osman, Surface Quality of Electrochemically Machined Surfaces, *Proc. 10th Int. Symp. Electromachining,* Magdeburg Technical University, Germany, 1992, p 543-552
11. K.P. Rajurkar, J. Kozak, and B. Wei, Study of Pulse Electrochemical Machining Characteristics, *Ann. CIRP,* Vol 42 (No. 1), 1993, p 231-234

Electropolishing

Electropolishing is used for polishing of metal parts. The principle is just the reverse of that of electroplating. The workpiece is made the anode in an electrolyte, with a cathode added to complete the electrical circuit. In the resulting deplating, material is removed most rapidly from raised, rough spots, producing a very smooth, polished surface (Ref 12). During the process, products of anodic metal dissolution react with the electrolyte to form a film at the metal surface. Two types of films have been observed: a viscous liquid and an anodically discharged gas, usually oxygen (Ref 13). Neither film adheres closely to the microroughness of a metal surface, and both types conform to the macrocontour. Therefore, the film is essentially thinner over microprojections and thicker at microdepressions. Resistance to electric current flow over the microprojections is less, so more current can flow over the microprojections than in the microdepressions. The result is a more rapid dissolution process at the projections, causing microleveling of the surface. This gives a metal surface with so little scattering of incident light that a mirror-like glossy appearance is obtained.

This process is primarily used for obtaining mirror-like surfaces from highly smooth initial surfaces. A final finish of less than 0.05 μm can be obtained if the initial surface roughness (root mean square) does not exceed 0.18 to 0.20 μm. Electropolishing was primarily developed for polishing metallurgical specimens and for polishing of irregular shapes that were difficult to buff. Now electropolishing is used for polishing stainless steel sheets and parts.

References cited in this section

12. E. DeGarmo, P. Black, J. Temple, and R.A. Kohser, *Materials and Processes in Manufacturing,* Macmillan, 1984
13. *Surface Cleaning, Finishing, and Coating,* 9th ed., Vol 5, *Metals Handbook,* American Society for Metals, 1982, p 303-309

Electrodischarge Machining

Electrodischarge machining (EDM) is a thermoelectric process that removes material from the workpiece by a series of discrete sparks between a work and tool electrode immersed in a liquid dielectric medium. The method of removal of material from the workpiece is by melting and vaporizing minute amounts of electrode material, which are then ejected and flushed away by the dielectric (Ref 1, 14).

The two major types of EDM are die sinking EDM and wire EDM (WEDM). Die sinking EDM is traditionally performed vertically, but it may also be conducted horizontally. WEDM is a special form in which the electrode is a continuously moving conductive wire. In the WEDM process, spark discharges are generated between a small wire electrode (usually smaller than 0.5 mm diameter) and a workpiece with deionized water as the dielectric medium. The electroerosion process is used to produce complex two- and three-dimensional shapes, even in harder materials. According to the most agreed-on process mechanism, when a voltage is applied through a dielectric medium across the gap between the tool and the workpiece, an electric field builds along the path of least resistance. This causes a breakdown of the dielectric and initiates the flow of current. In the second stage, electrons and ions migrate toward the anode and cathode at high current density, forming a column of plasma and initiating the melting of the workpiece. When the application of voltage is stopped, the column collapses, a portion of the molten metal is ejected from the workpiece, and a crater is formed. The debris remaining on the workpiece is flushed away by the dielectric.

In EDM the erosion rate and tool wear, and the resulting surface integrity and geometry, depend on the current, voltage, on-time, off-time, polarity, pulse shape, work and tool material properties, dielectric flushing conditions, dielectric

properties, electrode geometry, and machine characteristics. A general overview of the EDM process is given in Volume 16 of the *ASM Handbook.*

EDM Equipment

All EDM systems include the machine (including the frame, ram, worktable, tool and workpiece holders, and clamping devices), pulse-power supply, tool electrode, dielectric system, and servo control system. Figure 8 is a schematic of an integrated die sinking EDM system. The EDM power system transforms the utility ac power into pulsed dc power with 30 to 300 V and from several milliamperes to 100 A of peak current. Various types of power supply systems exist today. Among those that are suitable for EDM are the relaxation power system, which consists of a charge loop and a discharge loop, and the independent power system, which consists of a dc power source, pulse controller, and a power controller. The pulse controller in this type of power supply sets a time basis and controls the "on" and "off" states of the power controller. The power controller delivers the pulse to the gap with the required power. Some EDM machines are equipped with power supplies that combine the relaxation and independent power supplies in order to improve surface roughness.

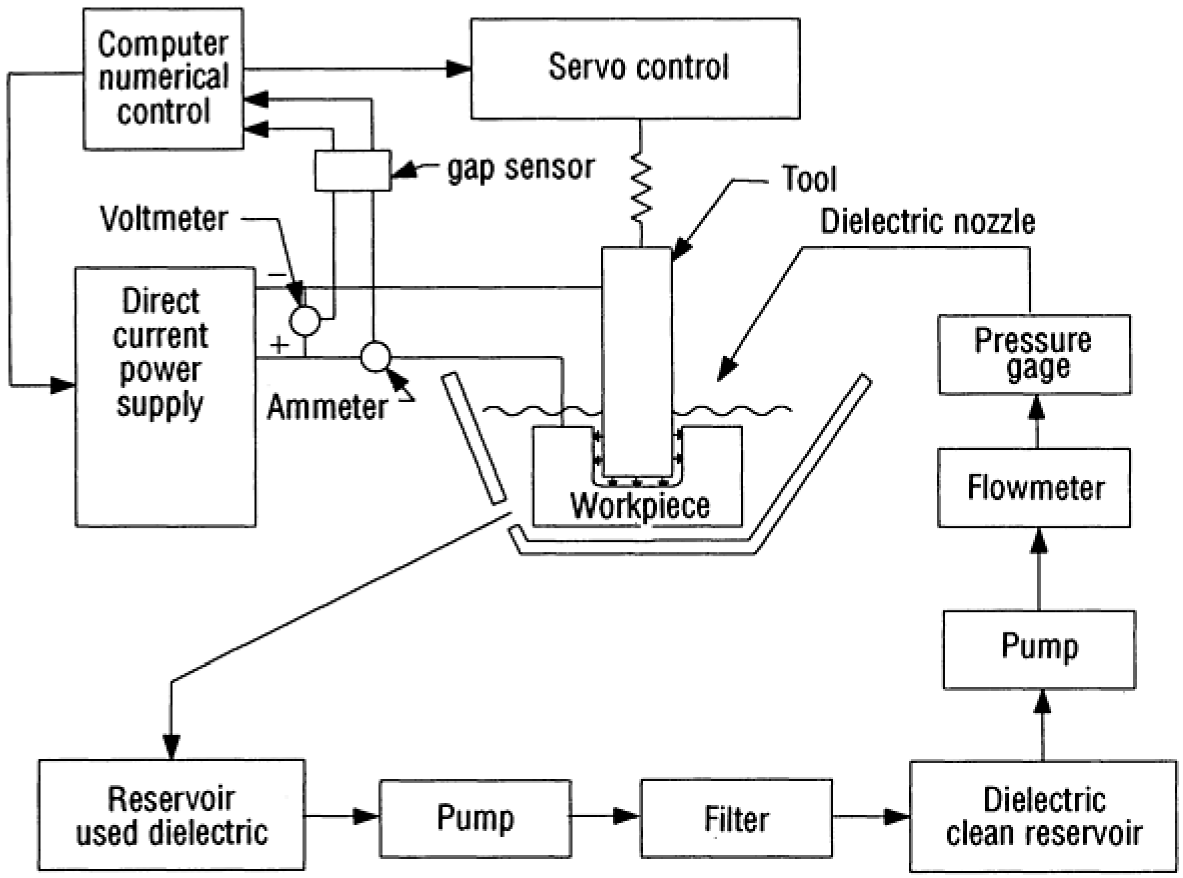


Fig. 8 Schematic of die-sinking electrodischarge machining system

Five-axis computer numerical control WEDM is now routinely employed in complex three-dimensional contour machining jobs (Ref 1). Another application of EDM is electrical discharge grinding, which is used for precision machining of electrically conductive workpieces. Electrical discharge grinding uses a rotating electrically conductive grinding wheel as the "electrode" or cutting tool. (See Volume 16 of the *ASM Handbook.*)

Tool Material. The basic requirements for a tool material are high electrical conductivity, high melting point, and high thermal conductivity. The tool materials should be easy to machine and inexpensive. Some of the most frequently used tool materials include graphite and bronze for machining steels and copper-tungsten for machining carbides. Bronze and copper tungsten are often used for producing smooth surfaces and for high-precision EDM.

Dielectric Fluid. The main functions of the dielectric fluid are to insulate the gap between the tool and the workpiece before high energy is accumulated, to concentrate the discharge energy to a tiny area, to recover the gap condition after the discharge, and to flush away the discharge products. The two most commonly used dielectric fluids are petroleum-based hydrocarbon mineral oils and deionized water. Dielectric flushing is very important in EDM operations. The commonly used flushing methods are immersion, spray, or jet.

Controls. A servo control is used to keep the interelectrode gap within a small range of variations around a desired setting during machining. Typical values of the gap that are used during EDM are 0.010 to 0.050 mm, though gaps as small as a few microns or as large as several hundred microns can be used, depending on the voltage, current, dielectric media, and surface finish requirements. In order to maintain a constant gap size, the tool feed rate should equal the material removal rate in the feed direction. However, because the removal rate is often not constant, a servo control is used that takes the gap signals (the average voltage) as the measure of the gap size and compares them with the servo reference voltage. Action as to whether to retract the tool or to move it faster toward the workpiece is taken, depending on this comparison.

EDM Process Characteristics

In the case of EDM, the metal removal rate and the surface roughness depend on the peak current, pulse on-time, peak voltage, frequency of pulses, and the flow rate of the dielectric. The surface roughness obtained by EDM can range from 2.5 to 30 μm R_a for rough machining. The metal removal rate achieved by EDM can range from 50 to 200 cm^3/hr for rough cuts. As the removal rates increase, the surface finish deteriorates.

Electrodischarge polishing (EDP) uses exactly the same principle as that of EDM; however, the objective is to produce smooth, lustrous surfaces. Hence EDP is carried out with very low discharge energy. EDP can be used to produce smooth surfaces (0.2 μm R_a) that exhibit extremely thin, homogeneous, crack-free surface layers of uniform width (Ref 15). In this process, the high metal removal rate associated with deep craters is undesirable. The aim is to achieve melting of roughness peaks with ensuing resolidification, while avoiding molten metal spinoff. It has been found that EDP with a positive workpiece electrode produces flat craters with a smooth surface and a crater rim raised only slightly above the surrounding workpiece surface (Ref 15). EDP makes use of a gradual reduction of the discharge energy of the individual pulses of less than 3 μJ and a simultaneous increase of the frequency to around 100 kHz. It has been found that the surface roughness rises sharply with increasing discharge current and is found to decrease with increasing polishing depth. The higher smoothing of the surface achieved as a result of the increased polishing depth increases the processing time drastically, however. Because gap widths in EDP are extremely small and difficult to control, flushing is another significant factor influencing the variables for physical conditions in the working gap. With continuous flushing, the workpiece roughness decreases with a decreasing flow rate. In EDP, planetary motion is necessary to avoid undulating workpiece surfaces, because this technique entails relative movement of the electrodes, producing a surface that is microscopically as well as macroscopically smooth.

Applications, Process Capabilities, and Limitations. EDM is capable of machining difficult-to-cut materials such as hardened steels, carbides, high-strength alloys, and even ultrahard conductive materials such as polycrystalline diamond and some ceramics. The process is particularly well suited to sinking cavities and drilling irregularly shaped holes. The only limit in machinability is the electrical conductivity of the workpiece material. The other problems in EDM include tool wear and the irregularity of the tool wear, and limitations of EDM to machine very sharp corners because of the existence of the gap between the tool and the workpiece. A recently developed EDM process called micro-EDM expands the capabilities of EDM with respect to fine part fabrication. This process can achieve a surface roughness of 0.1 μm R_{max} and a high accuracy (roundness of 0.1 μm, and the straightness of some fine parts as small as 0.5 μm).

Recent Advances in EDM as a Surface Finishing Process. As described earlier, EDM and WEDM are performed by passing a dc pulse anywhere between several tens to several hundreds of volts between the tool (the negative wire in case of WEDM) and the positive workpiece. In the case of WEDM, water is generally used as the machining fluid. During WEDM, there is some electrolysis during machining. Consequently, besides being affected by the heat at the time of electric discharge, the electrolysis results in a drop in the machined surface quality. In a recent development, engineers at Mitsubishi Electric have developed a WEDM with an antielectrolysis (AE) power source (Ref 16). Experiments using AE power supply show that the corrosion of the workpiece surface is totally preventable. One of the problems of EDM is the formation of microcracks, which must be avoided, and the use of AE power supply with uniform pulses has also been found to reduce the number of microcracks in EDM surfaces (Ref 16).

In an attempt to achieve extremely fine surface finishes by EDM, different kinds of powders such as silicon, aluminum, and graphite have been suspended in the working fluid (Ref 17). In the case of conventional EDM, during finishing

operations, the gap distance between the electrode and the work is very small, resulting in frequent abnormal discharges. Use of a suspended powder in the working fluid results in an increase in the working gap distance. The effective working gap distance depends on the concentration of the powder and the type of the powder (Ref 17, 18). In fact, experiments show that the working gap distance increases ten times compared to that of the conventional working fluid. The powder suspension is also found to disperse the electrical discharge very well. A good dispersion of the electrical discharge is extremely important for a fine surface finish. The work surface machined using a fluid with suspended powder also has strong corrosion resistance. The surface finish achieved by the use of a fluid with suspended powder was in the range of 0.6 to 1.8 μm R_{max}.

Because EDM is becoming a key process for die manufacturing, it has also become necessary to realize full automation of the EDM process. Engineers at the Toyota Technological Institute have developed a technique to eliminate manual polishing after EDM. During die manufacturing, cusps are left on the workpiece after milling, and in this research, the cusps were removed by EDM under high-wear conditions with planetary motion of the electrode (Ref 19). In order to realize a mirror-like surface on the workpiece, electrically resistive material such as silicon was used as an electrode. This improved the surface finish remarkably; surface roughnesses in the range of 2 to 3 μm were achieved. However, because silicon is hard and brittle, forming an electrode in a complicated shape was extremely difficult. Hence silicon powder was suspended in the working fluid and EDM was carried out. EDM carried out by suspended powders also helps improve the surface finish rapidly.

All of the above methods have been demonstrated in the laboratory to result in mirror-like finishes. However, in most of these cases, large areas (i.e., greater than 300 mm^2) cannot be successfully machined by EDM for a good surface finish. A new method of achieving mirror-like finishes with EDM has recently been attempted (Ref 20). In this method, narrow spark duration and small discharge current (i.e., with the smallest of discharge energies) have been used. In order to reduce the dependence of surface roughness on the working area, a partially induced electric field is used during machining. The concept is to reduce the space in which the electric energy is stored before breakdown.

It has also been demonstrated that surface roughness achieved after EDM can be improved by the use of a radio-frequency (RF) controller (Ref 21). In the presence of bad flushing conditions, the occurrence of stable arcs results in thermal damage to the workpiece surface. Hence it is important to detect the occurrence of stable arcs. Research shows that normal spark discharges generate intense high-frequency (HF) noise signals that are a component of the discharge voltages and are emitted as RF signals. The intensity of the HF or RF signal drops as the gap conditions change from normal sparking to harmful arcing (Ref 21). The RF controller has been modified to include an isoenergetic function, and the sensing gain of the RF detecting circuit has been improved. The EDM operations carried out with the RF controller have been shown to improve the surface finish by 40%.

As mentioned earlier, a uniform surface finish on large areas is difficult to achieve by EDM. However, an electrical discharge texturing system has been developed to obtain improved machining performance and precise control of the surface roughness (Ref 22). The electrical discharge texturing system incorporates an RF monitoring and controlling unit, a unique gap voltage measuring circuitry, and MOSFET (metal oxide semiconductor field-effect transistors) for power switching.

In another attempt to achieve good surface finish by EDM, surface modification by the use of composite electrodes has been performed (Ref 23). In this new technique, the electrode used for EDM is made from fine powder or green compact and shows higher wear than a conventional solid electrode. The machined surface shows the presence of components of the electrode, and there are fewer microcracks in the machined surface layer.

EDM has recently become an important method for machining advanced ceramic materials for many applications, due to the fine finishes that it provides. It has been found that the grain size of the dispersed phase plays the dominant role in affecting the surface roughness (Ref 24).

New developments in the field of materials science have led to new engineering methods for metallic materials, composite materials, and high-tech ceramics. EDM (both rough and finishing) of ceramics turns out to be a very good alternative to traditional machining techniques such as grinding, milling, turning, and sawing. Because EDM is a thermal machining process, it provides a means of machining ceramic materials, irrespective of their hardness and strength. Recorded machining speeds when EDM is applied on those ceramics are much better than those obtained with traditional machining techniques. This, combined with the extremely good surface finishes obtained makes EDM a viable alternative to traditional finishing techniques for ceramic materials (Ref 25).

However, because ceramic materials have higher melting points compared to metals, in general the metal removal rate of ceramics is lower. The removal mechanism during EDM of metals is based on melting and vaporization phenomena. In the case of ceramics, metal removal is due to two types of mechanisms, depending on melting point. The lower-melting-point ceramics exhibit metal removal due to failure by thermal shock (spalling). Spalling occurs when high internal stresses created by steep temperature gradients cause the material to flake. Ceramics that are machined by spalling exhibit very smooth surfaces (1.11 to 1.67 μm). It has been observed that EDM of ceramics results in higher machining speeds compared to the traditional machining techniques for the same surface roughnesses (Ref 25).

In other recent research into the machining of new materials, polycrystalline diamond (PCD) has been machined by WEDM (Ref 26). PCD is challenging to shape due to its hardness, high strength, and high toughness. Diamond grinding is one of the most commonly used techniques for shaping of PCD. However, diamond grinding results in rapid tool wear during machining of PCD, and WEDM has been found to be a much more cost-effective method. The surface quality of workpieces machined by WEDM is very good, and there is not much difference in the surface roughness with a change in the diamond grain size.

References cited in this section

1. G.E. Benedict, *Nontraditional Manufacturing Processes,* Marcel Dekker, 1987
14. E.J. Weller, Ed., *Nontraditional Machining Processes,* Society of Manufacturing Engineers, 1984
15. H.C. Konig and L. Jorres, Electrodischarge Polishing as a Surface Finishing Process, *EDM Technology,* Vol 1, EDM Technology Transfer, 1993, p 12-16
16. Y. Hisashi, M. Takuoi, S. Kiyoji, Y. Tsuyoshi, and K. Kazuhiko, High Quality Electrical Discharge Machining Using an Anti-Electrolysis Power Source, *EDM Technology,* Vol 1, EDM Technology Transfer, 1993, p 25-30
17. H. Narumiya, N. Mohr, N. Saito, H. Ootake, Y. Tsunekawa, T. Takawashi, and K. Kobayashi, EDM by Powder Suspended Working Fluid, *Proc. 9th Int. Symp. Electromachining* (Nagoya, Japan), Japan Society of Electromachining, 1989, p 5-8
18. O. Yoshihara, M. Furuya, N. Saito, and N. Mohri, Finish EDM on Large Surface Area, Report No. 1--Finish Machining Phenomena, *Toyota Tech. Rev.,* Vol 41 (No. 1), Dec 1991
19. N. Mohri, N. Saito, and M. Higashi, A New Process of Finish Machining on Free Surface by EDM Methods, *Ann. CIRP,* Vol 40/1, 1991, p 207-210
20. Y.F. Luo, Z.Y. Zhang, and C.Y. Yu, Mirror Surface EDM by Electric Field Partially Induced, *Ann. CIRP,* Vol 37/1, 1988, p 179-181
21. K.P. Rajurkar and W.M. Wang, Improvement in EDM Surface Roughness and Other Performances with an R.F. Control System, *Proc. 10th Int. Symp. Electromachining,* Magdeburg Technical University, Germany, 1992, p 383-394
22. S.M. Ahmed, "Texturing Large Surface Areas by EDM," Increase Machining Precision and Efficiency with EDM--Conf. Proc., Society of Manufacturing Engineers, 1987
23. N. Mohri, H. Momiyama, N. Saito, and Y. Tsunekawa, Surface Modification by EDM--Composite Electrode Method, *Proc. 10th Int. Symp. Electromachining,* Magdeburg Technical University, Germany, 1992, p 587-593
24. A.M. Gadalla and N.F. Petrofes, Surfaces of Advanced Ceramic Composites Formed by Electrical Discharge Machining, *Mater. Manuf. Process.,* Vol 5 (No. 2), 1990, p 253-271
25. D.F. Dauw, C.A. Brown, J.P. van Griethuysen, and J.F.L.M. Albert, Surface Topography Investigations by Fractal Analysis of Spark-Eroded, Electrically Conductive Ceramics, *Ann. CIRP,* Vol 39/1, 1990
26. S.Z. Wang, K.P. Rajurkar, and J. Kozak, Effect of Grain Size on Wire Electrical Discharge Machining of Polycrystalline Diamond, *Proc. Int. Conf. Advanced Material Processing* (Gaithersburg, MD), S. Jahanmir, Ed., Special Publication 847, National Institute of Standards, and Technology, 1993, p 535-542

Mass Finishing

Revised by Edward H. Tulinski, Harper Surface Finishing Systems, Inc.

Introduction

MASS FINISHING normally involves loading components to be finished into a container together with some abrasive media, water, and compound. Action is applied to the container to cause the media to rub against the surfaces, edges, and corners of the components, or for components to rub against each other, or both. This action may deburr, generate edge and corner radii, clean the parts by removing rust and scale, and modify the surface stress. The basic mass finishing processes include:

- Barrel finishing
- Vibratory finishing
- Centrifugal disc finishing
- Centrifugal barrel finishing
- Spindle finishing
- Drag finishing

Mass finishing is a simple and low-cost means of deburring and surface conditioning components. Consistent results from part to part and batch to batch are generally ensured. All metals and many nonmetals in a variety of sizes and shapes can be handled. Processes range from heavy radiusing and grinding operations to very fine finishing.

A basic advantage of mass finishing is that the action is effective on all the surface edges and corners of the part. Normally, preferential treatment to one area is impossible. Action is greater on corners than other similarly exposed surfaces. Action in holes and recesses is less than on exposed areas.

The mass finishing processes are used to:

- Clean, descale, and degrease
- Deburr
- Radius edges and corners
- Change surface condition
- Remove surface roughness
- Brighten
- Inhibit corrosion
- Dry
- Stress relieve
- Impart compressive stress

Barrel Finishing

The rotary barrel, or tumbling barrel, utilizes the sliding movement of an upper layer of workload in the tumbling barrel, as shown in Fig. 1. The barrel is normally loaded about 60% full with a mixture of parts, media, compound, and water. As the barrel rotates, the load moves upward to a turnover point; then the force of gravity overcomes the tendency of the mass to stick together, and the top layer slides toward the lower area of the barrel.

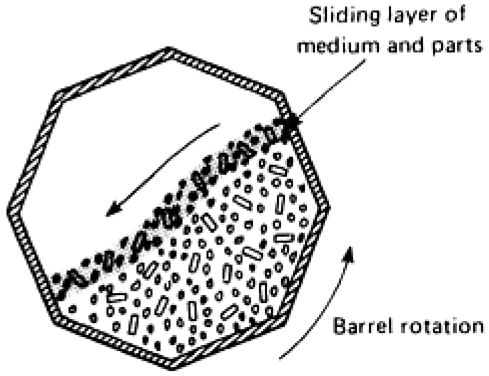


Fig. 1 Action of media and parts within a rotating barrel

Although abrading action may occur as the work load rises, about 90% of the rubbing action occurs during the slide. In the case of a horizontal barrel that is just over half full, the most effective action occurs to produce the longest slide. As may be judged from Fig. 1, the faster the rotation of the barrel, the steeper the angle of the slide. With all but the shallowest of angles of slide, there is invariably more tendency for tumbling of the load, as well as sliding. The faster the rotation of the barrel, the faster the action will take place. However, the faster the action, the poorer the surface and edge condition will be, and the greater the likelihood of parts being damaged.

Typical equipment for barrel tumbling is shown in Fig. 2 and includes:

- Open-ended, tilted-type barrel (concrete mixer)
- An adaptation known as the bottle-neck barrel
- Horizontal barrel
- Submerged barrel
- Fixtured barrel

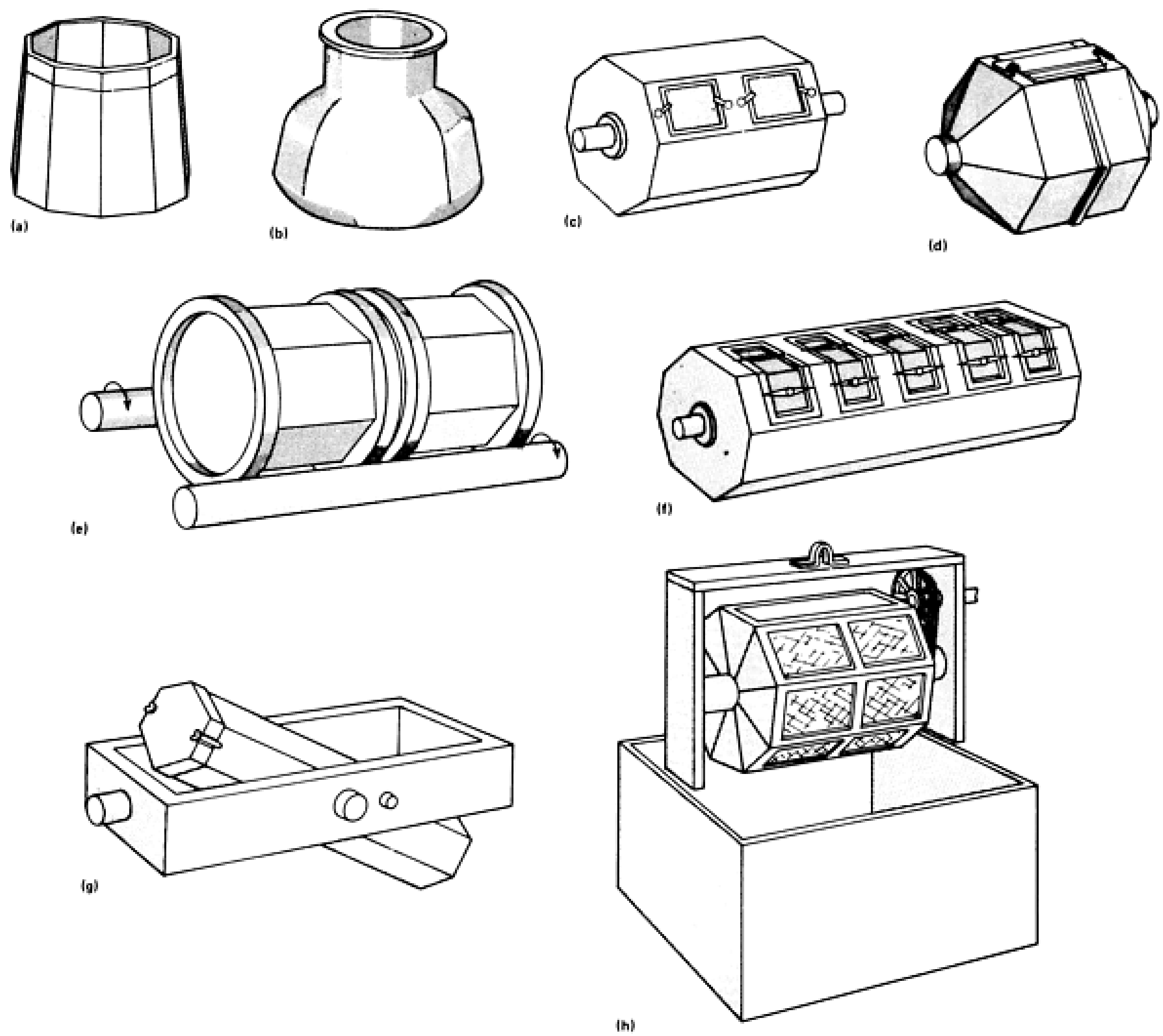


Fig. 2 Barrels available in a variety of sizes. (a) Standard open-end, tilting. (b) Bottlenecked. (c) Horizontal octagonal. (d) Triple-action, polygonal. (e) Multiple drums. (f) Multicompartment. (g) End loading. (h) Submerged

The open-ended, tilting barrel is used for light finishing and also for drying. The bottle-neck shape provides essentially the same action, but more effectively, because parts and media remain better mixed. The horizontal barrel, usually of octagonal cross section, is the standard or most used tumbling barrel, capable of achieving a variety of results and maintaining real consistency. Rotational speeds of these barrels range from as low as 4 rpm for large barrels to 60 rpm for small barrels; surface speeds range from about 6 to 60 m/min (20 to 200 sfm); the higher speeds are used for cutting, the slower speeds for burnishing and fine finishing.

Ratio of media to parts ranges from about 3-to-1 to 15-to-1 by volume. Rough work can be loaded only with parts, so that parts self-tumble against each other. Some of the factors to be considered in determining the media to parts ratio are:

- Size and complexity of the workpiece
- Possibility of media lodging in the parts
- Possibility of the parts nesting
- Required quality of final finish

Automation of barrel tumbling equipment is possible. The barrel can rotate in a clockwise direction to deburr and finish the parts. At the end of the process, the barrel rotation is reversed and parts feed out through a scroll, then through a screener into a material handling unit.

The capital cost of barrel tumbling equipment is low and generally maintenance costs are also low. Because barrel tumbling is a very well-established process, the basic conditions are well understood and guidance on best process techniques is readily available. Barrel tumbling is, however, a slow process, almost invariably involving several hours and on occasion several days. The process is space consuming with a high level of work in progress. More modern mass finishing processes offer greater versatility and convenience, with better use of labor and consistency of quality in production. For these reasons, and because higher operator skills are needed, barrel tumbling has been replaced in most modern production facilities.

Vibratory Finishing

A vibratory finishing machine is an open-topped tub or bowl mounted on springs, usually lined with polyurethane. Parts and media are loaded in a fashion similar to that of a tumbling barrel. With a vibratory machine, the container can be almost completely filled. Vibratory action is created either by a vibratory motor attached to the bottom of the container, by a shaft or shafts with eccentric loads driven by a standard motor, or by a system of electromagnets operating at 50 or 60 Hz. The action of media against components takes place throughout the load, so that process cycles are substantially shorter than conventional tumbling in barrels. Components can be inspected and checked during the process cycle. This process is faster, more convenient, and more versatile than tumbling barrels. The vibratory machine is able to handle larger parts and is more readily automated. The process achieves more abrasive action in the recessed areas of components, is easier to operate, and is cleaner.

Two important variables for operation of vibratory equipment are frequency and amplitude of vibration. Frequency may range from 900 to 3000 cycles/min. Amplitude can range from 2 to 10 mm ($\frac{1}{16}$ to $\frac{3}{8}$ in.). Most equipment operates in the range of 1200 to 1800 cycles/min and 3 to 6 mm ($\frac{1}{8}$ to $\frac{1}{4}$ in.) amplitude.

The tub vibrator consists of an open container where the cross section is either U-shaped, a round inverted keyhole shape, or a modification of these. Figure 3 shows three types of tub vibrators. The modifications from the U-shaped cross section are constructed to develop more uniform flow of the mass, because the U-shaped cross section has a tendency for some back flow against one of the walls. The means of creating the vibratory action is with a single shaft mounted directly underneath the tub. At each end of the shaft, or along its length, are eccentric weights and a facility to add or reduce some of the weights. The greater the weight, the more amplitude. The faster the action, the rougher the surface finish and the greater the media wear. The shaft may be driven from a motor coupled to the shaft through a flexible coupling or by belts. Variable speed of rotation of the shaft is fairly easily obtained and gives variable frequency of vibration. The higher the frequency, the faster the cut, but the rougher the surface. Modifications of the drive system include:

- Use of double shaft, as shown in both Fig. 3(b) and 3(c), to maintain greater uniformity of the parts and media mix and offer somewhat faster action
- Use of eccentric shaft, rather than eccentric weights at the ends of a shaft, to give greater consistency of action throughout the load
- Location of eccentric weights or shaft on one side, at top of tub wall, or at both sides

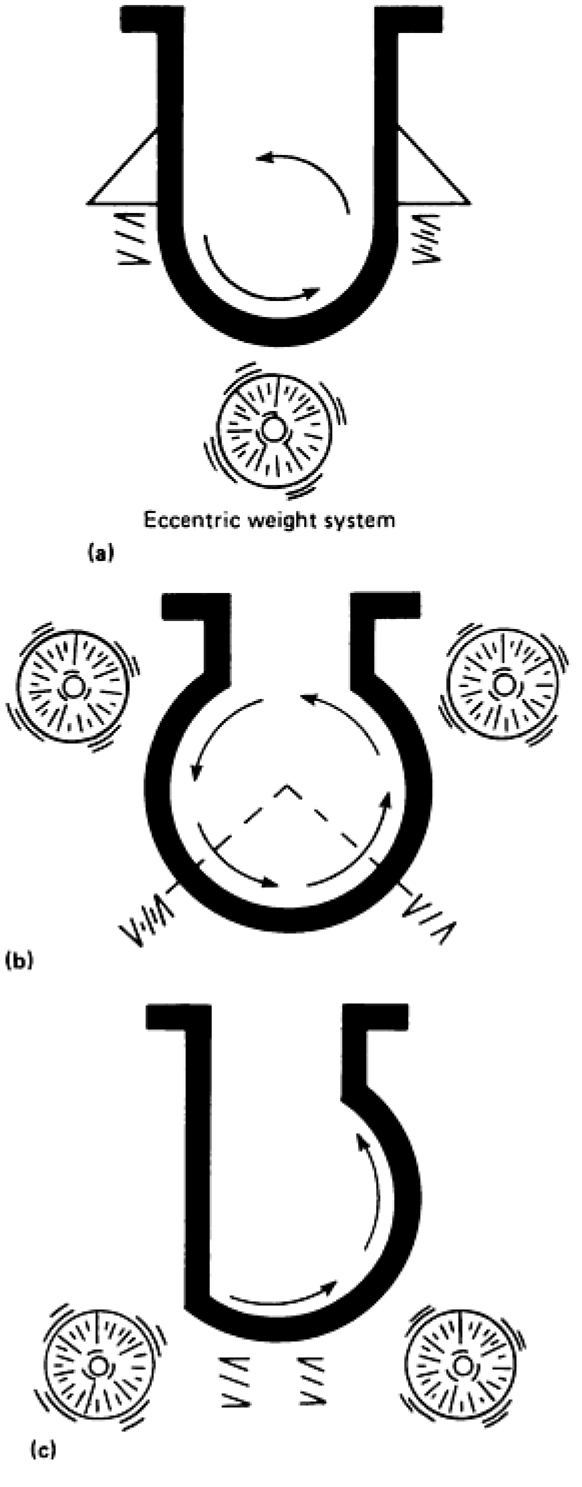


Fig. 3 Tub vibrators

Tub vibratory equipment can be sized to suit the largest components. Units are in production to handle parts as long as 12 m (40 ft), and other equipment has been built to handle parts of cross section as much as 2 m (6 ft) by 2 m (6 ft).

Separation of parts and media is sometimes accomplished by dumping the total contents of the vibratory tub into a material handling system. Most tub vibrators have unload doors at one end, which may be opened manually or automatically and through which the total load is fed. Some units have a system for emptying by inverting the complete tub.

Tub vibratory equipment is readily automated for continuous production. A long tub vibrator may have parts and media fed in at one end of the container. These proceed along the tub until finished parts and media exit at the other end. The discharge end is lower than the parts' entry end, causing the media and parts to move to the discharge end. Parts are then screened out from the media. The media is returned with a simple belt conveyor directly or through a storage unit. Such systems are suitable for processes where satisfactory results are achieved with process cycles of up to 30 min.

Other automated tub vibratory systems include storage for different media that may be automatically selected for different processing tasks. Tub vibratory machines can be highly versatile and permit process cycles normally $\frac{1}{5}$ to $\frac{1}{10}$ of those achieved with tumbling barrels. They are capable of handling all sizes of workpieces, including complex shapes. Materials handling is usually accomplished by units added onto the vibrator itself, designed and built to meet specific applications.

Bowl vibrators are round bowl- or toroidal (doughnut)-shaped and, like the tub vibrator, have a container mounted on springs. The principle of this type of equipment is shown in Fig. 4. Vibratory action is imparted to the bowl by eccentric weights mounted on a vertical shaft at the center of the bowl. Eccentric weights at either end of the shaft are adjustable in their relationship to one another. This is referred to as the lead angle. When set within the normal range established by the manufacturer, a spiral motion is imparted to the mass of parts and media. Changing the relationship of the weights alters the spiral path, the speed at which the load moves around the bowl, and the amplitude of vibration. The bowl vibrator is capable of more gentle action than tub equipment because parts hold their relationship to one another as they proceed around the bowl; consequently there is less chance of part-on-part impingement. Another advantage of bowl vibrators is that they require less floor space than most tub units of similar capacity.

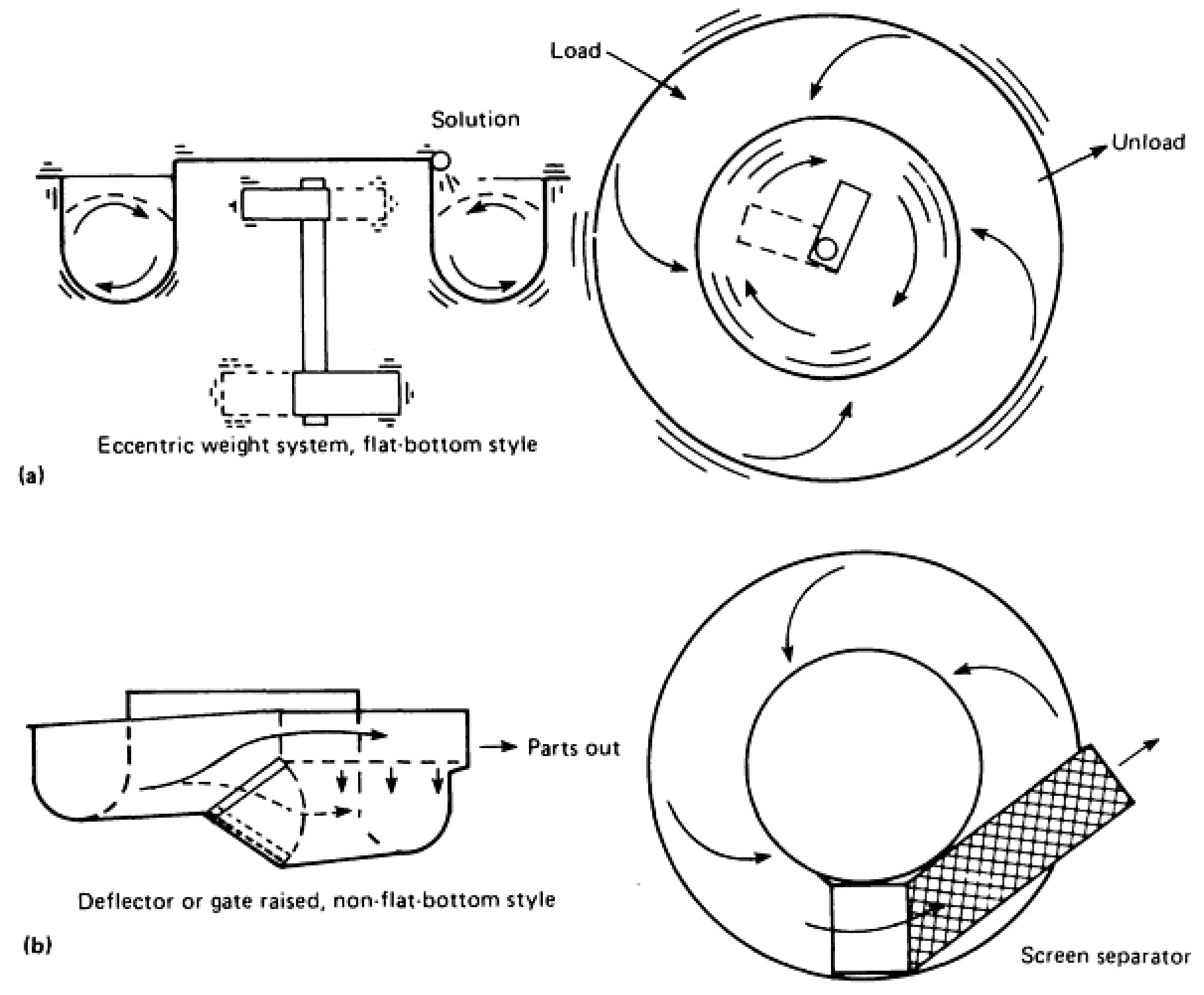


Fig. 4 Bowl vibrators

The major advantage of bowl vibrators is that an integral separation system can be incorporated, such as that shown in Fig. 4(b). To separate parts from media, a dam is placed in the channel so that parts and media are forced up and over. At the top of the dam is a screen over which parts and media pass. Media fall through the screen back into the vibrator bowl. Parts are deflected off the screen into a collection hopper or conveyor. Bowl vibrators with integral separation may have a non-flat-bottom base, so the dam has a shorter distance to travel. Parts and media do not have to lift as high to reach the screen, excellent separation is achieved, and there is less likelihood of parts piling up at the dam with danger of impingement. Action of the dam may be automatic; some equipment has automatic reversal of the action and increased vibration to promote faster and more complete separation. Therefore, the round vibrators can be fully automated. For short process cycles up to about 30 min, flow-through automation can be achieved with the dam permanently in place.

Bowl vibratory equipment is preferred if integral separation meets all requirements, and if there is no need for frequent media change. Bowl vibrators are somewhat slower than the tub units. They cannot handle very large parts, but they are gentle and can handle parts in individual compartments.

Causes of Problems. Some causes of sluggish, ineffective vibratory action include:

- Water flow rate that is too high or drains that are clogged, resulting in excessive dampening
- Use of wrong type of compound, little or too much compound
- Frequency of vibratory action that is not best for the partsAmplitude that is too great
- Equipment that is underpowered and therefore does not develop enough vibratory action for effective performance

Unacceptable finishes may be the result of:

- Insufficient cutdown of surface
- Improper media for amount of cut needed on workpieces
- Dirt, oil, or metal fragments in the solution that work back into the surface of parts
- Insufficient flushing and cleaning of media from processing tub
- Use of wrong type of finishing compound and/or wrong concentration
- Vibratory action that is too harsh
- Incorrect ratio of parts to media
- Careless handling in auxiliary operations

Spindle Finishing Machines

Spindle finishing is categorized as a mass finishing process, although parts to be deburred or finished are mounted on fixtures. The process uses fine abrasive media for finishing. The spindle machine is a circular rotating tub that holds the abrasive media, and a rotating or oscillating spindle to which the part is fixed. The workpiece mounted on the spindle is immersed into the rapidly moving abrasive slurry, causing the abrasive to flow swiftly over rough edges and over the surfaces of components. In some designs, the media container is stationary, and the fixtures move the parts rapidly through the media. Figure 5 shows a layout of a spindle machine.

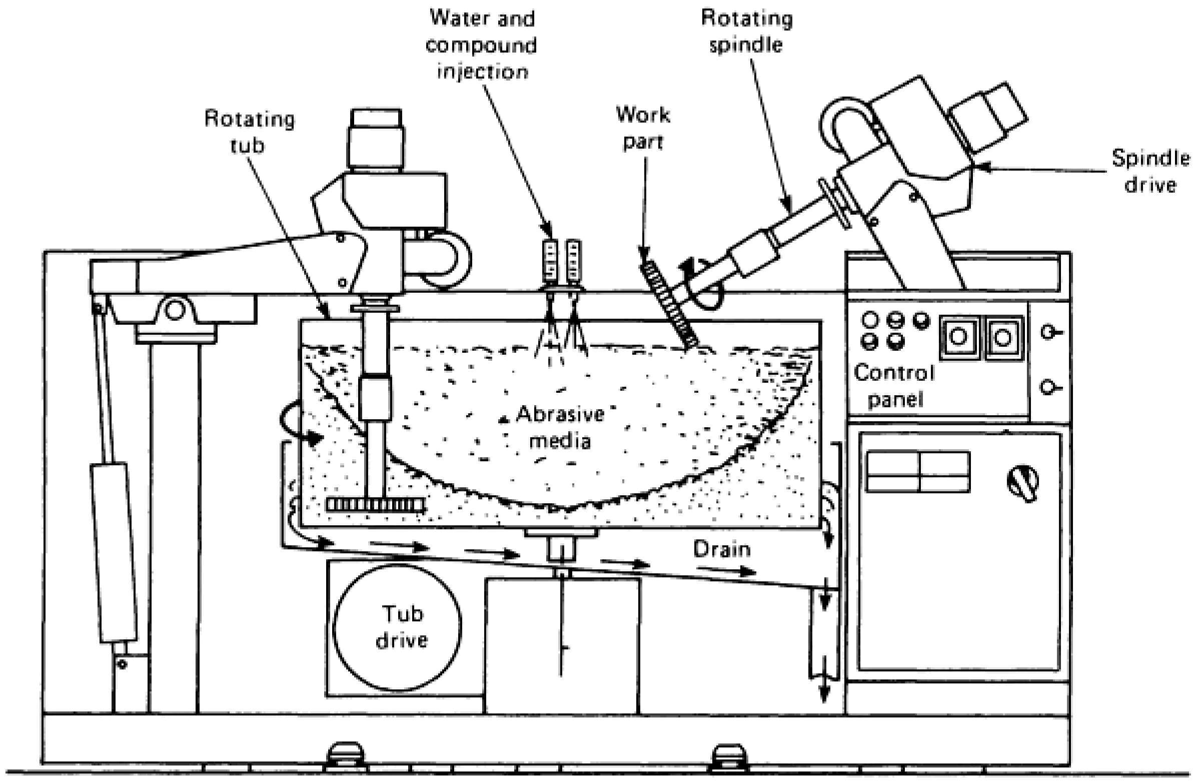


Fig. 5 Two-spindle mass finishing machine

The media used are usually small aluminum oxide nuggets, although all forms of small finishing media are applicable. Most operations are carried out in a water solution, although very fine finishing of some components can be achieved by dry operation using media composed of fine abrasives and corncob or walnut shells.

Process cycles in spindle equipment rarely exceed 20 min and are frequently less than 30 s. The equipment is well suited for parts such as gears, sprockets, and bearing cages where parts cannot be allowed to contact one another. Equipment can deburr, edge radius, and produce very fine surface finishes. Because parts are fixtured, part-on-part impingement does not occur during the process or at reload time. The limitations of this process result primarily from the need to fixture the workpieces. Where parts can be handled entirely satisfactorily in bulk in vibratory equipment, centrifugal barrel machines, or centrifugal disc equipment, the operation will be more economical, convenient, and versatile.

Centrifugal Disc Finishing

The centrifugal disc process is a high-energy mass finishing process. The basic design is a vertical cylinder with side walls that are stationary. The top of the cylinder is open. The bottom of the cylinder is formed by a disc that is driven to rotate at a high speed. Media, compound, and parts are contained in the cylinder. As the disc rotates with peripheral speeds of up to 10.2 m/s (2000 ft/min), the mass within the container is accelerated outward and then upward against the stationary side walls of the container, which act as a brake. The media and parts rise to the top of the load and then flow in toward the center and back down to the disc.

The action achieved in the centrifugal disc machine, shown in Fig. 6, is substantially faster than in vibratory equipment because of the centrifugal forces of as much as ten times gravity pressing abrasive media against components. Process cycle times are up to $\frac{1}{20}$ those of vibratory processing. The short process cycles result in reduced floor space requirements in the finishing department, increased versatility, and less work in progress. As with vibratory equipment, parts can be readily inspected during the process cycle and variable speed can occasionally combine deburring with a final, more gentle surface refinement operation. The faster process speeds create a much greater rate of media wear and increase demands on the compound solution and its flow rate.

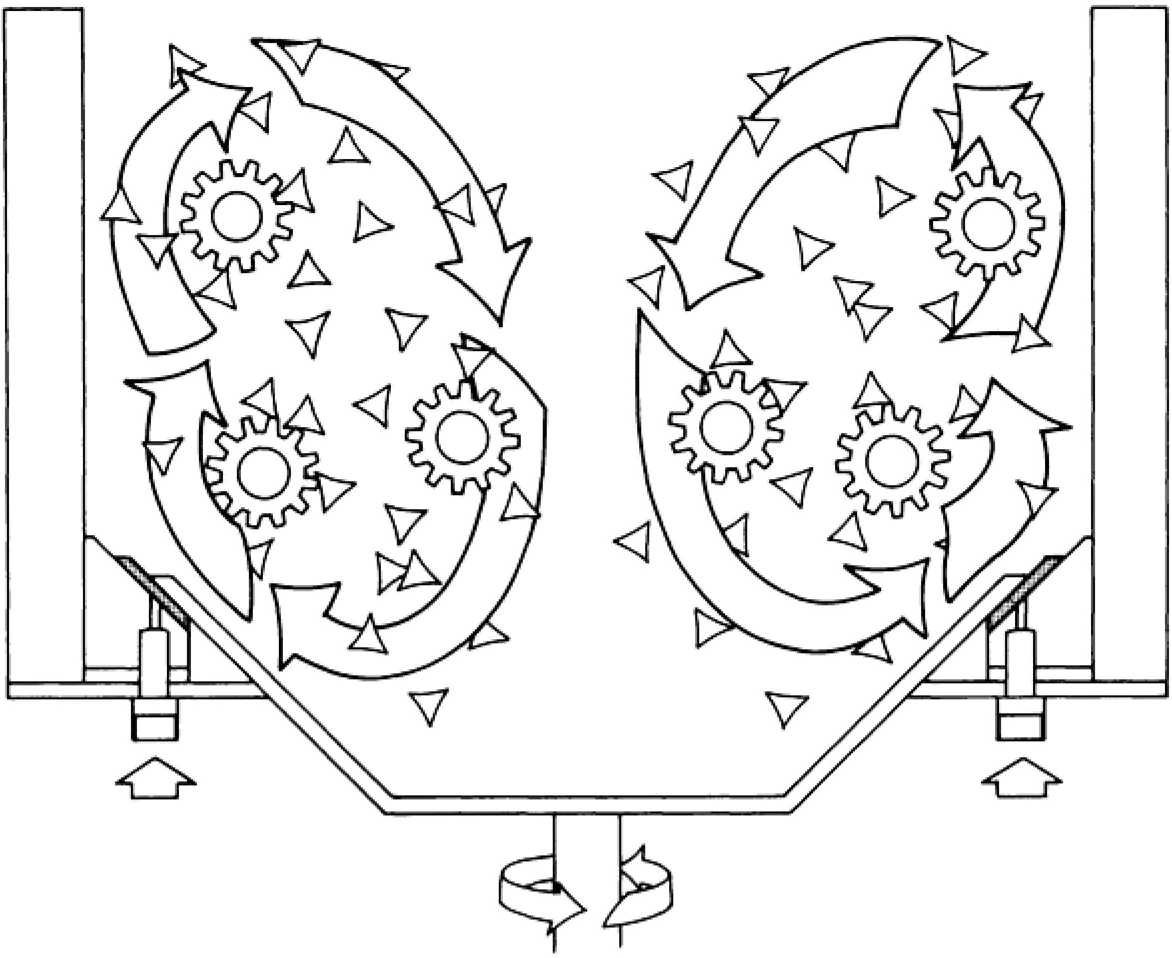


Fig. 6 Centrifugal disc machine

Centrifugal disc equipment is available with capacities ranging from 0.04 to 0.6 m^3 (1.5 to 20 ft^3). This equipment is easily automated. The load is emptied through a door in the side of the container through which parts and media can be fed, or by tilting the whole bowl through 180° to dump the load. Subsequent separation, classification, washing systems, and the return of media to the container for the next operation are similar to those techniques used with tub vibratory machines.

Centrifugal Barrel Finishing

Centrifugal barrel equipment is comprised of containers mounted on the periphery of a turret. The turret rotates at a high speed in one direction while the drums rotate at a slower speed in the opposite direction. The drums are loaded in a manner similar to normal tumbling or vibratory operations with parts, media, water, and some form of compound. Turret rotation creates a high centrifugal force, up to 100 times gravity. This force compacts the load within the drums into a tight mass. Rotation of the drums causes the media to slide against the work load, to remove burrs and to refine surfaces. The action of a centrifugal barrel machine is shown in Fig. 7.

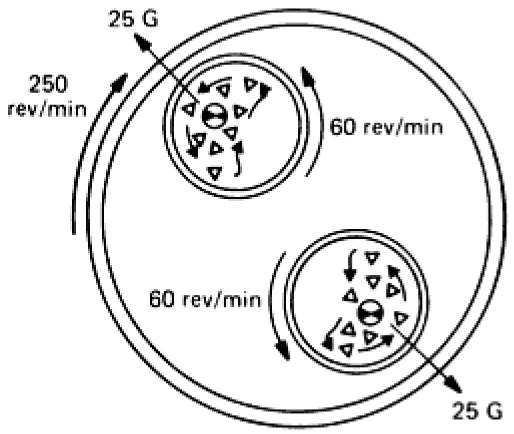


Fig. 7 Action of turret and drums within a centrifugal barrel finishing machine

The abrading action, under high centrifugal force, results in short process cycles, generally less than $\frac{1}{50}$ of the time taken in vibratory equipment. Because of the counter rotation of drums to turrets, a completely smooth sliding action of media against components is generated, with little possibility of one part falling or impinging against another. This completely smooth action achieves consistent and reproducible results. Very high tolerances are maintained even with fragile parts, and very high surface finishes are achieved.

Process variables are similar to those of other mass finishing processes, but an advantage of centrifugal barrel finishing is the ability to control the force with which media are pressed against components. This gives greater latitude in choice of media. For example, hard and low-abrasion media may be used to deburr by running at high speed. Then the same media refine surfaces when the machine is switched to a low speed. Therefore, two operations can be combined into a single cycle. Particle size of media is selected to meet requirements of uniformity and to ease separation without increasing the time of the process cycle.

One important application of centrifugal barrel equipment is to impart a high compressive stress to the surface layer of components and to increase resistance to fatigue failure. The capability of imparting improved fatigue strength is used in bearings, aircraft engine parts, springs, and compressor and pump components. The improved fatigue strength is generally greater than that of the other finishing processes combined with shot peening. It is almost always significantly lower in cost.

Economic considerations frequently dictate the choice between centrifugal barrel equipment and the other mass finishing processes. If satisfactory results are achieved with a process cycle of less than 1 h, a vibratory process is the more economical method. If the process cycle is much longer, if there is a wide variety of components to be handled, or if there are special finishing requirements or parts of very high precision, centrifugal barrel machines are usually better suited.

Centrifugal barrel equipment is available in sizes ranging from less than 0.01 m^3 ($\frac{1}{4}$ ft^3) capacity to 1.4 m^3 (50 ft^3) capacity. The process is fully batch automated but not subject to continuous flow-through of workpieces.

Other Types of Mass Finishing Equipment

The mass finishing processes discussed so far are the well-established mechanical finishing techniques throughout industry. Equipment comes in a variety of shapes and sizes to meet special requirements. Equipment has been developed to suit changing requirements and is frequently built to meet special purposes. Other mass finishing machines offered with slightly different actions from those that have been discussed include the following:

- *Vibratory rotary barrel machines* are conventional tumbling barrels that are vibrated as they rotate. They were originally developed to avoid some of the problems of parts migrating out of the media in tub

vibratory equipment. These machines do not appear to have any substantial merit for modern general-purpose deburring and finishing.

- *Reciprocal finishing:* As in spindle finishing systems, parts are attached to a holding device and placed into a tub of media, water, and compound. The component is moved through the mass of media in a reciprocating motion. This process permits the handling of parts too large for spindle finishing machines. Action is concentrated on just one side of the component for specialized finishing. Process cycles are generally much longer than with spin finishing machines, and equipment is special and of limited purpose.
- *Chemically accelerated centrifugal barrel finishing:* A combination of chemical polishing with centrifugal barrel finishing has found many worthwhile applications, particularly with high-precision, complex-shaped ferrous components. The process is substantially more costly than normal centrifugal barrel finishing and is only suited to very special purposes.
- *Electrochemically accelerated mass finishing equipment:* For special purposes, a combination of electropolish and vibratory or tumbling barrel action achieves very fast stock removal. The process is expensive and inconvenient and is not commercially used in the United States.
- *Orboresonant cleaning and finishing:* Parts clamped on fixtures are oscillated at very high frequency in a bed of fluidized media, with some capability for removing internal burrs and cleaning internal surfaces.

Selecting Mass Finishing Equipment

Factors to be considered when selecting the most suitable mass finishing process include:

Production requirements

- Size and configuration of parts
- Batch size
- Part material
- Variety of parts
- Hourly production
- Annual production

Quality requirements

- Consistency of quality entering department
- Consistency of quality leaving department
- Surface finish
- Edge condition required
- Cleanliness of parts
- Uniformity over edges and surfaces
- Uniformity part to part

Process variables

- Relationship to other manufacturing processes
- Automation requirements
- Process time
- Total investment
- Operation and maintenance costs
- Consumable materials
- Energy
- Water and effluent removal and treatment

- Preventive maintenance and repairs
- Available floor space
- Inventory requirements
- EPA and OSHA considerations
- Labor, direct, supervisory, and quality control
- Future and current needs

Traditionally, mechanical finishing has been a centralized service operation for all manufacturing operations within an organization. Although the centralized finishing department is still suitable in many organizations, deburring and mechanical finishing is frequently incorporated in the production line. In reviewing mechanical finishing requirements, as in buying any metal-forming equipment, one should consider that equipment as part of a system with all controls between the system and all ancillary and handling equipment.

Some of the advantages and disadvantages of mass finishing processes that should be considered are included in Table 1.

Table 1 Advantages and disadvantages of mass finishing processes

Process	Advantage	Disadvantage
Industry standard		
Tumble barrel	Low initial cost Low operating cost for supplies Very low equipment maintenance cost	Slow process Skillful operator essential Automation impractical Wet working area No in-process inspection
Vibratory tub	Fast operation Handles all part sizes Open for in-process inspection Practical full batch automation Practical in-line automation	Slower than high-energy process External material handling required
Vibratory bowl	Open for in-process inspection Practical full batch and continuous operations Requires no auxiliary equipment to automate Internal separation Space saving Lowest cost for general purpose work Simple selection and operation with little operator skill required Can produce cleanest parts and excellent surface finish	Somewhat slower than vibratory tub
High-energy		
Spindle	Fast processing Possible automation, robot load and unload No part-on-part impingement	Limited part geometry Parts must be fixtured High labor cost
Centrifugal disc	Fast processing Open for in-process inspection Practical automated batch process Compact operation	Part size limitation High initial investment

Centrifugal barrel	Fast processing Fragile part handling High precision part handling Potential automated batch processing Automatic change from grind to super finish Produces finest finish Improves fatigue strength	No in-process inspection High initial investment

Mass Finishing Consumable Materials

For the vast majority of mass finishing processes, equipment is loaded with components to be finished, media, compound, and water. Media are solid stones or chips. Compounds are the materials that dissolve in water to form solutions to facilitate or modify the action of media against components.

There are very few occasions when media can be used with no water and, therefore, no compound. There are some occasions when the parts themselves act as the media; this is a self-tumbling process.

Clearly, the selection of media and compounds for the mass finishing operation is as important as the selection of the correct tooling for any forming operation, and an understanding of the materials available is essential for effective use of equipment.

Mass Finishing Compounds. The correct use of compound-water solutions is vital to good and consistent mass finishing processing in any equipment. The compound solution is used to:

- Develop and maintain cleanliness of parts and media during the process
- Control pH, foam, and water hardness
- Wet surfaces
- Emulsify oily soils
- Remove tarnish or scale
- Control part color
- Suspend soils
- Control lubricity
- Prevent corrosion
- Provide cooling
- Ensure effluent meets EPA, OSHA, and plant standards

Compounds may be liquid or powder. Addition of compound to the mass finishing equipment may be made in three ways:

- *Batch:* This is the simplest technique, used in closed machines, barrels, small centrifugal barrels, and vibrators with no drains. The machine is charged with compound and water, which is flushed away at the end of the process cycle.
- *Recirculation:* The solution is mixed in a tank and pumped into the process, allowing it to drain back into the tank for reuse. This process is simple and has the basic benefit that there is no continuous drainage, and the effluent can be treated on a batch basis. The major disadvantage of this system is that the solution deteriorates during its life and, therefore, results vary. For this reason, recirculation should be avoided if at all possible.
- *Flow-through:* This system pumps fresh solution into the machine, allows it to act, and then drains it out. Modern compound solutions can be very dilute and economical. For example, a 0.3 m^3 (10 ft^3) machine normally uses less than 4 L (1 gal) of compound per shift. When using flow-through systems with liquid compounds, automatic addition through a compound metering pump is possible, further reducing waste and improving consistency of the process.

Because the use of a flow-through compound solution system permits close control and is readily automated, liquid compounds are normally preferred for consistent results. When mass finishing in closed-batch systems, powdered compounds can be economical. Powdered compounds can include loose abrasives that enhance cutting capabilities of media. Abrasives are seldom recommended in vibratory systems.

Finishing Media. The media in the mass finishing operation are equivalent to the tooling used in any machining operation. The functions of media are to abrade or burnish edges and surfaces of components to be finished and to keep parts separate from one another to avoid or limit any part-on-part impingement. Media may be selected from any of the following materials:

- *Natural media:* Stones that have been quarried, crushed, and graded were the original media for mass finishing operations. Natural media have been largely replaced by synthetic materials that are harder with longer life; greater consistency of cut, wear, and dimension; and greater variety of capabilities.
- *Agricultural materials:* Sawdust, corncob, and walnut shells are frequently used in mass finishing machines for drying. Mixed with fine abrasives, these materials are suited for some fine polishing operations, particularly in the jewelry industry. Wood pegs may be coated with fine abrasives or waxes for edge radiusing and finishing of some wooden and plastic components.
- *Synthetic random media:* Fused and sintered aluminum-oxide media, crushed and graded, are available in a number of grades, both heavy cutting and fine finishing. Generally they are much tougher than natural media and more consistent.
- *Preformed ceramic media:* Porcelain or other vitreous material is mixed with abrasives and formed into shapes, then fired to vitrify. These media are available in a large range of shapes, sizes, grades of abrasive, proportions of abrasive to binder, and types of binder to enable selection of material to suit virtually every application. The consistency of quality can be ensured. This type of material is the present standard for the mass finishing industry.
- *Preformed resin-bonded media* are abrasives bonded into polyester or urea-formaldehyde resins. Like the ceramic materials, these are available in a broad range of shapes and sizes with different types, grades, and quantities of abrasive to meet a range of applications. Plastic media are somewhat softer than ceramic, and for a given degree of abrasion they usually have shorter life, but they also have somewhat lower cost and lower density. These softer materials achieve better preplate finish than other media and are better suited for handling soft metals.
- *Steel:* Hardened steel preformed shapes are available in a variety of shapes and sizes and are well suited for burnishing. Steel applications also include cleaning and light deburring. The basic benefit is that these media wear very little. Although there is a high initial investment, they are not consumable and do not need reclassification. Steel pins and tacks used with abrasive compounds can be useful means of removing somewhat inaccessible burrs.

Final selection of the best media must be made on a trial and error basis, but the following factors affecting selection should be understood and considered before any form of testing is started:

Shape and size of media

- To remove burrs
- To achieve uniform edge and surface finishes
- To avoid jamming in holes and recesses
- To achieve ease of separation
- To achieve shortest cycle time

Availability and cost of media

- From consistent supplier
- For economical cost per pound or unit volume

- For consistent quality

Ability and versatility of media

- For minimum wear and reclassification
- For handling a range of products within a given machine
- For minimum break-in requirements
- For cushioning action between parts

Optimum media-to-part ratio is another consideration for choosing the best media (Table 2).

Table 2 Typical media-to-part ratios for vibratory and tumbling mass finishing processes

Media to part ratio, by volume	Commercial application
0:1	No media, part-on-part, used for beating off burrs, no media for cutting, sometimes suitable for burnishing
1:1	Equal volumes of media and parts, forgings, and castings; crude, very rough surfaces
2:1	More gentle, more separation, still severe part-on-part damage is possible
3:1	About minimum for nonferrous parts, considerable part-on-part contact, fair to good for ferrous metals
4:1	Probably average conditions for nonferrous parts, fair to good surfaces, good for ferrous metals
5:1	Good for nonferrous metals, minimal part-to-part contact
6:1	Very good for nonferrous parts, common for preplate work on zinc with plastic media
8:1	For higher-quality preplate finishes
10:1 to 15:1 or more	Better, used for very irregularly shaped parts or parts that tangle or bend
No contact	Absolutely no part-on-part contact, one part per machine or compartment, part fixturing

Mass Finishing Process Considerations

The mechanical finishing department in virtually every metal-working plant is used as a general rectification shop. This is inevitable because metal forming machinery does not produce consistent burrs or truly consistent surface and edge finish conditions. Equipment in the mechanical finishing department should be sufficiently versatile to meet the changing quality of parts.

Cleanliness. Most mass finishing processes tolerate some oil, scale, and dirt on components. In fact, mass finishing is frequently used as a highly effective means of cleaning components, having both mechanical and chemical action; however, some operations, particularly super finishing on very high-precision parts, demand cleanliness or at least consistency of any surface contamination. The finishing department should be notified of any changes in prior operations, such as change of machining lubricants or heat treatment methods.

Ancillary Equipment. Most mass finishing processes are wet operations. After parts are unloaded from the mass finishing equipment, parts are rinsed, corrosion protection is applied, and the parts are dried. A decision must be made whether these processes are separate from the mass finishing machine or if combination compounds could incorporate these steps in the finishing machine.

There is a requirement to separate parts from media by screening or magnetic separation. Media reclassification is also frequently incorporated into a screening separator.

Automation. Opportunities to automate mass finishing should be investigated. Mass finishing operation requires measured quantities of parts and media to be placed into the equipment; controlled addition of compound solution with change of solution at some point during the process cycle; unloading of the equipment; separation of parts from media; washing, drying, and conveying parts; and classification, conveying, and storage of media. Such a sequence may represent a substantial labor involvement and many opportunities for errors that are difficult to control. The cost of automation is repaid by improved work flow, improved quality, and lower labor costs.

Process Instructions and Control. Process instructions should cover all variables, which include:

- Machine cycle, including process times, barrel speeds, or vibratory frequency and amplitude, or G force and speed, depending on type of equipment
- Load levels, total load, and proportion of parts to media
- Compound and water flow rates
- Media and compound variables
- Pretreatment and post-treatment variables

Masking and Fixturing. Holes in components with rubber or plastic are plugged to keep media from being jammed into those holes during processing. Corners and edges that must be left sharp can also be masked. Some components are processed on fixtures in the mass finishing equipment. This is essential for spindle finishing. In some mass finishing equipment, large components are better processed in individual compartments within the machine. Occasionally, threads are masked that might get damaged or abraded too much during processing.

Causes of Difficulties Commonly Encountered in Mass Finishing. The following is a list of difficulties encountered during mass finishing processes:

Excessive impingement on part surface

- Insufficient amount of media in chamber
- Parts in work load too large for the machine
- Excessive equipment speed or amplitude
- Low solution level or flow rate
- Insufficient or wrong compounds
- Undesirable handling methods
- Media too large for part size
- Wrong type of media

Rollover of edges, corners, and burrs

- Abrasive action too slow
- Wrong type of media
- Media particles too large for part size
- Excessive equipment speed or amplitude
- Excessive work load for volume of media
- Incorrect water level

- Processing time too long

Persistent lodging of media in holes, slots, or recessed areas

- Wrong size of media
- Wrong shape of media
- Excessive wear or depreciation of media
- Media fracturing during operation
- Failure to classify media as required

Poor surface finish

- Insufficient cutdown in process
- Inadequate flushing and cleaning of equipment
- Incorrect compound
- In-process corrosion
- Water flow not correct
- Media too aggressive or too hard
- Part-on-part impingement

Safety Precautions

In addition to the normal hazards with rotating machinery, other hazards in finishing are generation of gas, usually flammable, in a closed barrel, and handling of acid or alkaline compounds. Accidents caused by a buildup of gas pressure within a closed barrel have ranged from the blowing off of a cover during its removal to the fracture and fragmentation of portions of a barrel during operation. All closed barrels should have a cover-locking device that permits loosening of the cover but restrains it so that it cannot be blown off. Ventilation of the barrel, preferably automatic, is also highly recommended.

Hazards connected with the use of acids and alkalis are generally recognized. The use of rubber gloves and face masks is recommended.

Waste Disposal

Some compounds used in barrel finishing are harmful and their disposal may pose problems. In all instances, local regulations should be checked before establishing any procedure for waste disposal.

Most compounds are alkaline when mixed with water, although some are acid. Compounds containing cyanides or chromates are toxic and are not recommended.

Methods of waste treatment include:

- Neutralizing acid or alkaline waste before disposal
- Removing oils by running the solution under a skimming bar
- Settling out solid wastes in a basin, preferably after neutralization

Shot Peening

Revised by Ted Kostilnik, Wheelabrator Corporation

Introduction

SHOT PEENING is a method of cold working in which compressive stresses are induced in the exposed surface layers of metallic parts by the impingement of a stream of shot, directed at the metal surface at high velocity under controlled conditions. It differs from blast cleaning in primary purpose and in the extent to which it is controlled to yield accurate and reproducible results. Although shot peening cleans the surface being peened, this function is incidental. The major purpose of shot peening is to increase fatigue strength. The process has other useful applications, such as relieving tensile stresses that contribute to stress-corrosion cracking, forming and straightening of metal parts, and testing the adhesion of silver plate on steel.

Peening Action

When individual particles of shot in a high-velocity stream contact a metal surface, they produce slight, rounded depressions in the surface, stretching it radially and causing plastic flow of surface metal at the instant of contact. The effect usually extends to about 0.13 to 0.25 mm (0.005 to 0.010 in.) but may extend as much as 0.50 mm (0.02 in.) below the surface. The metal beneath this layer is not plastically deformed. In the stress distribution that results, the surface metal has induced or residual compressive stress parallel to the surface, while metal beneath has reaction-induced tensile stress. The surface compressive stress may be several times greater than the subsurface tensile stress. This compressive stress offsets any service-imposed tensile stress, such as that encountered in bending, and improves fatigue life of parts in service markedly.

Peening action improves the distribution of stresses in surfaces that have been disturbed by grinding, machining, or heat treating. It is particularly effective on ground or machined surfaces, because it changes the undesirable residual tensile stress condition that these processes usually impose in a metal surface to a beneficial compressive stress condition. Shot peening is especially effective in reducing the harmful stress concentration effects of notches, fillets, forging pits, surface defects, and the low-strength effects of decarburization, and the heat-affected zones of weldments.

Strain Peening. The magnitude of residual stress that can be induced by shot peening is limited. In hard metals, it is slightly more than half the yield strength. A higher residual stress, approaching the full yield strength, can be obtained by strain peening, which consists of peening the surface as it is being strained in tension. The effectiveness of strain peening is limited to parts such as springs, gears, and shafts, that are subjected to unidirectional service loads.

Surface Coverage and Peening Intensity

The workpiece surface being peened is affected by the amount of the target surface peened and the effectiveness of the peening action on that target surface.

Surface coverage is a measure of how completely an area has been hit by the myriad of impinging shot particles. Without 100% coverage or saturation, the improvement in fatigue characteristics conventionally produced by shot peening is not obtained.

As stated in SAE Recommended Practice J443, "Procedure for Using Shot Peening Test Strip," a definite and quantitative relationship between coverage and exposure time exists, which may be expressed as follows:

$$C_n = 1 - (1 - C_1)^n$$

where C_1 is the percentage of coverage (decimal) after 1 cycle, C_n is the percentage of coverage (decimal) after n cycles, and n is the number of cycles.

This relationship indicates that coverage approaches 100% as a limit. Accurate measurements above 98% coverage are difficult to obtain, but a measurement at a lower degree of coverage serves as a means of determining the exposure time or equivalent time required to obtain any desired coverage. Because accurate measurement can be made up to 98%

coverage, this value is arbitrarily chosen to represent full coverage or saturation. Peening at less than saturation is ineffective because of the amount of unpeened surface. Beyond this value, the coverage is expressed as a multiple of the exposure time require to produce saturation. For example, 1.5 coverage represents a condition in which the specimen or workpiece has been exposed to the blast 1.5 times the exposure required to obtain saturation. Figure 1 shows the relationship between exposure time and coverage and indicates that after a measurement of a low percentage of coverage has been established, the correct exposure time for any percentage of coverage can be readily determined.

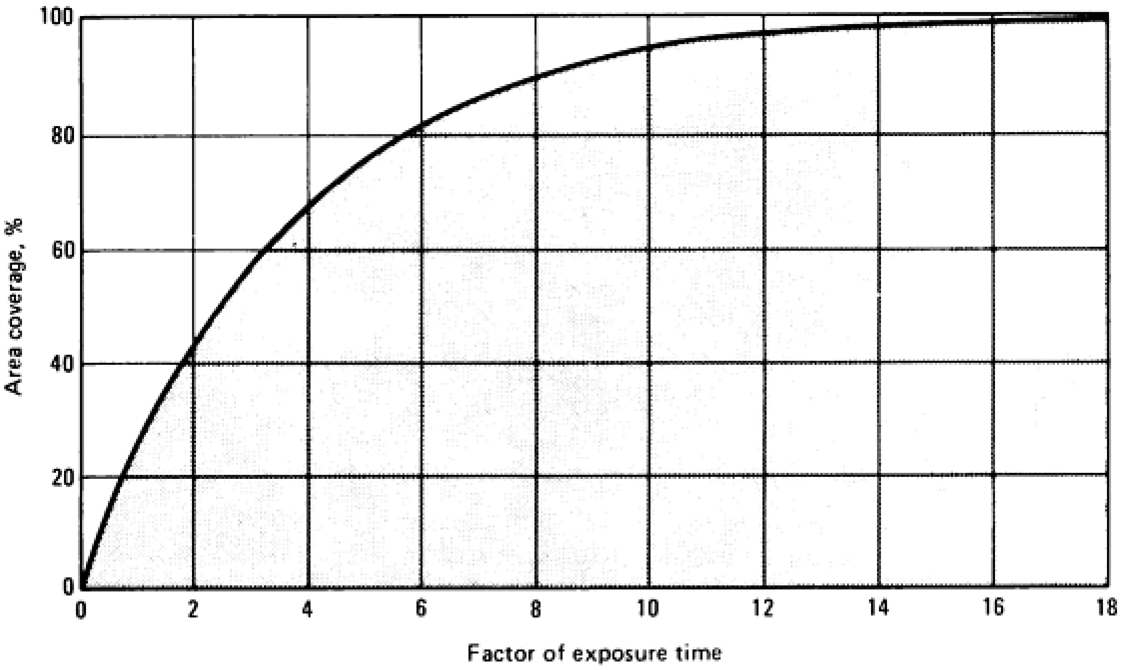


Fig. 1 Area coverage as a function of exposure time in shot peening

Measurement of Coverage. Direct methods for measuring coverage include visual methods and the Straub method. One of the indirect methods is the Valentine method, which involves layer removal.

Visual methods, although not quantitative, are almost universally used. The simplest of these consists of visual inspection, with or without the aid of optical (10×) magnification of the surface of the peened part. This method may be supplemented by a series of reference photographs illustrating various percentages of coverage.

Another visual method consists of preparing a transparent plastic replica of the peened surface and comparing it, by means of photographic projection, with reference replicas having various percentages of coverage.

The Straub method consists of exposing a polished surface to the shot stream, projecting the surface at a magnification of 50 diameters on the ground glass of a metallographic camera, tracing the images of the indented areas on translucent paper, and measuring the total area and the indented area with a planimeter. Percentage of coverage is expressed as the ratio of indented area to total area multiplied by 100. About 15 min is required to make one measurement.

The Peenscan method is offered in lieu of visual inspection in MIL-S-13165 and consists of painting a part before peening with a dye sensitive to ultraviolet light, shot peening the part, inspecting the part under the ultraviolet light for any missed areas, shot peening the part, and reinspecting the part under ultraviolet light. Complete removal of the dye indicates 100% coverage of the part.

The Valentine method consists of making a duplicate of the part from low-carbon steel, peening the part, annealing it for several hours to promote recrystallization and grain growth, and relating peening coverage to the amount and continuity of grain growth by metallographic examination of cross-sectional areas.

Because of the difficulty in quantitatively measuring coverage by these methods, percent coverage is usually estimated from the curve of Almen arc height against the duration of shot exposure. The Almen test is described in the section "Peening Test Strips, Holder, and Gage" in this article. The graph in Fig. 2 shows the relation between shot coverage and doubling exposure time. A change in arc height of 10% or less indicates saturation peening.

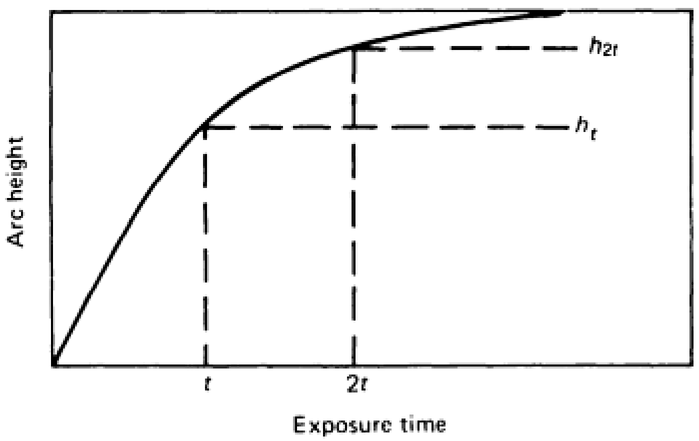


Fig. 2 Relation of measuring coverage to peening time. Coverage is considered full at time *t*, if doubling exposure to time 2*t* results in change in arc height less than 10%.

Peening intensity is governed by the velocity, hardness, size, and weight of the shot pellets, and by the angle at which the stream of shot impinges against the surface of the workpiece. Intensity is expressed as the arc height of an Almen test strip at or at more than saturation coverage. Arc height is the measure of the curvature of a test strip that has been peened on one side only. At or above saturation of the Almen strip, arc height is a measure of the effectiveness of the peening operation on a specific part. The Almen test is the primary standard of quality control and should be used at regular intervals, often on a day-to-day basis, and in the same location in the peening setup. Used correctly, a lower arc height indicates a reduction in peening intensity caused by a reduction in wheel speed or air pressure, excessive breakdown of shot, or other operational faults, such as undersized shot in the machine or clogged feed valves.

Selection of Intensity. The lowest peening intensity capable of producing the desired compressive stress is the most efficient and least costly, because the peening process can be achieved with the minimum shot size in the minimum exposure time. Conversely, an intensity may be considered excessive if, as with very thin parts, a condition is produced in which the tensile stresses of the core material outweigh the beneficial compressive stresses induced at the surface. Figure 3 presents data that indicate the relation of peening intensity to cross-sectional thickness.

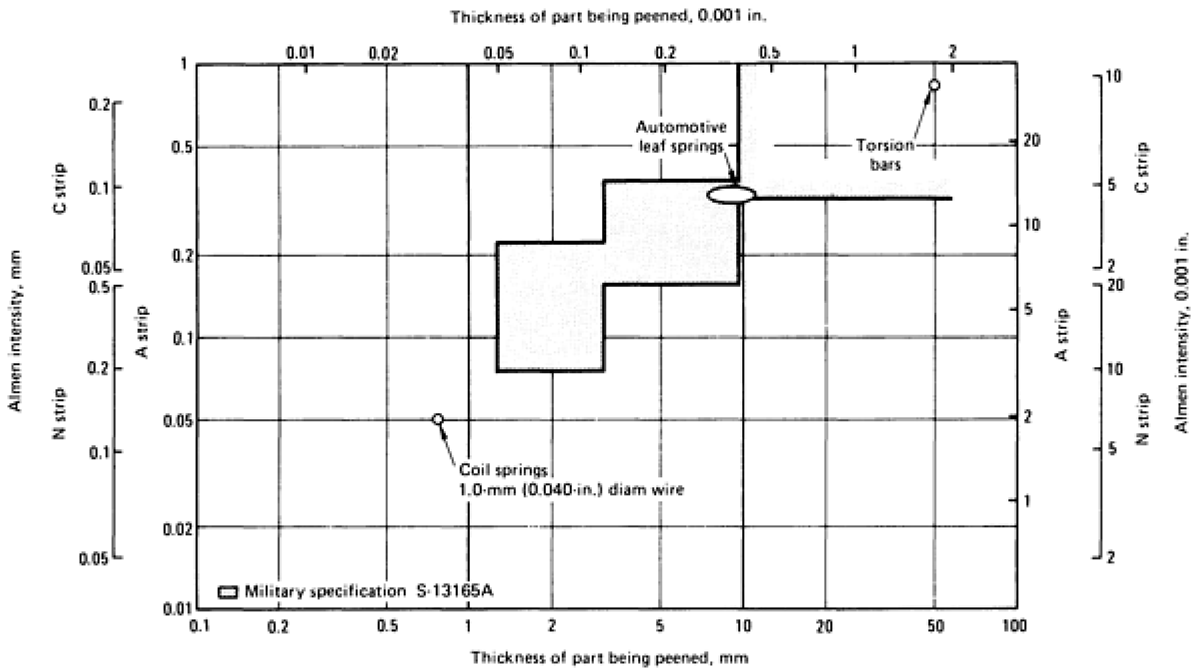


Fig. 3 Relation of peening intensity to cross-sectional thickness of parts peened

The depth of compressed layer to be produced by peening is a factor in selecting peening intensity. For instance, a heavy steel component with a partially decarburized skin requires a peening intensity high enough to induce a compressive stress beneath the decarburized layer. The relation between peening intensity and depth of compressed layer, for steel hardened to 31 and 52 HRC, is shown in Fig. 4.

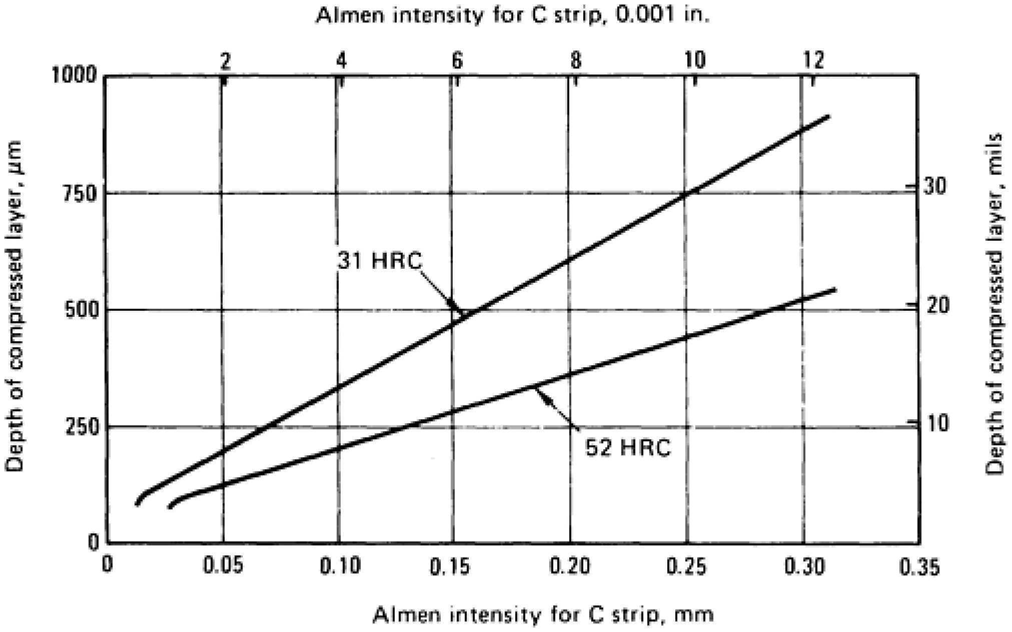


Fig. 4 Relation of depth of compressed layer to peening intensity for steel of two different hardnesses

Types and Sizes of Media

Media used for peening can be iron, steel, or glass shot, or cut steel or stainless steel wire. Metallic shot is designated by numbers according to size. Shot numbers, as standardized by MIL-S-13165, range from S70 to S930. The shot number is approximately the same as the nominal diameter of the individual pellets in ten thousandths of an inch. Standard size specifications for cast iron and steel shot are given in Table 1.

Table 1 Cast shot numbers and screening tolerances

Numbers in parentheses measured in inches

Peening shot size No.	All pass U.S. screen size	Maximum 2% on U.S. screen	Maximum 50% on U.S. screen	Cumulative minimum 90% on U.S. screen	Maximum 8% on U.S. screen	Maximum number of deformed shot acceptable
930	5 (0.157)	6 (0.1320)	7 (0.1110)	8 (0.0937)	10 (0.0787)	5[(a)]
780	6 (0.132)	7 (0.1110)	8 (0.0937)	10 (0.0787)	12 (0.0661)	5[(a)]
660	7 (0.111)	8 (0.0937)	10 (0.0787)	12 (0.0661)	14 (0.0555)	12[(a)]
550	8 (0.0937)	10 (0.0787)	12 (0.0661)	14 (0.0555)	16 (0.0469)	12[(a)]
460	10 (0.0787)	12 (0.0661)	14 (0.0555)	16 (0.0469)	18 (0.0394)	15[(a)]
390	12 (0.0661)	14 (0.0555)	16 (0.0469)	18 (0.0394)	20 (0.0331)	20[(a)]
330	14 (0.0555)	16 (0.0469)	18 (0.0394)	20 (0.0331)	25 (0.0280)	20[(b)]
280	16 (0.0469)	18 (0.0394)	20 (0.0331)	25 (0.0280)	30 (0.0232)	20[(b)]
230	18 (0.0394)	20 (0.0331)	25 (0.0280)	30 (0.0232)	35 (0.0197)	20[(b)]
190	20 (0.0331)	25 (0.0280)	30 (0.0232)	35 (0.0197)	40 (0.0165)	20[(b)]
170	25 (0.0280)	30 (0.0232)	35 (0.0197)	40 (0.0165)	45 (0.0138)	20[(b)]
130	30 (0.0232)	35 (0.0197)	40 (0.0165)	45 (0.0138)	50 (0.0117)	30[(c)]
110	35 (0.0197)	40 (0.0165)	45 (0.0138)	50 (0.0117)	80 (0.0070)	40[(c)]
70	40 (0.0165)	45 (0.0138)	50 (0.0117)	80 (0.0070)	120 (0.0049)	40[(c)]

(a) Per area, 1 in. square.

(b) Per area, $\frac{1}{2}$ in. square.

(c) Per area, $\frac{1}{4}$ in. square

Glass shot, used primarily for peening nonferrous material, is available in a wider range of basic diameters. Hardness of glass shot is equivalent to 46 to 50 HRC. For further information on glass beads, see the article "Mechanical Cleaning Systems" in this Volume. Table 2 shows the effect of shot size and peening intensity on fatigue life.

Table 2 Effect of shot peening on fatigue strength of aluminum alloys and carbon and low-alloy steels

Metal tested	Type of specimen	Stress cycle	Surface condition as-received
Aluminum alloys			
2014-T6	Plain, 38 mm (1.5 in.) diam	Reversed bending	Smooth turned[(a)]
2024-T4	Plain, 38 mm (1.5 in.) diam	Reversed bending	Turned[(a)]
7079-T6	Plain, 38 mm (1.5 in.) diam	Reversed bending	Turned[(a)]
7075-T6		Reversed bending	Turned[(a)]
Carbon and low-alloy steels			
5160 spring steel[(c)]	Flat leaf, 38 mm (1.5 in.) wide, 4.88 mm (0.192 in.) thick	Unidirectional bending	Machined before heat treatment[(d)]
1045 steel (165 HB)	Plain (R.R. Moore)	Rotating bending	Machined
1045 steel (285 HB)	Plain (R.R. Moore)	Rotating bending	Machined
9260 steel (526 HB)	Plain (R.R. Moore)	Rotating bending	Machined
Ingot iron (121 HB)	Plain (R.R. Moore)	Rotating bending	Machined
4340 steel (277 HB)	Plain (R.R. Moore)	Rotating bending	Machined

4118 steel (60 HRC)	Single gear tooth	Unidirectional bending	Machined
8620 steel (58 HRC)	Single gear tooth	Unidirectional bending	Machined
S-11 steel[n]	Grooved, 7 mm (0.3 in.) D[o]	Rotating bending	Machined
0.54% C steel[q]	Plain, 8 mm (0.315 in.) diam	Rotating bending	Decarburized
	Plain, 5.99 mm (0.236 in.) diam	Reversed torsion	Decarburized
	10.0 mm (0.394 in.) diam bars:		
	Smooth	Rotating bending	Polished
	Round-notched[r]	Rotating bending	Machined
	V-notched[s]	Rotating bending	Machined[t]
Music wire[u]	Coil spring	Not reversed	. . .
4340 steel[w]	14 mm (0.560 in.) diam[x]	Reversed torsion	Smooth turned
4340 steel[z]	6.4 mm (0.250 in.) diam[x]	Rotating bending	Highly polished
4340 steel[}]	6.4 mm (0.250 in.) diam[x]	Rotating bending	Highly polished

Metal tested	**Peening conditions**				**Fatigue strength**						**Strength gain by peening, %**		**Ref**
	Shot		**Intensity**		**As-received**		**Polished**		**Peened**		**Over as-rec'd**	**Over polished**	
	Type	**Size No.**	**0.025 mm**	**0.001 in.**	**7 MPa**	**1 ksi**	**7 MPa**	**1 ksi**	**7 MPa**	**1 ksi**			
Aluminum alloys													
2014-T6	Cast steel	70	0.15	6 A	215	31[b]	. . .	. . .	260	38[b]	23	. . .	. . .
		230	0.76	30 A	215	31[b]	. . .	. . .	260	38[b]	23	. . .	. . .

		550	0.33	13 A	215	31[b]	. . .	. . .	260	38[b]	23	. . .	. . .
2024-T4	Cast steel	230	0.25	10 A	180	26[b]	. . .	. . .	240	35[b]	34	. . .	. . .
7079-T6	Cast steel	230	0.25	10 A	195	28[b]	. . .	. . .	250	36.5[b]	30	. . .	. . .
7075-T6		MIL-5	0.15	6 A	220	32[b]	. . .	. . .	275	40[b]	25	. . .	[~]
Carbon and low-alloy steels													
5160 spring steel[c]	Chilled iron	230[e]	0.15	6 C[f]	880	128[g]	. . .	. . .	1340	194[g]	51	. . .	[!]
		230[e]	0.15	6 C	880	128[g]	. . .	. . .	1215	176[g]	37	. . .	. . .
		230[e]	0.15	6 C[h]	880	128[g]	. . .	. . .	970	141[g]	10	. . .	. . .
1045 steel (165 HB)	Chilled iron	[i]	[j]	[j]	. . .	. . .	275	40[k]	305	43.8[k]	. . .	10	[?]
1045 steel (285 HB)	Chilled iron	[i]	[j]	[j]	. . .	. . .	560	81[k]	515	75[k]	. . .	-7	[?]
9260 steel (526 HB)	Chilled iron	[i]	[j][l]	[j][l]	. . .	. . .	750	109[k]	730	106[k]	. . .	-2	[?]
Ingot iron (121 HB)	Chilled iron	[i]	[j][l]	[j][l]	. . .	. . .	185	27[k]	185	27[k]	. . .	0.7	[?]
4340 steel (277 HB)	Chilled iron	[i]	[j]	[j]	. . .	. . .	455	66[k]	540	78[k]	. . .	18	[?]
4118 steel (60 HRC)	Cast steel	110	0.20-0.25	8-10 A	16,200	2,350[m]	. . .	. . .	20,900	3,025[m]	29	. . .	[>]
8620 steel (58 HRC)	Cast steel	230	0.41	16 A	86,185	12,500[m]	. . .	. . .	105,150	5,250[m]	22	. . .	[>]
S-11 steel[n]	. . .	280	[p]	[p]	260	38	. . .	. . .	420	61	62	. . .	[<]
0.54% C steel[q]	Chilled iron	460	0.48	19 A	310	45	. . .	. . .	475	69	54	. . .	[+]

	Chilled iron	460	0.48	19 A	225	33	. . .	. . .	325	47	43	. . .	. . .
	Chilled iron	460	0.48	19 A	585	85	. . .	. . .	600	87	3	. . .	[+]
	Chilled iron	460	0.48	19 A	285	43	. . .	. . .	395	57	33	. . .	. . .
	Chilled iron	460	0.48	19 A	185	27	. . .	. . .	325	47	73	. . .	. . .
Music wire[u]	. . .	110	. . .	. . .	825	120[v]	. . .	. . .	1310	190[v]	58	. . .	[++]
4340 steel[w]	Cast steel	170	0.20	8 A	275	40[g]	. . .	. . .	515	75[g][y]	87	. . .	[*]
4340 steel[z]	. . .	. . .	0.25	10 A	570	83	270	39[{]	675	98[|]	. . .	150	[**]
4340 steel[}]	. . .	. . .	0.25	10 A	725	105	380	55[{]	710	103[|]	. . .	87	[**]

(a) 0.50 μm (20 μin.).

(b) Values at 1,000,000 cycles.

(c) Oil quenched and tempered at 370 °C (700 °F), hardness is 46 to 50 HRC.

(d) 0.2 to 0.3 μm (7 to 12 μin.).

(e) Shot peened only on side subjected to tension in fatigue test.

(f) Peened under a strain +0.60, 1240 MPa (180 ksi).

(g) Fatigue limit based on 5,000,000 cycles.

(h) Peened under zero strain.

(i) Equal parts of 170 and 280.

(j) Depth of cold work, peening, 150 µm (6 mils).

(k) Fatigue limit based on 10,000,000 cycles.

(l) Stress relieved at 205 °C (400 °F) for 20 min after peening.

(m) Fatigue limit in kilograms (pounds) load based on 5,000,000 cycles.

(n) 3% nickel-chromium steel, oil quenched from 830 °C (1525 °F), tempered at 600 °C (1110 °F), tensile strength 930 MPa (135 ksi).

(o) 0.79 mm (0.031 in.) semicircular groove.

(p) Air pressure, 345 kPa (50 psi).

(q) Tensile strength, 1410 MPa (205 ksi).

(r) Notch depth 1.0 mm (0.040 in.), radius 0.051 mm (0.002 in.).

(s) Notch depth 1.0 mm (0.040 in.).

(t) Root of notch not hit by shot.

(u) 0.99 mm (0.039 in.) diam.

(v) For 400,000-cycle life.

(w) Tensile strength 1860 MPa (270 ksi).

(x) Chromium plated.

(y) Same value obtained for peened and chromium plated; not peened and plated is less than 275 MPa (40 ksi).

(z) Tensile strength 1520 MPa (220 ksi).

({) Fatigue limit for chromium plated and baked.

(|) Fatigue limit for peened, chromium plated, and baked.

(}) Tensile 1990 MPa (288 ksi).

(~) Fatigue Strength of 7075-T6 Aluminum Alloys When Peened with Steel Shot or Glass Beads, Potters Industries PII-I-74, 1974.

(!) R.L. Mattson and J.G. Roberts, The Effect of Residual Stresses Induced by Strain-Peening upon Fatigue Strength, *Internal Stresses and Fatigue in Metals*; Elsevier, Amsterdam, 1958.

(?) J.M. Lessells and W.M. Murray, *Proc. ASTM*, 41, 659 (1941).

(>) J.A. Halgren and D.J. Wulpi, *Trans. SAE*, 65, 452 (1957).

(<) W.J. Harris, *Metallic Fatigue*, Pergamon, 1961.

(+) S. Takeuchi and M. Honma, Effect of Shot Peening on Fatigue Strength of Metals, *Reports of the Research Institute for Iron, Steel and Other Metals*, Tohoku University, Sendai, Japan, 1959.

(++) H.C. Burnett, *Proc. ASTM,* 58, 515 (1958).

(*) "Effect of Chromium Plate on Torsion Fatigue Life of Shot Peened 4340 Steel," Douglas Aircraft Co. Report No. MP 20.005 (Sept. 13, 1960); available through SAE.

(**) B. Cohen, "Effect of Shot Peening Prior to Chromium Plate on the Fatigue Strength of High Strength Steel," WADC Technical Note 57-178, U.S. Air Force, June 1957

Cast steel shot is made by blasting a stream of molten steel with water and forming globules that rapidly solidify into nearly spherical pellets. This process is also called atomizing. The pellets are screened for sizing, reheated for hardening, quenched, and tempered to the desired hardness. According to SAE Recommended Practice J827, "Cast Steel Shot," 90% of the hardness measurements made on the representative sample should fall within the range equivalent to 40 to 50 HRC. To maximize the peened effect, shot should always be at least as hard as the workpiece. For hard metals, special hard-cast steel shot, 57 to 62 HRC, should be used.

Cast steel shot is the most widely used peening medium. With suitable heat treatment, it has a useful life many times that of cast iron shot. Its improved impact and fatigue properties markedly lower the rate of shot breakage, increase peening quality, and extend the life of components of peening machines.

Cast iron shot or chilled iron is brittle, with an as-cast hardness of 58 to 65 HRC. It breaks down rapidly; however, its inherently high hardness yields higher peening intensities for a given shot size, in comparison to softer materials. A high rate of shot breakage complicates the control of peening quality and increases the cost of equipment maintenance and cost of shot, because broken shot must be eliminated for best results.

Glass beads are used for peening stainless steel, titanium, aluminum, magnesium, and other metals that might be contaminated by iron or steel shot. They are also used for peening thin sections. Relatively low Almen A shot peening intensities, seldom exceeding 0.15 to 0.25 mm (0.006 to 0.010 in.), are used. Glass beads can be used in either wet or dry peening processes.

Cut wire is generally manufactured from carbon steel or stainless steel. The cut wire is mechanically manufactured and as a result is more uniform than cast steel or iron shot in size distribution. For peening applications, it is "conditioned" or

blasted into a spherical shape. This conditioning process also hardens the cut wire media. For information about sizing and related subjects, see the article "Mechanical Cleaning Systems" in this Volume.

Control of Process Variables

Major variables in the shot peening process are shot size and hardness, shot velocity, surface coverage, angle of impingement, the resulting peening intensity, and shot breakdown. The quality and effectiveness of shot peening depend on the control of each of these interdependent variables.

Size of Shot. When other factors, such as shot velocity and exposure time, are constant, an increase in shot size results in an increase in peening intensity and depth of the compressed layer, plus a decrease in coverage. Selecting the minimum shot size capable of producing the required intensity is preferable to take advantage of the more rapid rate of coverage obtained with smaller shot.

The selection of a particular shot size may be dictated by the shape of the part to be peened. In shot peening of the fir-tree serrations of steel compressor blades, complete coverage can be obtained only if the radius of the shot does not exceed the radius of the serrations. The same principle applies to the selection of shot size for peening the root radius of threads. When peening fillets, the diameter of the shot used should not exceed one half the radius of the fillet.

Hardness of Shot. Variations in the hardness of shot do not affect peening intensity, provided the shot is harder than the workpiece. If the shot is softer than the workpiece, a decrease in intensity occurs.

Velocity of Shot. Peening intensity increases with shot velocity; however, when velocity is increased, shot must be inspected for breakdown more frequently for purging the system of broken shot.

Angle of Impingement. By definition, the angle of impingement is the angle, 90° or less, between the surface of the workpiece and the direction of the blast. As this angle is decreased from 90°, peening intensity is reduced. Peening intensity varies directly as the sine of the angle of impingement. When a low impingement angle is unavoidable, increases in shot size and velocity may be required to attain a desired intensity.

Breakdown of Shot. To maintain the required intensity and to provide consistent peening results, a production peening unit must be equipped with a separator that continuously removes broken or undersized shot from the system. The rate of removal should approximate the rate of wear and breakdown. The percentage of full-size and rounded shot in the system should never fall below 85%. Higher percentages are preferred. Sharp-edged broken media can scratch a part, generating a stress raiser; therefore, rounded shot, like minuscule peening hammers, is mandatory. Integral shot conditioners on peening machines consist of screens of air wash systems, neither of which can fully discriminate whether shot is broken because these devices are designed to handle only the specific weight of the shot. The only practical method of maintaining 85% good shot in the machine is to remove the entire shot load and reclassify it in a separate machine that distinguishes both size and shape.

Equipment

The equipment used in shot peening is essentially the same as that used in abrasive blast cleaning, except for certain auxiliary equipment made necessary by the more stringent controls imposed in the shot peening process. For a description of basic equipment, such as cabinets, wheels, nozzles, and conveyors, see the article "Mechanical Cleaning Systems" in this Volume.

The principal components of shot peening equipment are a shot-propelling device, shot recycling and classification arrangements, and a work handling conveyor. All portions of equipment that are exposed to the stream of shot are enclosed to confine the shot and permit it to be recycled.

Propulsion of Shot. Two methods of propelling the shot are used widely in shot peening. One uses a motor-driven bladed wheel, rotating at high speed. The other uses a continuous stream of compressed air.

In the wheel method, shot is propelled by a bladed wheel that uses a combination of radial and tangential forces to impart the necessary peening velocity to the shot. The position on the wheel from which the spot is projected is controlled to concentrate the peening blast in the desired direction. Among the advantages of the wheel method of propulsion are easy

control of shot velocity when equipped with a variable-speed drive, high production capacity, lower power consumption, and freedom from the moisture problem encountered with compressed air.

The air blast method introduces the shot, either by gravity or by direct pressure, into a stream of compressed air directed through a nozzle onto the work to be peened. Aside from being more economical for limited production quantities, the air blast method can develop higher intensities with small shot sizes, permits the peening of deep holes and cavities by using a long nozzle, consumes less shot in peening small areas on intricate parts, and has lower initial cost, especially when a source of compressed air is already available.

In the late 1970s, another peening method was developed that uses gravitational force to propel the shot. Kinetic energy of the peening media is closely controlled by requiring the media to pass through a labyrinth before falling on the substrate from specified heights. Utilizing 1 to 2 mm (0.04 to 0.08 in.) hardened and polished steel balls as a peening media, surface finishes of less than 0.38 μm (15 μin.) are obtained while peening in the range of 0.23 to 0.38 mm (0.009 to 0.010 in.) Almen N shot peening intensities. Gravity peening has the drawback of requiring much more time for saturation, due to much lower impact velocities and greater shot diameter.

Cycling of Shot. Equipment for shot recycling consists of devices for the separation and removal of dust and undersize shot from the used shot mix. An air current or air wash, adjusted to the size of shot being processed, passes through a thin curtain of used shot as it falls through the separator. The air draws the dust and undersized shot from the mix, allowing the reusable shot to fall into a hopper for storage until needed at the peening machine. The major differences between the low-volume and the high-volume separators, illustrated in Fig. 5 and 6, are the use of trash removal screen in the low-volume separator (Fig. 5) prior to the air wash and the direct dumping of used shot from the elevator buckets into the separator (not shown), in contrast to the hopper and screw conveyor feed of used shot into the high-volume separator (Fig. 6). The effectiveness of the separator depends on careful control of the velocity of the air.

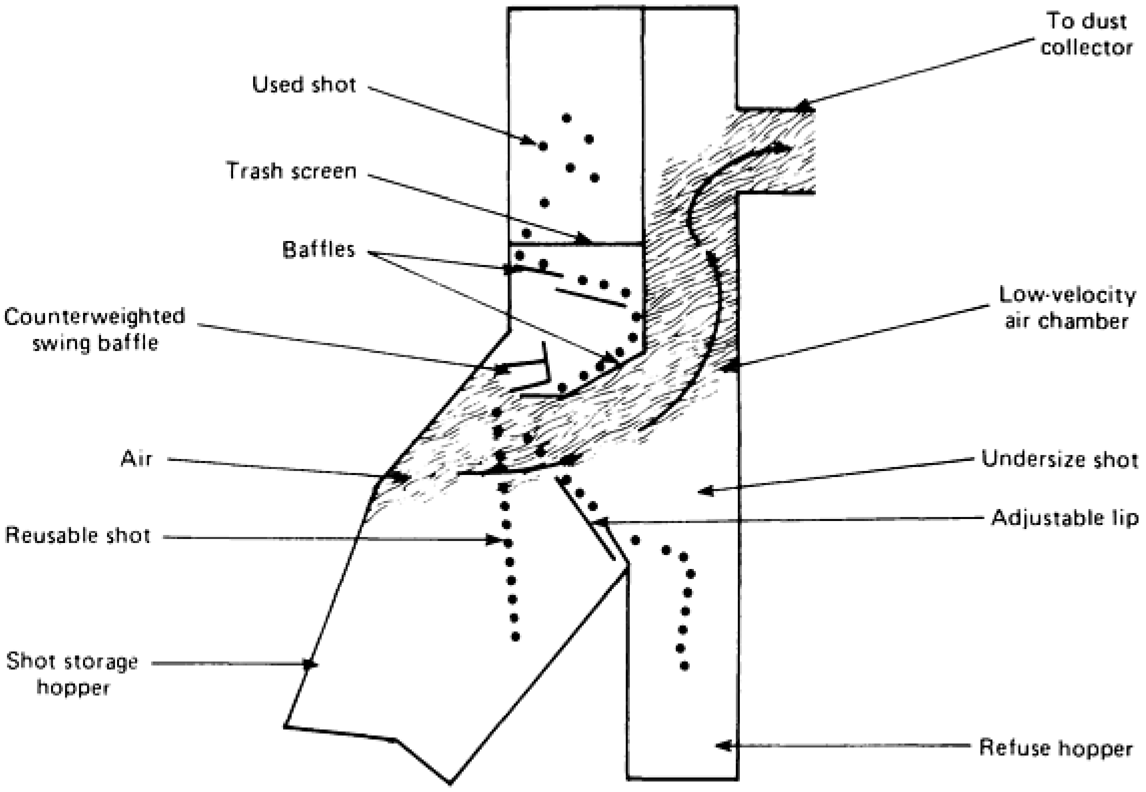


Fig. 5 Shot separator for use with a low-volume shot peening machine. Shot elevator not shown

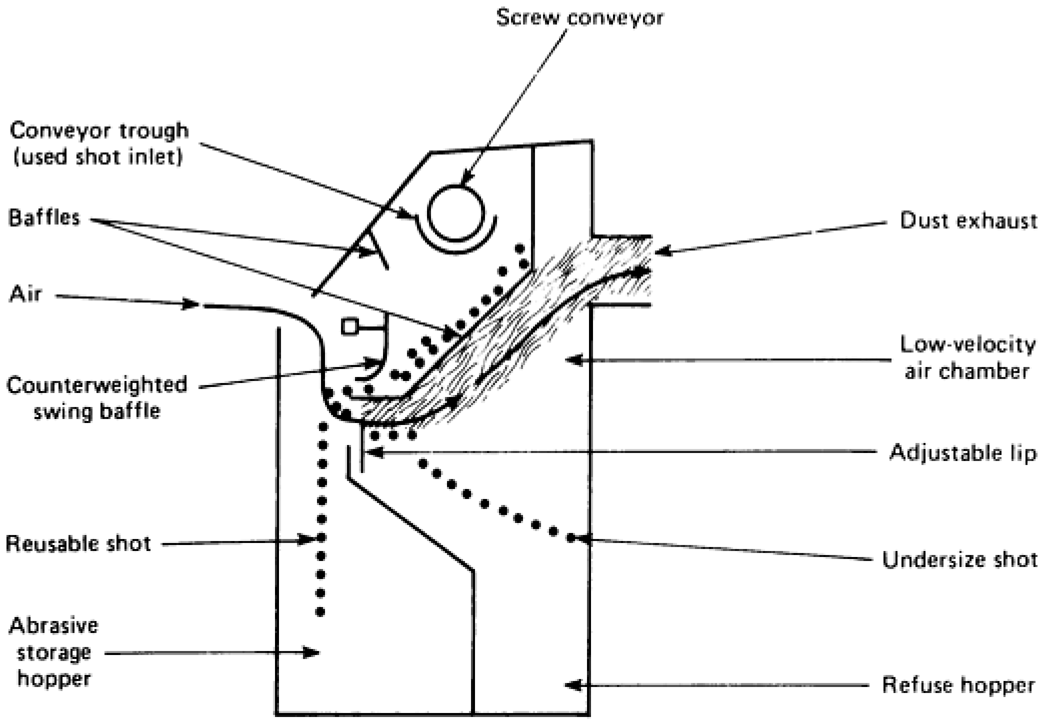


Fig. 6 Shot separator for use with a high-volume shot peening machine. Shot elevator and overflow not shown

Shot-adding devices automatically replenish the machine to maintain an adequate quantity of shot at all times. They are equipped with a capacitance switch or similar device to control the level of shot in the storage hopper and to add shot, as required, from a supply hopper.

Work Handling. The effectiveness of shot peening depends largely on peening intensity and adequate exposure of the workpiece to the blast stream. Proper exposure is facilitated by using efficient work-handling fixtures, conveyors, and mechanisms. Figure 7 shows six types of work-handling mechanisms, which incorporate several basic motions for effective exposure of parts with a variety of shapes.

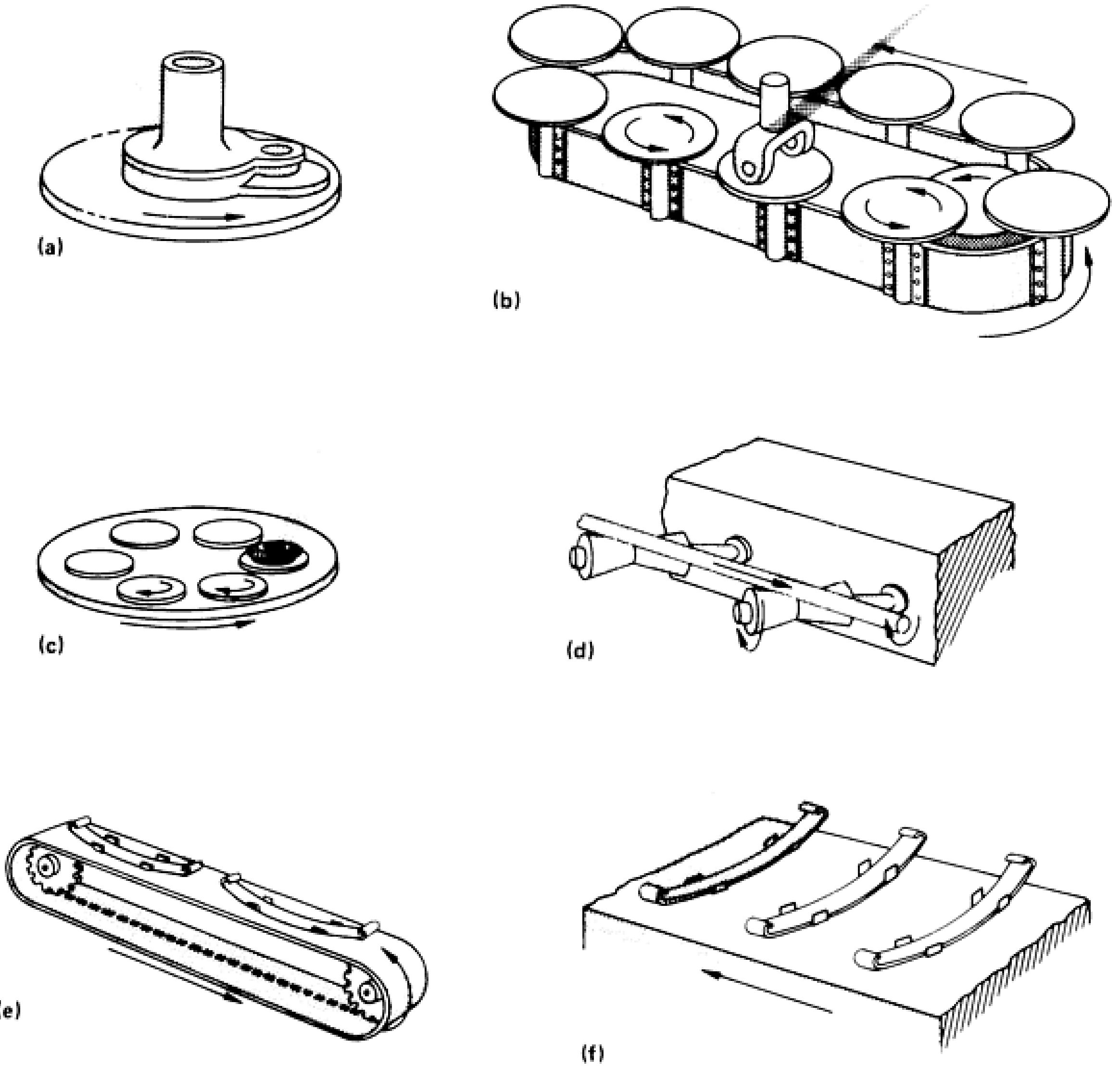


Fig. 7 Motion and fixturing used in work-handling equipment. (a) Rotation of work around a vertical axis in indexed position. (b) Rotation of work around a vertical axis, with straight-line travel. (c) Rotation of work around a vertical axis, with circular travel. (d) Rotation of work around a horizontal axis, with straight-line travel parallel to the axis of rotation. (e) Straight-line travel of work with no rotation. (f) Straight-line travel of work in a transverse direction

Stopoffs. Various methods and materials have been developed for masking parts that require shot peening on localized areas. Masking with tape is economical when low production quantities are involved, but its cost is prohibitive on a large-scale basis.

When fabrication of special masks is warranted, masks usually are designed to serve as holding fixtures as well as stopoffs. Ordinarily, masks of this type are made of molded urethane or rubber, as shown in Fig. 8. Large parts sometimes are protected with masks made of steel, carbide, polypropylene, or urethane.

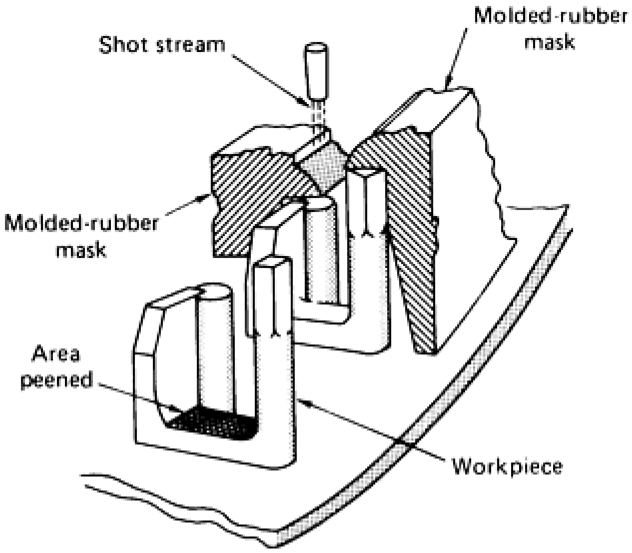


Fig. 8 Special mask made of molded rubber for shot peening a selected area and for holding the work during peening

Testing. Control of the shot peening process depends on systematic, periodic testing to determine intensity, coverage, and other important control factors. Standardized equipment for measuring peening intensity is illustrated and described in SAE Standard J442, "Holder and Gage for Shot Peening." A digest for measuring intensity is given in the section "Peening Test Strips, Holder, and Gage" in this article.

Dry Peening with Glass Beads. The methods used for dry peening with glass beads are comparable to the methods that use dry metallic shot. Separation of broken or damaged beads, as well as dust and other contamination, is accomplished by a centrifugal cyclone air separator, with final classification performed by a vibrating screen.

Wet Peening with Glass Beads. Wet glass peening is performed with glass beads, usually mixed in water and contained in a suitable hopper. In the automatic machine shown in Fig. 9, a mixer pump maintains a slurry of beads in water, and a feed pump forces the flow of slurry to the nozzle. The movement of slurry through the nozzle is accelerated by compressed air. The nozzles are attached to an oscillating bar that directs the flow of slurry at the workpiece. After making contact with the workpiece, the slurry is fed back to the hopper and recycled.

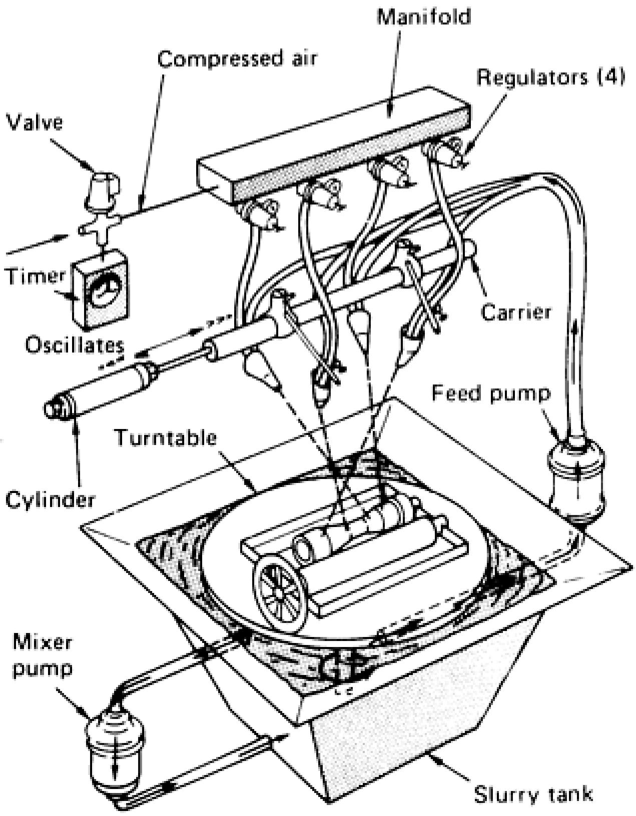


Fig. 9 Automatic machine for wet peening with glass beads

The principal controls in wet peening with glass are similar to those used in conventional shot peening. The peening pattern of the slurry is controlled by the oscillating nozzles. Air pressure is controlled at each nozzle by separate regulators. Exposure time for the peening cycle is controlled by automatic timing devices. Intensity of peening must be carefully matched to bead size, both to sustain maximum fatigue life of the peened part and to minimize bead breakage.

Applications

Although the major application of shot peening is related to improvement of fatigue characteristics, other useful applications have been developed, such as metal forming, straightening, improving resistance to stress corrosion, and testing the adhesion of plated deposits of silver on steel.

Improving Fatigue Properties. The improvement in fatigue strength obtained on several aluminum alloys and carbon and low-alloy steels is indicated in Table 2, which lists the type and size of shot, the peening intensity used on most of the materials, and data on the fatigue test specimens, the type of fatigue test, and the surface condition of specimens.

Forming. Shot peening is well suited for certain operations in the forming of thin sections. It has been used to form, as well as to strengthen, structural components of aircraft. An example is integrally stiffened aircraft wing panels. These were machined from slabs of aluminum alloy 2024-T6, 7075-T6, or others, which had to be curved for aerodynamic reasons. The large size of these panels, 10 m (32 ft) by 1.2 m (46 in.), precluded the use of hot forming. Cold forming produced surface tensile stresses of 140 MPa (20 ksi) or more, which were alleviated by shot peening the panels on the tension side. Proper curvature of the panels could be obtained by shot peening alone, with careful control of intensity. The need for conventional cold forming methods was avoided, and the high compressive stresses induced by peening reduced the probability of early fatigue failure.

Other parts that have been successfully formed by peening techniques include precision collets and large aluminum tubes that were preformed in halves in a press brake and peened to the desired diameter.

Straightening and correcting of distortion by peening have been used in salvaging parts. For example, large ring gears, 915 mm (36 in.) outside diameter by 19 mm ($\frac{3}{4}$ in.) thick, developed 3 mm ($\frac{1}{8}$ in.) out-of-roundness as a result of heat treating. Shot peening restored the gears to within 0.13 mm (0.005 in.) of perfect roundness. In another instance, shafts 50 mm (2 in.) outside diameter by 2 m (80 in.) long developed a 19 mm ($\frac{3}{4}$ in.) bow, which was straightened to within 0.8 mm ($\frac{1}{32}$ in.) by shot peening.

Improving Resistance to Stress Corrosion. Stress corrosion is a complex interaction of sustained tensile stress at a surface and corrosive attack that can result in brittle failure of a ductile material. Cracking due to stress corrosion has been associated with several metals, including brass, steel, stainless steel, aluminum, zinc, titanium, and magnesium. The surface tensile stresses that cause stress corrosion can be effectively overcome by the compressive stresses induced by shot peening, with either steel shot or glass beads.

In one case, test bars, 11.1 mm (0.437 in.) in diameter were cut in the short transverse direction from a 7075-T6 aluminum alloy hand forging and stressed to 75% of the yield strength. During alternate immersion tests in $3\frac{1}{2}$% sodium chloride solution, unpeened specimens failed in 1, 5, 17, and 28 days, respectively. Specimens peened in the unstressed condition with S230 cast steel shot lasted 365 and 730 days, when failure occurred in the unpeened grip outside the test area. During exposure to an industrial atmosphere, similar unpeened test bars failed in 20, 37, 120, and 161 days, respectively, whereas a peened specimen under the same conditions as above was uncracked when it was removed from testing after an exposure of $8\frac{1}{2}$ years.

Salt-fog tests on axial tension-test specimens of martensitic stainless steel showed that failure could be expected in a few days at stresses between 275 MPa (40 ksi) and 965 MPa (140 ksi). Shot peened specimens stressed at 690 MPa (100 ksi) lasted 14 to 21 days, as compared to 2 to 4 days for unpeened specimens. At a stress of 415 MPa (60 ksi), no failure of a peened specimen had occurred in 75 days, at which point the test was discontinued. Peening was beneficial, but it could not prevent stress corrosion at high stress levels. Table 3 presents stress-corrosion data indicating the life of peened and unpeened specimens of magnesium alloys, brass, and stainless steel in various corrosive mediums. All of these materials showed a high degree of improvement in resistance to stress corrosion as a result of shot peening.

Table 3 Effects of shot peening on stress-corrosion life of alloys

Material	Solution to which exposed	Time to failure	
		Unpeened	Peened
Magnesium, AZ31B-H	Potassium chromate and sodium chromate	110 s	>10 days
Magnesium, AZ61A-H	Potassium chromate and sodium chloride	$9\frac{1}{4}$ min	430 h
Brass cups, cold drawn	Ammonia	$2\frac{1}{2}$ h	19 and 47 h

Testing Adhesion of Silver Plate. The successful use of silver as a heavy-duty bearing material depends on a uniform high-strength bond between the silver plate and the steel substrate. Evaluating the integrity of the bond by peening has been accomplished with a high degree of reliability. Use of this technique on other electrodeposits is

unknown. In the poorly bonded areas, the silver deforms plastically under the peening action of the shot and forms wrinkles or blisters.

Shot peening intensities required for revealing defectively bonded areas may be determined experimentally, using the data in Fig. 10 as a guide. Figure 10(a) shows the minimum shot peening intensity required to blister poorly bonded silver plate in relation to the thickness of the plate. Silver is plated at least 60% thicker than the finished dimensions require. The plate is then machined to a uniform extra thickness for peen testing. The intensity is adjusted to +0.004, -0 of that indicated in Fig. 10(a). Uniform coverage and exposure time should be maintained. Masking is applied to the unplated areas. After peening, the surface is machined again to final dimensions. Data in Fig. 10(b) show the relation between the minimum thickness of silver for peen testing and the maximum finished thickness of silver.

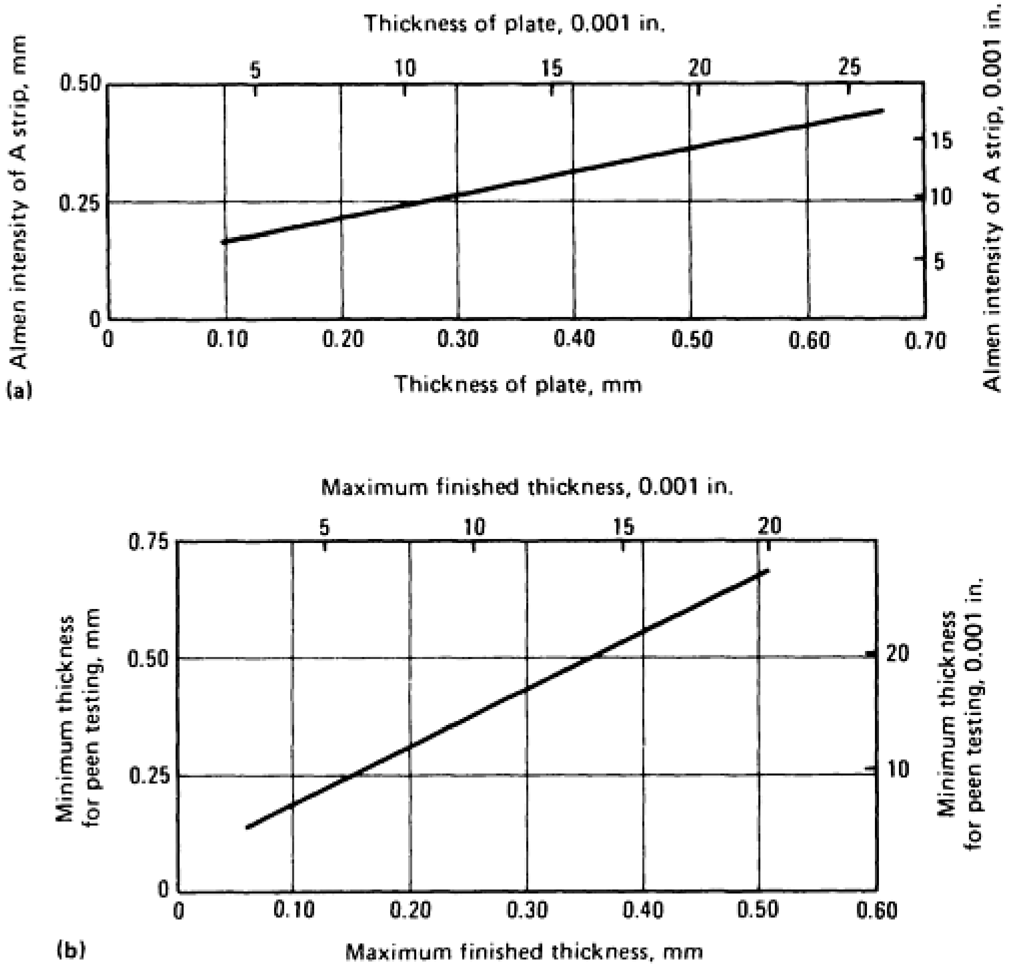


Fig. 10 Peen testing of silver plate on steel. (a) Minimum shot peening intensity required to blister poorly bonded silver plate, shown as related to plate thickness. (b) Relation between minimum thickness of silver plate for peen testing and maximum finished thickness of plate.

Limitations

Shot peening has few practical limitations in terms of the materials or the size, shape, quantity, surface condition, and surface hardness of parts that can be peened. Major limitations are not related to the mechanical aspects of the peening process, but to subsequent processing, such as the effects of machining and post-peening elevated temperature, that can nullify the beneficial results of shot peening.

Size and Shape of Workpiece. The size of the peening cabinet is usually the only limitation on the size of workpiece that can be peened. To some extent, even this limitation can be overcome by the use of portable mechanized peening equipment. Provided the surface to be peened is accessible to the blast, the shape of a workpiece is seldom a limitation. The peening of small radii in fillets and thread roots is limited by the smallest available media size, currently 0.0200 mm (0.001 in.) diameter glass beads. Sharp edges that must retain their sharpness should not be peened.

Surface condition, provided the workpiece surface is free of gross contaminants, is seldom a limitation in shot peening. Water, oil, and grease seriously contaminate the shot and interfere with peening quality and effectiveness. An as-forged surface usually shows greater improvement in fatigue strength than a polished surface as a result of peening. Cast surfaces respond as well to peening as wrought surfaces. Peened aluminum parts may be bright-dipped before being anodized.

Temperature Limitations. Low tempering temperatures, such as those conventionally used for carburized parts, have no adverse effect on peening stresses. Low-alloy steels can be heated to about 175 to 230 °C (350 to 450 °F) for about a half hour before significant decrease in the compressive stresses occurs. Steels intended for elevated-temperature application usually withstand temperatures of 260 to 290 °C (500 to 550 °F) without undergoing a significant stress-relieving effect; however, exposure at 540 °C (1000 °F) or above relieves induced stresses in all high-temperature alloys. Exposure to temperatures above 175 °C (350 °F) can eliminate the induced compressive stresses in some alloys of aluminum.

Problems in Production Peening

Problems in the shot peening of production parts have been corrected by a variety of solutions. A small forging, as shown in Fig. 11(a), contained two holes with thin-wall sections. The inner bearing surfaces had to be held to a tolerance of 0.013 mm (0.0005 in.). In shot peening a hole with a heavy walled section, the size of the hole is reduced by the peening action. With the thin-wall section here, the size of the hole was not reduced, but the hole became oval shaped. The solution to this problem required the establishment of new dimensions before shot peening that permitted a light honing operation after shot peening to bring the hole size to within dimensional requirements.

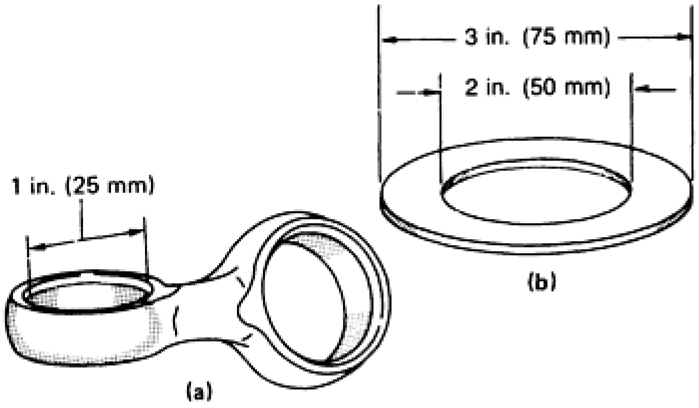


Fig. 11 Production parts that presented problems in shot peening

In another instance, a flat ring, as shown in Fig. 11(b), failed in fatigue either by cracking from the inside diameter to the outside diameter or by flaking. Shot peening eliminated the fatigue failures but caused the parts to dish as well as to warp. These parts were required to retain flatness to within a tolerance of 0.013 mm (0.0005 in.). After various intensities were tried, the distortion problem was solved by peening one side of the ring at a higher intensity than that used on the other side, depending on warpage direction.

In shot peening the fir-tree serrations of type 410 stainless steel compressor blades used in a jet aircraft engine, as shown in Fig. 12, it was determined that a maximum improvement of 26% in the fatigue life of serrated blade roots could be obtained only if a closely controlled peening procedure was followed. Certain variations from this procedure actually proved harmful to blade life. An alteration in peening intensity had a marked effect on fatigue characteristics. Variations in blast intensity that could be obtained by changing nozzle size, aspirator size, or the distance from the nozzle to the work are given in Table 4.

Table 4 Peening intensity as affected by nozzle and aspirator sizes and distance from nozzle to work

Test	Nozzle size	Aspirator size	Almen intensity, A strip, 0.025 mm (0.001 in.),

No.[a]					at given distance from nozzle to work, mm (in.)				
	mm	in.	mm	in.	200 (8)	180 (7)	150 (5)	120 (5)	100 (4)
1	9.5	$\frac{3}{8}$	4	$\frac{5}{32}$	5.5	4	5	5.5	5
2	9.5	$\frac{3}{8}$	5.5	$\frac{7}{32}$	4	5.5	5	5.5	5
3	13	$\frac{1}{2}$	4	$\frac{5}{32}$	3	2.5	3	3	3.5
4	13	$\frac{1}{2}$	5.5	$\frac{7}{32}$	5	6	7	7	7
5	16	$\frac{5}{8}$	4	$\frac{5}{32}$	7	6	5.5	7	7-8
6	16	$\frac{5}{8}$	7	$\frac{9}{32}$	6	6.5	7	7	7.5

(a) Tests made using suction shot peening test cabinet, 70 steel shot; pressure 635 kPa (92 psi); flow of shot to nozzle 3.3 kg/min ($7\frac{1}{4}$ lb/min)

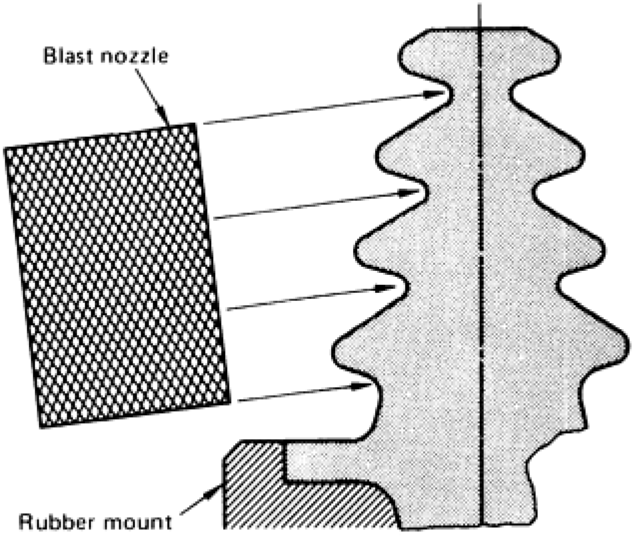


Fig. 12 Relation of nozzle angle, angle of load face, and resulting angle of impingement in peening root serrations of compressor blades. Angle of impingement, 83°

The procedure adopted consisted of peening the root serrations with S70 steel shot at an intensity of 0.007 to 0.008 A at an impingement angle of 83°. The intensity indicated was measured at an impingement angle of 90°. The true intensity on various portions of the root serrations was considerably less, depending on impingement angle; however, maximum intensity was obtained at the critical root radius, using the 83° impingement angle calculated to have this effect. The relation between impingement angle and intensity is shown in Fig. 13.

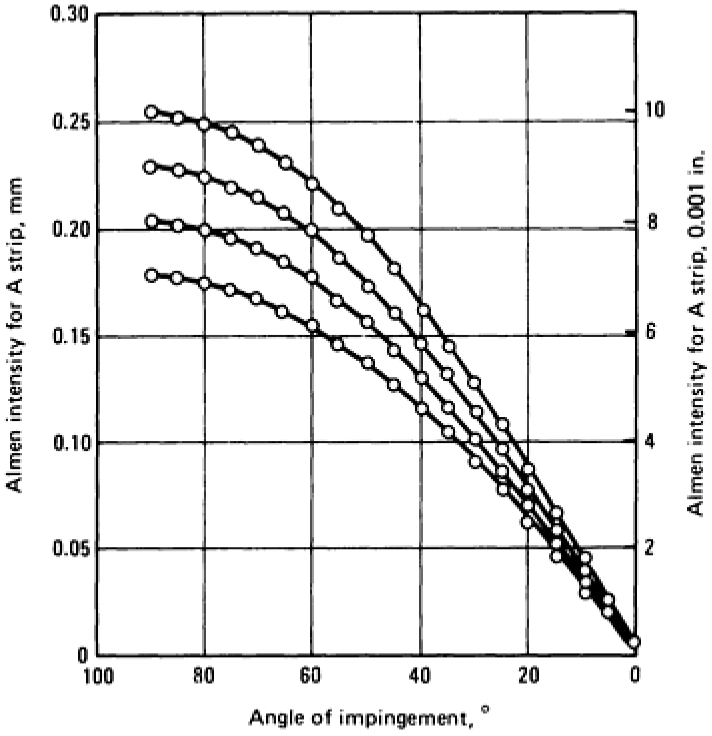


Fig. 13 Peening intensity as a function of angle of impingement

Peening was performed in a gravity-feed, continuous-conveyor production cabinet, using a 16 mm ($\frac{5}{8}$ in.) bore diameter nozzle, a 4 mm ($\frac{5}{32}$ in.) aspirator, 635 kPa (92 psi) air line pressure, and a shot flow of 3.4 kg/min (7.5 lb/min). The distance from the nozzle to the work was set at 100 mm (4 in.). The cabinet conveyor moved at a fixed speed that exposed the work to the blast for a period of 5 s. The peening operation required two passes under the nozzle, one for each side of the blade root. The airfoil sections of the blade were protected from the blast by a sheet rubber covering.

Costs

The cost of shot peening on a production basis depends on several factors, including the size, shape, and hardness of parts, the total area to be peened, and the required intensity and coverage. Shot type, size, and velocity also influence costs, because they affect peening intensity, rate of shot breakdown, and the rate at which the desired coverage is obtained.

With an increase in shot velocity, the rate of shot breakdown increases far more rapidly than the intensity of the peening blast; however, the weight of a shot pellet varies directly, while the number of pellets per kilogram (pound) of shot varies inversely, with the cube of the diameter of the pellet. Consequently, for a given Almen intensity, coverage is obtained much more rapidly with smaller shot and higher velocity. Because of these opposing factors, the number of kilograms (pounds) of shot used per part is virtually the same for various shot sizes, assuming similar intensity, coverage, and control of uniform shot size. The use of small shot at high velocity increases production rate and reduces labor costs.

Processing after Peening

Shot peening itself is a finishing treatment, and usually no further processing of peened work is required, except for the application of a rust preventive on low-alloy steels. The as-peened surfaces of these steels are clean and chemically active and are highly susceptible to corrosion from fingerprints and other contaminants. Such surfaces are also highly receptive to oils for rust prevention and lubrication, and they provide an excellent base for organic or inorganic coatings that do not require thermal treatment other than low-temperature baking. Temperatures high enough to relieve the beneficial compressive stresses imposed by peening must be avoided.

Stainless steel that has been peened with iron or steel shot should be passivated to counteract contamination by iron particles, which causes rusting. Passivation is not required for use at elevated temperature. Secondary peening with glass beads, after peening with steel shot, removes contaminating ferrous residue and increases the fatigue life of the peened part.

Because the compressive layer induced by peening is relatively thin, subsequent grinding or machining of peened surfaces should be avoided, except for aluminum and magnesium alloys that have been peened to a greater depth. As much as 0.13 mm (0.005 in.) may be removed from the surface of these alloys without harmful effect to the peened layer, and the improved surface finish may prove beneficial to fatigue properties; however, a knowledge of stress gradients must be available before stock removal.

Steels may be lightly honed or lapped after peening. There is limited evidence that these operations for fine-particle abrasive blasting have a beneficial effect where maximum fatigue resistance is desired. After peening, straightening or cold forming by conventional methods should be avoided. These operations may result in a complete reversal of the stress pattern. Peen straightening and peen forming, however, are permissible, because these processes do not introduce harmful residual tensile stresses.

Peening Test Strips, Holder, and Gage

SAE standard J442 describes the test strips, strip holder, and gage used in measuring shot peening intensity.

If a thin flat piece of steel is clamped to a solid block and exposed to a blast of shot, it will be curved after removal from the block. The curvature is convex on the peened side. The extent of this curvature on a standard sample serves as a means of measurement of the intensity of the peening.

Standard test strips of three thicknesses used are shown in Fig. 14. Made of 1070 cold-rolled spring steel, these strips have a specified hardness of 44 to 50 HRC. Strip A is recommended for testing intensities that produce curvatures having arc heights ranging from 0.15 to 0.60 mm (0.006 to 0.024 in.). For lesser intensities, the N strip is recommended. For greater intensities, the C strip is used. The relationship between strips A, C, and N is shown in Fig. 15. The data represent readings for conditions of identical blast and exposure.

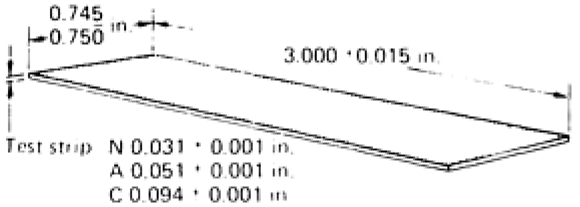


Fig. 14 Designations and dimensions of standard Almen test strips used in measuring shot peening intensity

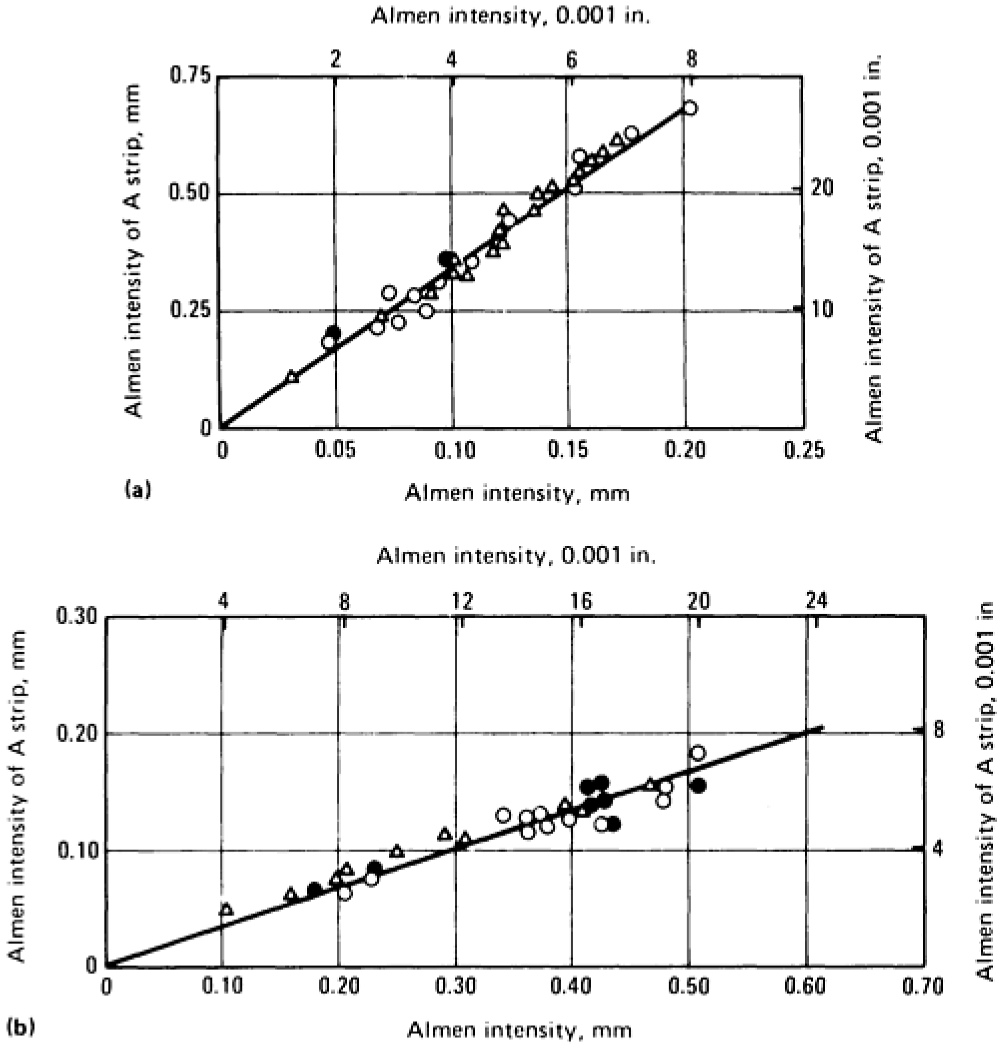


Fig. 15 Correlation of intensities as indicated by arc heights of A, C, and N strips peened under identical blast and exposure conditions. (a) C strip. (b) N strip (SAE J442)

During peening, the test strip is mounted on a holder as shown in Fig. 16. After being peened, the strip is removed and placed in an Almen gage (Fig. 17), located so that the dial indicator stem bears against the unpeened surface. The curvature of the strip is determined by a measurement of the height of the combined longitudinal and transverse arcs across standard chords. This arc height is obtained by measuring the displacement of a central point on the unpeened surface from the plane of four balls forming the corners of a rectangle. Almen gages are available with either analog or digital readout. In digital units, accuracy can be posted to four decimal places.

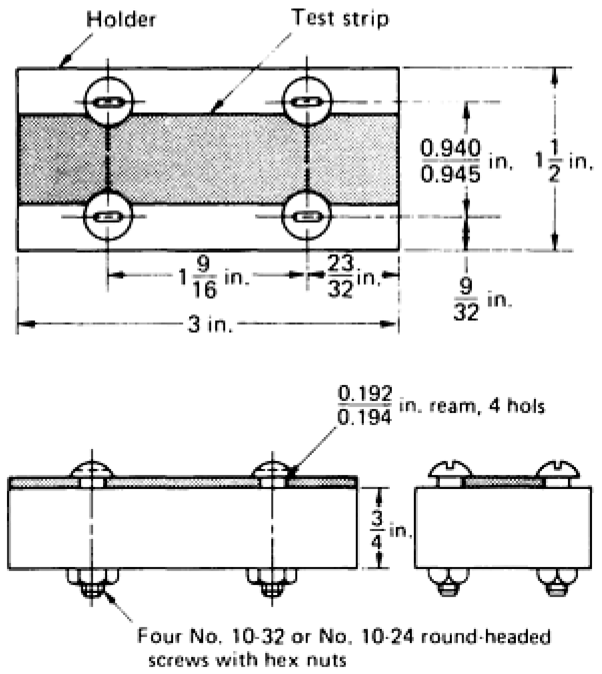


Fig. 16 Assembled Almen test strip and holder

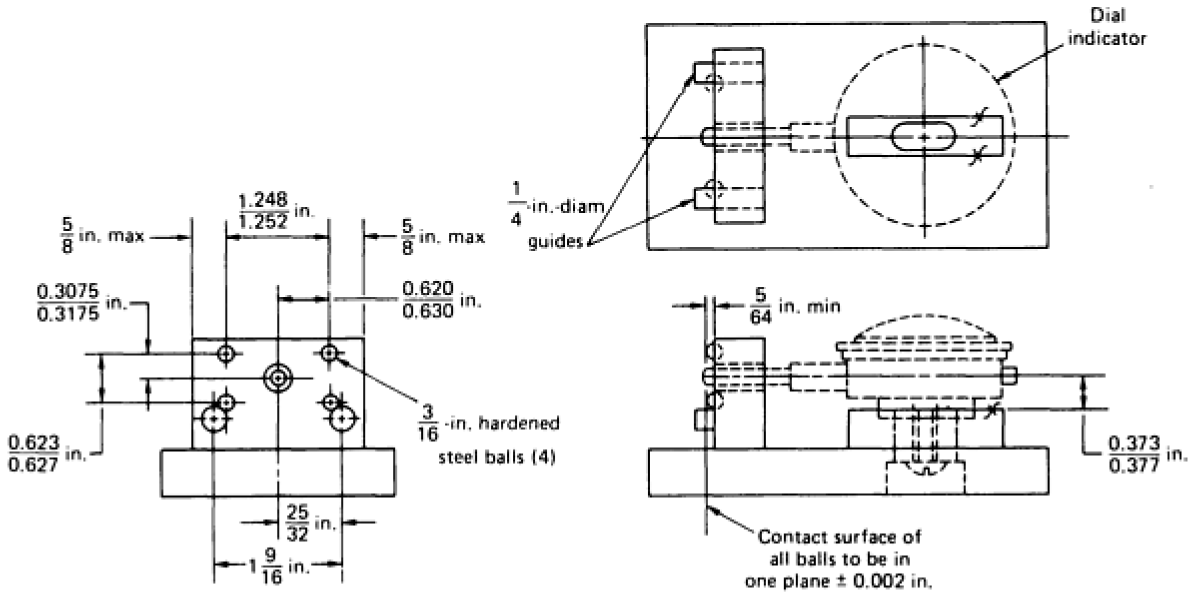


Fig. 17 Almen gage for measuring arc height for test strip

The standard designation of intensity includes the gage reading or arc height and the test strip used. For example, 0.013 A signifies that the arc height of the peened test strip is 0.33 mm (0.013 in.) and that the test strip used was of the A thickness. Uniform procedures for using the standard test strips described in the above digest of SAE J442 are provided in SAE Recommended Practice J443.

Topography of Surfaces

R.K. Morton, Rank Taylor Hobson Inc.

Introduction

MOST SURFACES have regular and irregular spacings that tend to form a pattern or texture on the surface. This surface texture is generated by a combination of various factors that are due either to the manufacturing process or the material being finished. Of the factors due to the material, the most fundamental is the microstructure of the material. For example, cast aluminum surfaces generally produce a granular surface when machined, while wrought aluminum alloys can be machined to produce a highly reflective, flat, and smooth topography. Internal stress in the material, released after machining, can also contribute to surface deformation.

The machining or finishing process itself has the greatest impact on the geometry of the surface. A major factor is the action of the cutting tool on the material. Elements such as tool shape, speed, feed, and cutting fluid can be varied to affect the surface topography. Other factors affecting the surface are the instability of the cutting tool due to chatter or imbalance in the grinding wheel, and errors in the machine tool guideway.

General Background

Reasons to Measure Surface Topography. The primary reason to measure a surface is to try to predict the performance of the component. As an example, a bearing surface requires a level of surface texture that allows lubricant to be retained in small pockets and at the same time allows the bearing to roll with a minimum of friction. If the surface is too rough, wear can quickly develop; however, if the surface is too smooth, inadequate lubrication and seizure might occur.

The other principal reason to measure a surface is to control the manufacturing process. By measuring the surface topography during processing, an operator can detect changes in the surface finish and adjust the manufacturing process to ensure that the process remains in limit.

The Components of a Surface. The topography of a surface is made up of a combination of three features (Fig. 1).

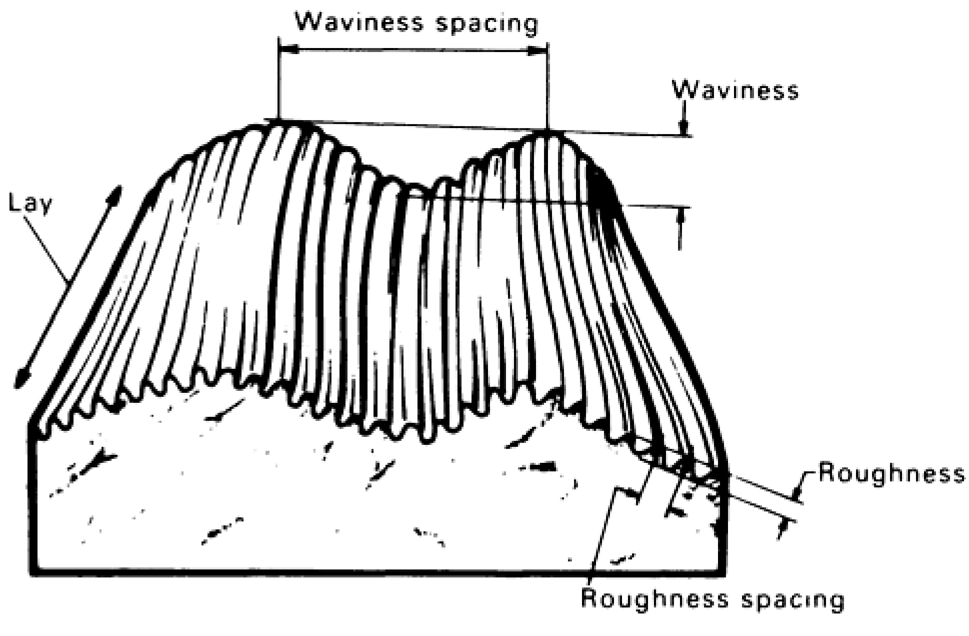


Fig. 1 Illustration of the roughness, waviness, and general form of a surface

Surface roughness refers to the high-frequency irregularities on the surface caused by the interaction of the material microstructure and the cutting tool action.

Surface waviness refers to the medium-frequency irregularities on the surface on which the surface roughness is superimposed. These forms can be caused by the instability of the cutting tool and errors in the machine tool guideway.

Surface form is the general shape of the surface, neglecting roughness and waviness, which are caused principally by errors in the machine tool guideway, and deformations due to stress patterns in the component.

Lay is another important feature of a surface. This is a machining pattern that has a distinctly directional characteristic, such as a parallel, circular, radial, or multidirectional pattern. The lay is an important consideration because surface topography measurements will differ depending on the direction from which they are taken. Measurement should be made perpendicular to the lay of the surface.

Measuring Surface Topography

Because the basic types of surface geometry are caused by different factors and tend to have different relationships to the performance of the component, it is conventional to consider them separately during analysis. In general, if control of aspects of component performance related to surface topography is required (e.g., wear characteristics, friction, reflectivity, resistance to stress failure, or lubrication properties), roughness is analyzed. If control of some aspect of machine tool performance or component performance (e.g., noise or vibration generation) is required, waviness is analyzed.

Surface Texture Recorder. The most common type of contact method for measuring surface topography is the surface texture recorder, the principle of which is shown in Fig. 2. The stylus of the instrument is moved across the surface via a guiding mechanism to produce the "traced profile," which is defined by the interaction of the stylus with the component. The transducer produces a signal that is the difference between the traced profile and a "reference profile" or "datum profile" provided by the guideway. The transducer signal is then converted into a digital signal via an analog-to-digital converter. At this point the transducer contains only the vertical or Z-component of the profile. The horizontal or X-component generated by the traversing mechanism is combined with the Z-component to produce the "total profile." The total profile is then filtered to remove unnecessary information, which produces a "primary profile." This profile can then be subjected to filtering techniques that can separate the roughness, waviness, and form features of the surface.

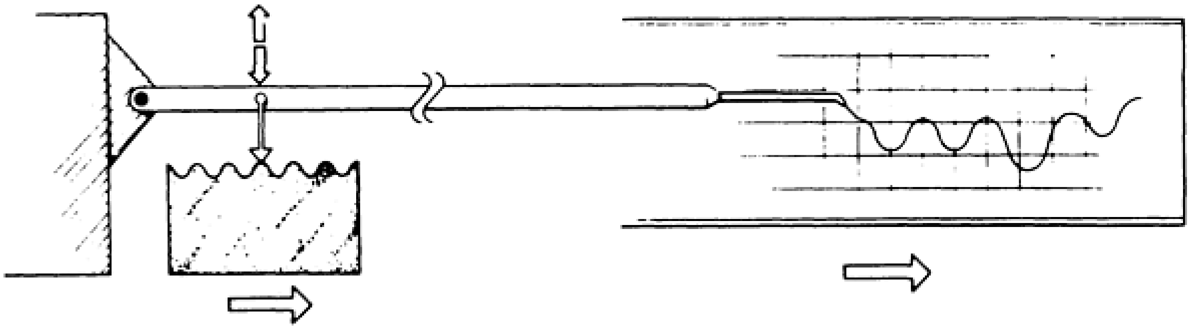


Fig. 2 Basic principle of a surface texture recorder

Noncontact techniques are becoming increasingly popular in the measurement of surface topography, especially for surfaces that may be subject to damage using contact techniques. The results obtained are very similar to those of stylus methods and can use the same parameter definitions. Some noncontact methods, such as diffraction measurement, can measure surfaces quickly and easily and can potentially be used on machine tools at the point of manufacture.

Some noncontact methods do have limitations in measuring certain surfaces. For instance, in surfaces with high slope, an insufficient intensity of light is reflected back to the detector and the focus lens begins to follow inaccurately. Another example is that on contaminated surfaces, the contamination is measured because there is no force to remove it, and this distorts the results. Oxide layers on surfaces such as aluminum can also present problems, because the focusing lens will oscillate between the top and bottom of the oxide layer, giving the false impression of a very rough surface.

The focus-follow method (Fig. 3) involves the use of a moving lens to try to keep a spot of light focused on the surface. The lens movement correlates to the profile of the surface and its vertical movement is controlled by an electric motor. The analog electrical signal generated to drive the motor is digitized and processed in the same manner as a

contact stylus. A variation of this method involves the use of a separate transducer to monitor the position of the lens; the electric signal from this transducer is used in the same manner as a contact stylus.

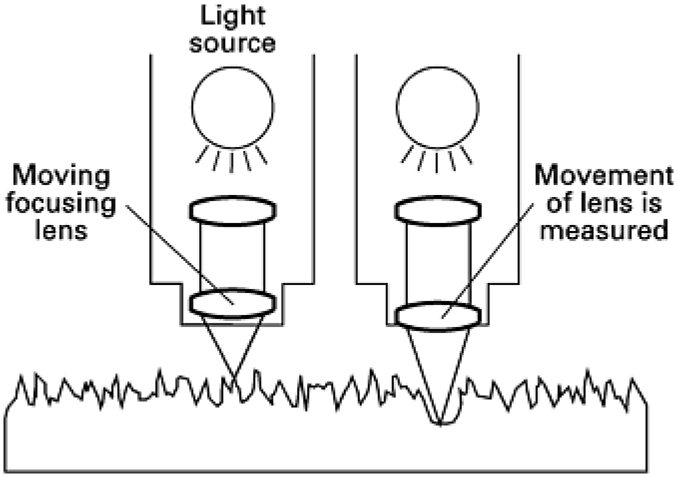


Fig. 3 Focus-follow method for noncontact measurement of roughness

Multiple-beam interferometers, such as the Fizeau interferometer, also have useful application in microtopography. They are used with a microscope to provide high resolution in three dimensions. The interference microscope divides the light from a single-point source into two or more waves. In multiple-beam interference microscopes, this is done by placing a partially transmitting and partially reflecting reference mirror near the surface of the specimen (Fig. 4).

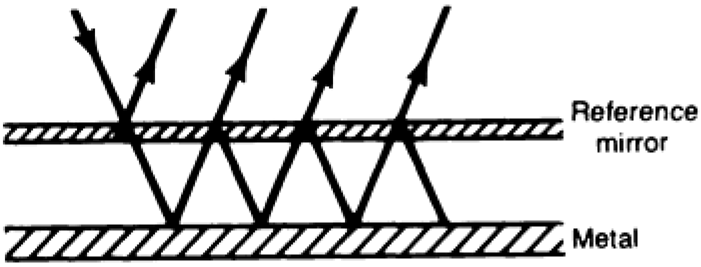


Fig. 4 General principle of a multiple-beam interferometer

The multiple beams illustrated in Fig. 4 are superimposed after traveling different lengths. This produces interference patterns, which are magnified by the microscope. The interference fringes having a perfectly flat surface appear as straight, parallel lines of equal width and spacing. Height variations cause the fringes to appear curved or jagged, depending on the unit used. With multiple-beam interferometers, height differences as small as $\lambda/200$ can be measured, where λ is the wavelength of the light source.

Lasers can provide a monochromatic light source, which is required in interference microscopes. Typical systems can provide displays of isometric plots, contour plots, and qualitative parameters, such as surface roughness, camber, crown, radius of curvature, cylindrical sag, and spherical sag.

The Profile. Before surface topography assessment can be understood clearly, an important factor needs to be explained concerning the measured profile generated from the surface. To obtain a reasonably clear display of the height and spacing of the surface profile, the vertical stylus deviation typically needs to be magnified by at least 5,000×, whereas the horizontal measurement length is magnified by about 100×. So it is important to note that the resultant display is not a magnified cross section of the surface. Figure 5 provides an illustration of this principle.

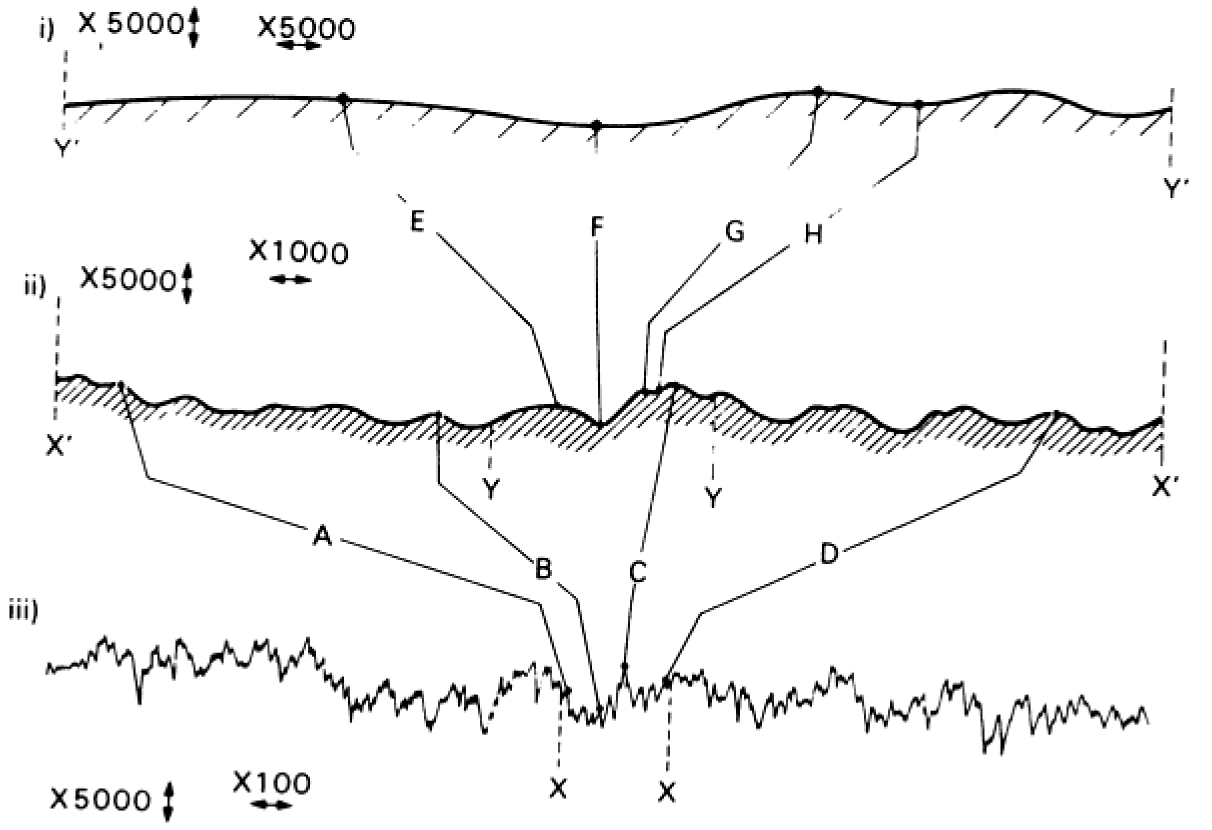


Fig. 5 Diagram illustrating how the profile shape varies as V_h, horizontal magnification, is reduced relative to V_v, vertical magnification. (i) Surface profile magnified 5000× equally in all directions. (ii) Profile with V_v:V_h ratio of 5:1. (iii) Profile graph recorded with a V_v:V_h ratio of 50:1. As the horizontal magnification of the profile is increased, the length X-X is expanded to X'-X' and the peaks A, B, C, and D appear flatter. Increasing the horizontal magnification still further until it equals the vertical magnification expands the length Y-Y to Y'-Y'. Peaks E and G and valleys F and H now appear much flatter, but the actual difference in heights of the corresponding peaks and valleys in (i), (ii), and (iii) are exactly the same.

Parameters

For effective analysis of surface roughness or waviness, the profile generated by the measuring instrument needs to be evaluated according to internationally recognized mathematical formulas, called parameters. The purpose of using a parameter is to apply a number that can characterize a certain aspect of the surface and hence remove the need for subjective operator assessment. It is not possible to characterize a surface completely with a single parameter, so a combination of parameters is normally used.

Parameters can be separated into four basic types:

- *Amplitude parameters* are measures of the vertical characteristics of the surface deviations.
- *Spacing parameters* are measures of irregularity spacings along the surface, regardless of the amplitude of these irregularities.
- *Hybrid parameters* analyze a combination of the amplitude and spacing of the surface irregularities.
- *Extended parameters* are not simply defined by the profile data and require further inputs or attributes.

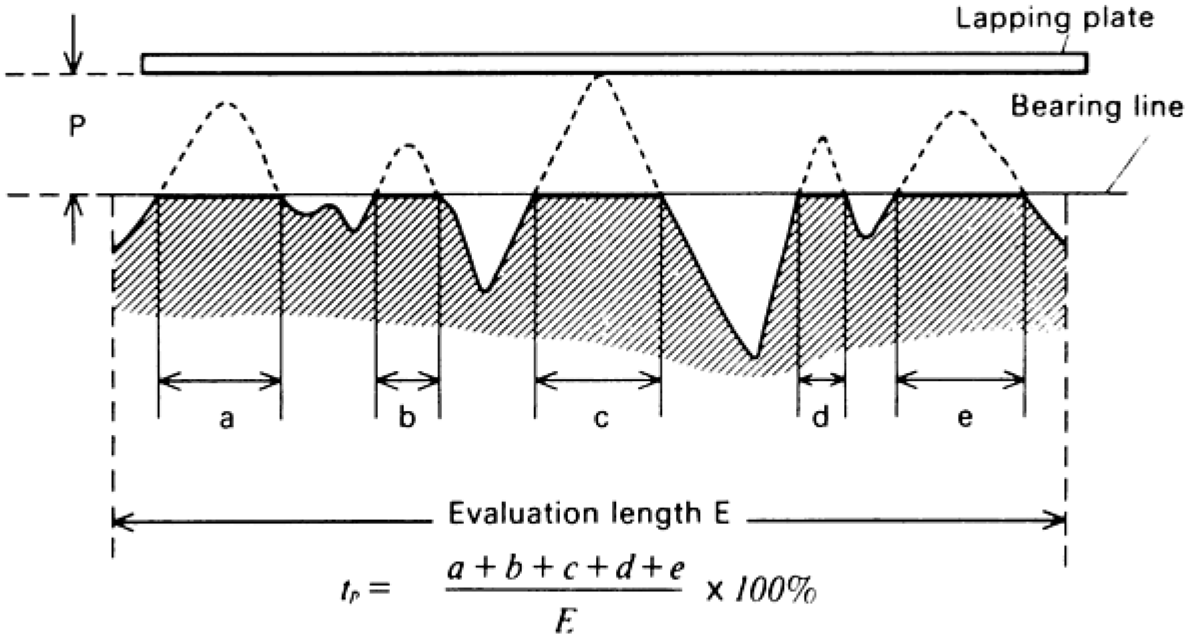
In order to characterize a surface using parameters, between three and six parameters must be chosen, including at least one of each of the types listed above. Examples of different types of parameters and how they are applied can best be described by discussing the various types of surfaces generated by finishing methods.

Ground, Turned, and Milled Machined Surfaces. One of the most commonly used roughness amplitude parameters is the roughness average (R_a), which is used to assess the coarseness of the surface such as those produced by grinding, turning, and milling operations. The parameter R_a is defined as the mean height of the roughness profile. It does have some significant drawbacks in that many differing profiles can have the same Ra and yet have very different performance characteristics. Another averaging parameter, R_q, takes the root mean square of the profile and is more sensitive to surface variations.

Surfaces Subject to Stress. For some surfaces it is sometimes desirable to specify the maximum roughness height, R_{max}, or the peak-to-valley height, R_z, rather than use the mean height given by R_a. The R_{max} parameter measures the highest and lowest points of the profile and is particularly valuable where components are subjected to high stresses. Any large peak-to-valley heights may be areas likely to suffer from crack propagation. However, because R_z is very susceptible to dirt or scratches, it is an unstable parameter. It is usual to take an average of the individual peak-to-valley heights, which can be done in slightly different ways with the parameters R_{tm} (R_z in DIN specifications) and R_z in ISO specifications.

Sheet Steel and Peak Counting. Although roughness amplitude is very important in most applications, the spacing of the roughness peaks can be equally important. Particularly in the manufacture and use of sheet steel, surface texture control is necessary to obtain consistent lubrication when forming the sheet, avoid scoring, and prevent the texture from showing through the paint on the finished product. Amplitude parameters such as R_a are not sufficient to specify the different types of texture that can be obtained from the rolling process. The peak count parameter, P_c, allows the operator to monitor and control the roughness peak spacing as well as the amplitude, thus producing a better bonding of finishes, a more uniform finish of plating and painting, and a reduced risk of cracking during drawing or forming operations. Peak spacing is also an important factor in the performance of friction surfaces such as brake drums. The high spot count is another spacing parameter; it is used frequently by the automotive industry on cylinder liners and other surfaces where the lubrication characteristics of the topography are important.

Bearing Surfaces. The most common use of engineering surfaces is to provide a bearing surface for another component moving relative to it, resulting in wear. The material ratio parameter, T_p (in %), is commonly used to simulate the effect of wear on a surface. Material ratio is defined as the ratio of the length of the surface to the evaluation length at a specified depth in the profile. A practical example is to imagine a surface plate resting on the highest peak of a profile as illustrated in Fig. 6. As the peaks wear and the material line (the top line of the remaining profile) descends, the length of the bearing surface (the length of the profile in contact with the lapping plate) increases. The parameter T_p can thus be used to control bearing surfaces as well as surfaces requiring lubrication.



$$t_p = \frac{a+b+c+d+e}{E} \times 100\%$$

Fig. 6 Illustration showing the derivation of material ratio, t_p

Plateau Honed and Lapped Surfaces. The R_k parameter uses the material ratio curve for analysis. It is commonly used to evaluate plateau honed surfaces, which are the result of multiple machining operations. Peaks are removed and large valleys are created to retain lubrication. The parameter has a wide application in the automotive field.

In using the R_k parameter five primary areas are analyzed. All measurements and parameters are scale dependent.

- *Core roughness depth* (R_k) is the working part of the surface that, after the initial running-in period, will carry the load and influence the life and performance of the surface.
- *Reduced peak height* (R_{pk}) is the top portion of the surface that will be worn away in the running-in period. Used in conjunction with this is the parameter M_{r1}, the associated percent length of the top portion of the profile that will be removed during the same process.
- *Reduced valley depth* (R_{vk}) is the lowest part of the surface that has the function of retaining the lubricant during its working life. Used in conjunction with this is the parameter M_{r2}, which is the associated percent length of the bottom part of the profile that will be used to retain lubricant.

Reflective, Painted, Elastic, and Wear-Resistant Surfaces. A useful hybrid parameter that has a close correlation to various surface properties is the average slope of the surface. The slope of the profile is the angle (in terms of the gradient) that it makes with a line parallel to the center line. It is defined as the mean of all the slopes at all points on the profile.

The parameter can be used to measure the actual profile length (i.e., the length that would be occupied if all the peaks and valleys were stretched out in a straight line). The steeper the average slope, the longer the actual length of the surface compared with its nominal length. The parameter is employed in painting and plating applications where the length of the surface available for keying is important. It is scale dependent.

Average slope is also useful in assessing other properties of engineering surfaces. It can be related to the hardness and elasticity of the surface, where the higher the slope, the greater the chance of surface deformation upon loading. In assessing surface reflectivity a high slope indicates a surface with low reflectivity. Also, the higher the level of average surface slope, the higher the level of friction and the greater the level of wear.

Microstructural Analysis of Finished Surfaces

Donald C. Zipperian, Buehler Ltd.

Introduction

MICROSTRUCTURAL ANALYSIS of a finished surface can provide important information regarding material properties and reliability. For example, surface cracks or other machining damage can act as stress risers in brittle materials. Additionally, improper machining techniques can create excessive heat that results in smearing or alteration of the microstructure. Microstructural analysis has been used extensively for characterizing ferrous and nonferrous metals, but it is also extremely useful for characterizing advanced materials such as composites and ceramics.

Traditional quantitative metallography or stereology relates two-dimensional features, as seen on photographs or images, to the actual three-dimensional microstructure. Common measurements include grain size, inclusion rating, phase determination, and density of dislocations. E.E. Underwood has described the basic measurement techniques and their relationships to traditional stereological analysis (Ref 1). Prior to the time when computers and image analysis software became accessible, feature counting methods were used (e.g., a grid is used to frame the object, or a line of known length is drawn on a photograph and the number of features or intersecting points are counted). Although these techniques were surprisingly accurate, they were time-consuming and subject to human bias.

Modern quantitative image analysis has expanded the capabilities of surface analysis significantly with the use of computer technology. For example, a typical computer-based image analysis system can measure and statistically analyze a variety of surface features over a number of fields of view very quickly and accurately. Table 1 provides a list of common image analysis features and field measurements.

Table 1 Quantitative image analysis

Field measurements (stereology)	**Object measurements (feature measurement)**
Area fraction	Area
Area percent	Length
ASTM E 112 grain size	Width
Count	Aspect ratio
Perimeter	Feret measurements
Mean intercept distance	Perimeter
Mean particle surface area	Sphericity
Density	Convex perimeter
	Roughness
	Breath
	Orientation

Reference

1. E.E. Underwood, Quantitative Metallography, *Metallography and Microstructure,* Vol 9, 9th ed., *Metals Handbook,* American Society for Metals, 1985, p 123-134

Quantitative Image Analysis

Computer-based image analysis is a contrast-based microstructural analysis tool that is finding widespread use because of significant improvements in computer speed and memory capabilities. The modern quantitative image analysis systems driven by personal computers can handle complex images quickly and accurately, with resolutions comparable to those of the human eye. The most economical image systems convert an analog camera signal to a digital signal through a hardware processor. Although digital cameras are available, they are significantly more expensive.

Image analysis consists of six basic steps (Ref 2):

1. *Image acquisition* for microstructural analysis is accomplished with a microscope and a video camera.
2. *Image enhancement* is required to correct for nonuniform illumination and to sharpen the digitized image. Image sharpening is required because the conversion from an analog signal to a digitized signal does not produce sharp edges. Delineation, the most commonly used image enhancement function, converts digitized signals to a square-wave function, thus producing sharper images.

3. *Feature detection* (also called *thresholding*) assigns specific contrast values to the image (0 to 255 gray levels). The most accurate and precise method for properly thresholding an image is to use a gray-level histogram. Figure 1 shows a porous steatite ceramic sample and the corresponding gray-level histogram. The darker phase (porosity) occurs at a lower value and is detected between gray levels of 0 to 129; the lighter phase (background matrix) is detected between gray levels of 130 to 255.
4. *Editing* is used to separate, delineate, or classify features based on their morphology or size. Examples of editing functions include dilation, erosion, grain-boundary reconstruction, filing, elimination, and chord sizing. These functions are used to add or remove pixels, rebuild missing or incomplete boundaries, fill in undetected features, or eliminate objects greater than a set pixel size. Another useful editing feature is the use of Boolean operators, such as AND, OR, XOR, NOR, NXOR, and NAND, to combine or separate features.
5. *Quantitative measurement and analysis* is performed for three categories of data. *Object measurements* analyze individual features such as area, length, width, aspect ratio, and sphericity (see Table 1). *Field measurements* analyze individual objects and report values over the entire field. Examples include area fraction, area percent, and density (see Table 1). *Total area measurements* analyze the cumulative values reported over multiple fields. Figure 2 shows the analysis of an etched steatite sample. Note that the phase percentages as well as the percent porosity have been measured.
6. *Report generation* presents the data in a clear and understandable fashion.

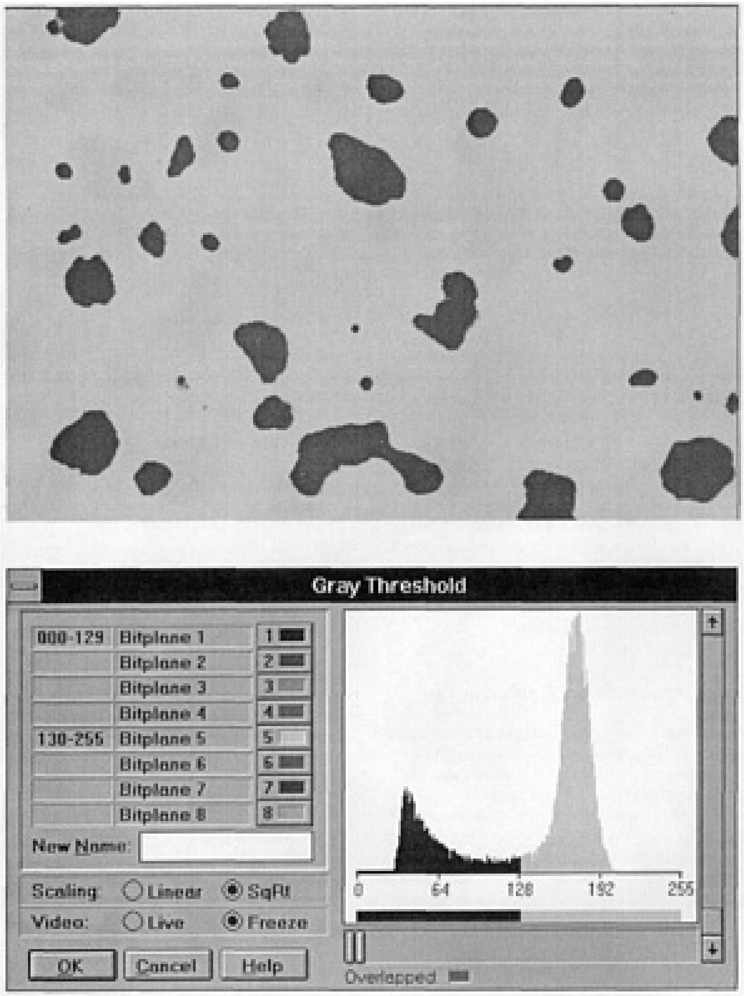


Fig. 1 Gray-level threshold for a porous steatite ceramic sample

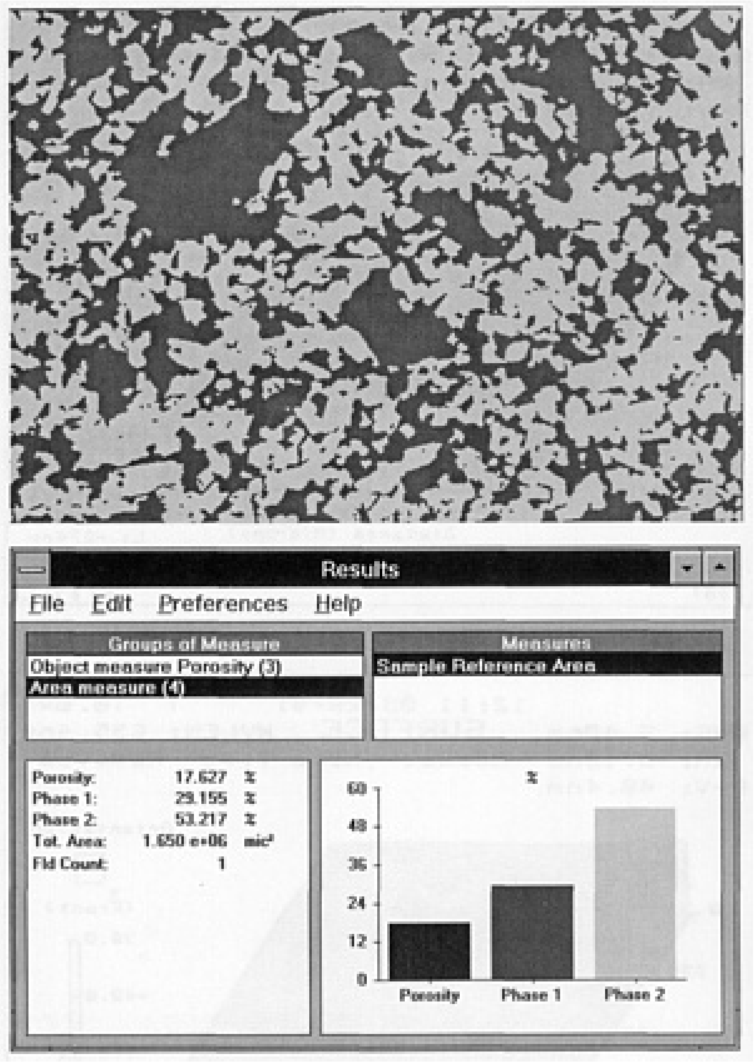


Fig. 2 Phase analysis of an etched steatite ceramic sample

Reference cited in this section

2. K. Leithner, Basics of Quantitative Image Analysis, *Adv. Mater. Proc.*, Nov 1993, p 18-23

Sample Preparation

Microstructural analysis requires a deformation- and damage-free sample for correct characterization. A typical preparation procedure includes sectioning, mounting, planar grinding (coarse grinding), sample integrity (rough polishing), polishing, etching, and examination. Ideally a specimen is prepared in such a way as to minimize the amount of damage produced at each stage. For example, the correct cutting blade can significantly reduce the amount of damage to the material, thus reducing the aggressiveness of the subsequent coarse grinding step (Ref 3, 4, 5).

To achieve the required surface finishes, combinations of grinding, lapping, polishing, and mechanochemical polishing techniques are used. For metallic samples, hardness is the critical feature for determining the preparation sequence, whereas ceramic preparation procedures depend on both hardness and fracture toughness. For metal samples, mechanical abrasives such as SiC, diamond, and alumina are commonly used in the preparation sequence. For ceramics, initial sectioning and grinding are accomplished with diamond abrasives; however, for the fine grinding steps, either diamond or softer mechanochemical abrasives (colloidal silica) are used. Nearly all ceramic materials that are final polished with colloidal silica produce damage-free samples. In the final-polished condition, surface features such as porosity, cracks, inclusions, and other defects can be observed.

In most cases, however, an etching step is used to reveal microstructural features such as grain boundaries or phase features. Common etching techniques include chemical, electrolytic, thermal, and plasma techniques (Ref 6). The commonly used techniques for metals are the chemical and electrolytic etching methods. For ceramics, thermal and plasma etching methods are very effective; however, chemical etching with very aggressive acids is also common. Another approach for etching both ceramics and composites is to relief polish the specimen. This technique requires a high-nap cloth and an alkaline-based colloidal silica suspension.

References cited in this section

3. S.N. Chanat, A.M. Trujillo, and D.C. Zipperian, Advanced Techniques for High Speed Precision Sectioning, *Buehler Digest,* Vol 27 (No. 1), 1993
4. D.C. Zipperian and S.N. Chanat, Readying Advanced Composites for the Microscope, *Adv. Mater. Proc.,* Aug 1993, p 15-21
5. D.C. Zipperian, S.N. Chanat, and A. Trujillo, Ceramic Microstructural Analysis for Quality Control, *Am. Ceram. Soc. Bull.,* Vol 71, July 1992, p 1077-1098
6. G. Petzow, *Metallographic Etching,* American Society for Metals, 1978

Optical Microscopy

For lower magnifications, 25× to 1000×, the optical microscope is the most important tool for the study of microstructure. For magnifications greater than 1000×, the scanning electron microscope is a useful tool. Today there are also other types of microscopes, including the scanning tunneling microscope and the confocal microscope.

The optical microscope offers a number of forms of illumination for revealing surface detail:

- *Bright-field illumination* is the most widely used. The incident light is reflected back through the objective, producing a bright background with dark features.
- *Dark-field illumination* is particularly useful for analyzing surface artifacts, such as surface scratches, and for studying grain structures. The incident light is supplied through the outside of the lens and is reflected back through the objective, producing a dark background with bright features.
- *Oblique illumination* is useful for low-magnification analysis that requires a three-dimensional appearance. It uses low-angle illumination, so higher magnifications are limited.
- *Polarized light* is especially useful for analyzing optically anisotropic metals, such as beryllium, α-titanium, and zirconium.
- *Differential interference contrast (DIC) illumination* is used to enhance topographic features in a surface. DIC illumination uses a Nomarski-modified Wollaston prism to split light into two wavefronts. Along with a polarizer, this enhances the relief effects on the surface.

Figures 3(a) to (c) show the same sample of machinable, reaction-bonded silicon-silicon carbide (SiSiC). In bright-field illumination, little information other than porosity is revealed, but in dark-field illumination, features such as grain boundaries and the porosity of the sample can be examined. In DIC illumination, the different phases of silicon and silicon carbide become very apparent.

Fig. 3 (a) Bright-field image of SiSiC. 200×. (b) Dark-field image of SiSiC. 200×. (c) Differential interference contrast illumination image of SiSiC. 200×

Abrasion Damage and Abrasion Artifacts

Machining ductile materials such as metals produces surface scratches as well as a plastically deformed surface layer. The depth of this deformed layer depends on the machining parameters as well as the metal type. For example, highly alloyed copper alloys such as 70-30 brass are among the most sensitive (Ref 7). To reveal the abrasion artifacts in 70-30 brass, etchants are used to remove the smeared layer. Figure 4 shows a polished 70-30 brass specimen along with its corresponding etched microstructure. Note that the artifacts have been highlighted by etching. To remove this abrasion damage, careful machining is required.

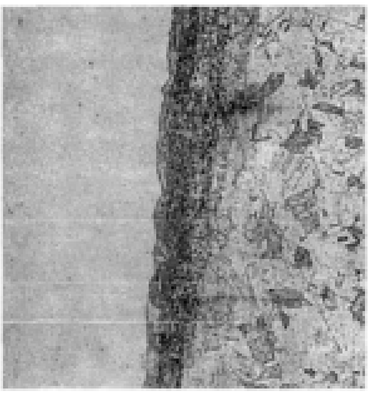


Fig. 4 Etching of 70-30 brass reveals smeared layer

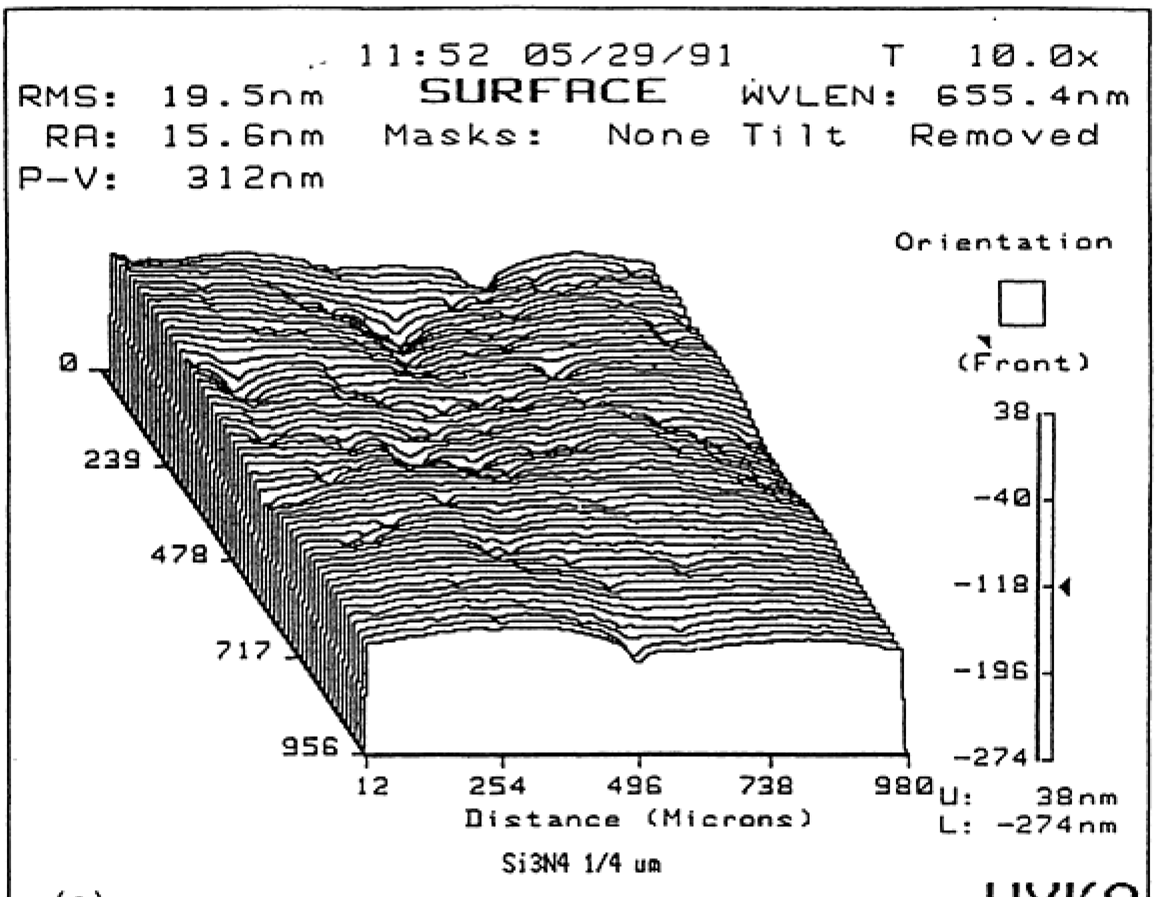
For ductile materials, the depth of the artifact-containing layer generally decreases with increasing specimen hardness. It also decreases with the use of finer abrasives. Additional examples of artifacts are given in Table 2. Other types of abrasion damage found in metals include hardening of the surface via cold working, embedded abrasives, and poor surface flatness.

Table 2 Common examples of abrasion artifacts for metals

Metal	Common artifacts	Solution
Austenitic steels	Deep surface layer artifacts	Extended rough polishing
Zinc	Mechanical twinning; Recrystallization abrasion layer	Avoid production of deep damage by severe grinding
Ferritic steels	Outer fragmented layer	Continued polishing beyond the scratch depth
Pearlitic steels	Disturbance in outer fragmented layer	Continued polishing
Tempered steels	Rehardened martensite caused by excessive heat	Appropriate cooling

Source: Ref 7

For ceramic and composite materials, the most important abrasion artifacts are surface and subsurface damage. For brittle ceramics in particular, grain pullout is a common abrasion artifact. Removal of this type of damage is difficult when only hard abrasives are used, such as diamond. The damage may be several orders of magnitude deeper than can be reached by the abrasives used in the final machining (polishing) stages, so it may not be removed. In fact, the most effective way to remove this type of damage is to use mechanochemical abrasives such as colloidal silica. Figure 5 compares the effects of 0.25 μm diamond polish and a mechanochemical polish on Si_3N_4.


11:52 05/29/91 T 10.0x
RMS: 19.5nm
SURFACE
WVLEN: 655.4nm
RA: 15.6nm
Masks: None Tilt Removed
P-V: 312nm
Orientation
(Front)
38
-40
-118
-196
-274
0
239
478
717
956
12
254
496
738
980
Distance (Microns)
U: 38nm
L: -274nm
Si3N4 1/4 um
WYKO
(a)

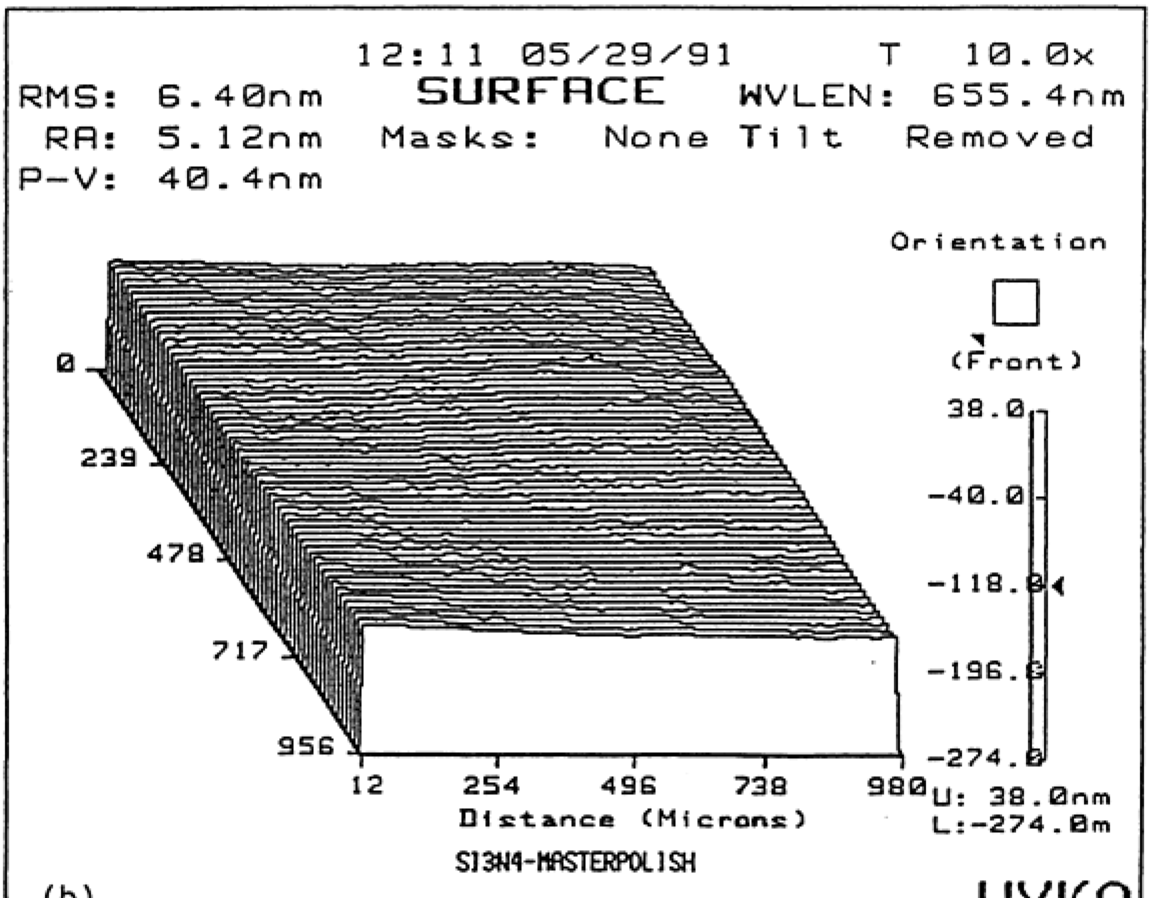

12:11 05/29/91 T 10.0x
RMS: 6.40nm
SURFACE
WVLEN: 655.4nm
RA: 5.12nm
Masks: None Tilt Removed
P-V: 40.4nm
Orientation
(Front)
38.0
-40.0
-118.0
-196.0
-274.0
0
239
478
717
956
12
254
496
738
980
Distance (Microns)
U: 38.0nm
L:-274.0m
SI3N4-MASTERPOLISH
WYKO
(b)

Fig. 5 Surface roughness of Si_3N_4 after (a) 0.25 μm diamond polish and (b) mechanochemical polish

Another aspect of subsurface damage is that unlike ductile materials, brittle materials can fracture, forming subsurface cracks that can continue to propagate with less aggressive surface finishing operations. Unless this damage is removed, the integrity and mechanical properties of the material can be compromised. In this respect, it is critical to minimize damage at each individual machining step. Analysis of a finished surface can provide a statistical analysis of the machining process and identify any significant changes in the material microstructure.

Reference cited in this section

7. L.E. Samuels, Mechanical Grinding, Abrasion, and Polishing, *Metallography and Microstructure,* Vol 9, 9th ed., *Metals Handbook,* American Society for Metals, 1985, p 33-47

Microhardness Testing

Microhardness testing is a useful tool for the microstructural analysis of a finished surface. Information such as phase identification and fracture toughness data can be determined. Hardness is defined as the resistance to penetration by an indenter, and the Knoop and Vickers measurements are the most common.

A Knoop hardness number (HK) is obtained by:

$$HK = P/A_p = 14.229\ P/d^2$$

where P is the load in kilogram force, A_p is the projected area of indentation in millimeters, and d is the length of the longest diagonal in millimeters.

The Vickers hardness number (HV) is obtained by:

$$HV = P/A_s = 1.8544\ P/d^2$$

where P is the load in kilogram force, A_s is the surface area of indentation in millimeters, and d is the length of the longest diagonal in millimeters.

Surface preparation is typically required before hardness testing to ensure that accurate reproducible results can be obtained. The surface finish used depends on the load to be applied to the indenter. For microhardness testing (1 to 1000 gf), a final polish is recommended.

Microhardness testing is a useful technique in characterizing different phases, and it has also been used to determine the fracture toughness in brittle materials. Fracture toughness is determined by initiating a controlled crack, then breaking the specimen, or by measuring crack lengths and applying fracture toughness equations (Ref 8, 9, 10, 11).

References cited in this section

8. J. Petrovic, L. Jacobson, P. Talty, and A. Vasudevan, *J. Am. Ceram. Soc.,* Vol 58 (No. 3-4), 1975, p 113-116
9. M. Mendiratta and J. Petrovic, *J. Am. Ceram. Soc.,* Vol 61 (No. 5-6), 1978, p 226-230
10. J. Petrovi and L. Jacobson, *J. Am. Ceram. Soc.,* Vol 59 (No. 1-2), 1976, p 34-37
11. J. Petrovic, R. Dirks, L. Jacobson, and M. Mendiratta, *J. Am. Ceram. Soc.,* Vol 59, 1976, p 177-179

Residual Effects of Finishing Methods

Marc Tricard, Norton Company

Introduction

THE CONCEPT OF "SURFACE INTEGRITY," originally defined in 1964 (Ref 1) for grinding operations, applies to any finishing operation. It can be extended to encompass six different groups of key factors: visual, dimensional, residual stress, tribological, metallurgical, and other factors as described in Fig. 1. This article shows the importance of these factors in the performance and behavior of various manufactured parts. Special emphasis is given to residual stresses and their influence on the final mechanical properties of a part.

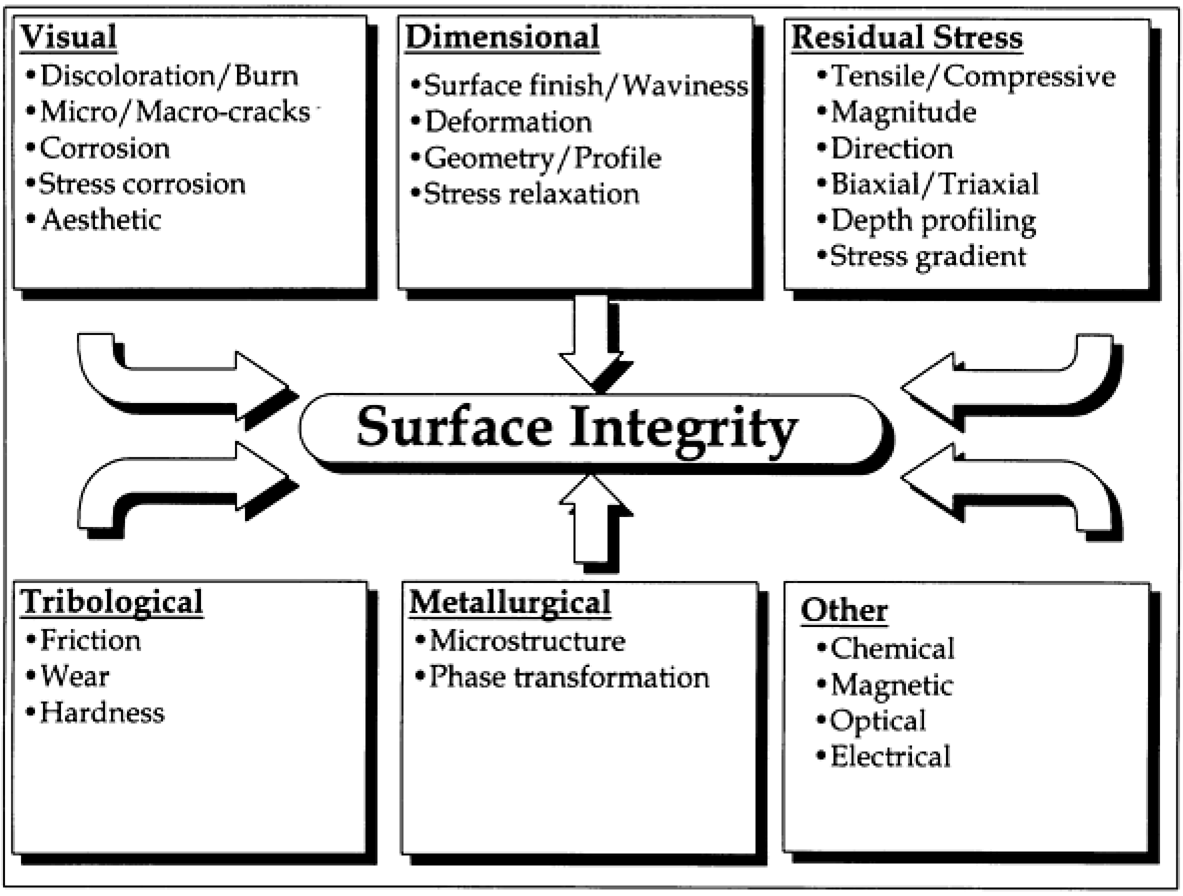


Fig. 1 The six different groups of key factors that define the surface integrity of a finished material

Acknowledgements

The author thanks K. Subramanian for his helpful comments on this manuscript, as well as Carol Cooper, Anna Durilin, Frank Esposito, Mary Silverberg, and Bruce Vigeant.

Reference

1. M. Field and J.F. Kahles, Review of Surface Integrity of Machined Components, *Ann. CIRP*, Vol 20 (No. 2), 1971, p 153-163

Systems Approach to Finishing

Finishing methods, like any manufacturing operation, can be looked at efficiently using a systems approach (Ref 2). As can be seen from Fig. 2, a systems approach can also be used to consider a finishing operation and its resulting surface integrity:

- *Input:* Finishing processes involve a vast array of variables pertaining to four categories (i.e., the work material, the machine tool, the processing tool used, and the operational factors).
- *Process:* The four inputs define the microscopic aspects of a finishing operation, especially the thermal and mechanical interactions that condition the final surface integrity. These microscopic aspects can be measured macroscopically with forces, power, energy, or temperature transducers during the finishing operation.
- *Output:* The process leads to a finished part that has a given surface integrity and specific visual, dimensional, residual stress, tribological, metallurgical, and other factors (Fig. 1). The resulting surface integrity of the finished part conditions its operational performance.

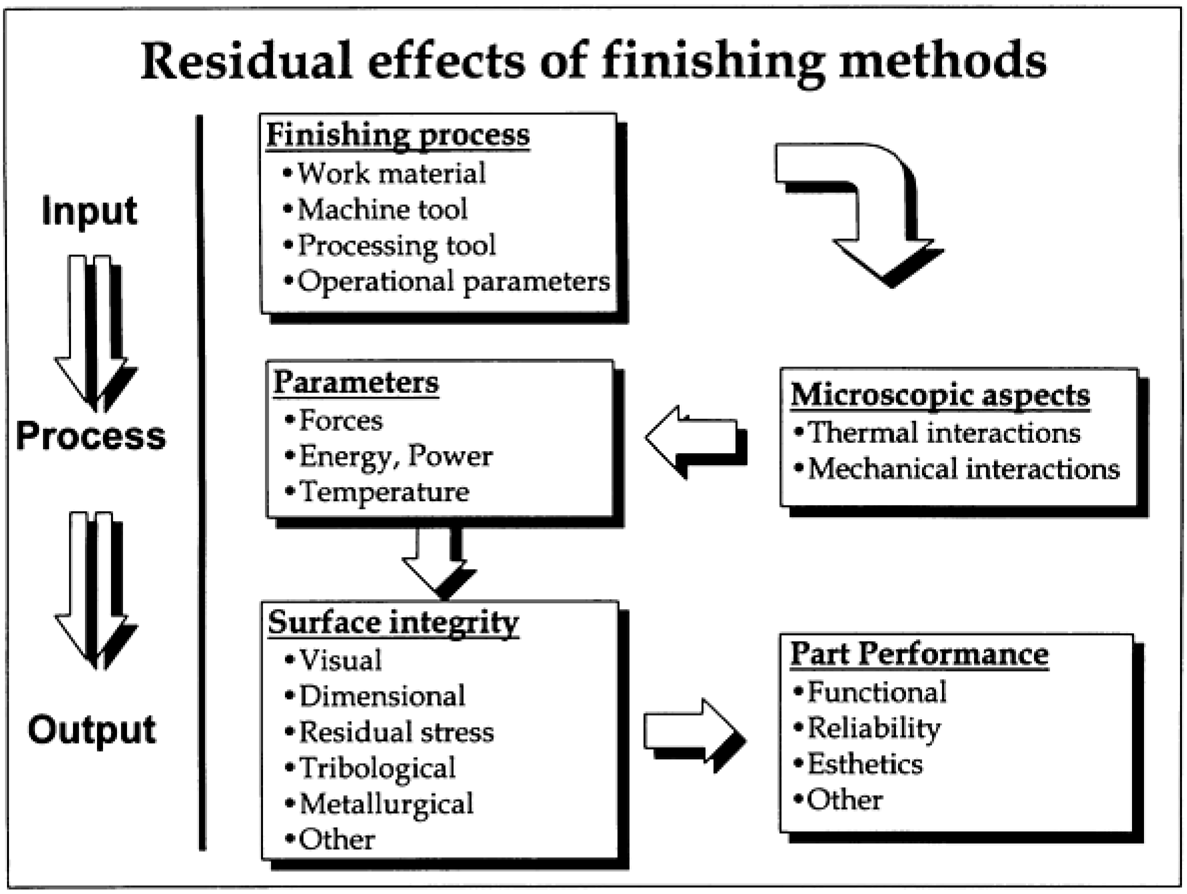


Fig. 2 Systems approach to the residual effects of finishing methods

As the name implies, finishing methods occur at the end of a manufacturing process, and thus the residual effects they leave on the part are of crucial importance. Manufactured components typically result from a succession of operations, but in most cases it is the last operation that governs the residual stress profile imparted to the component prior to its use or service. Exceptions occur when the final machining operation has a penetration depth smaller than the previous ones (Ref 3). In such situations, the superimposition of residual stress must be considered (Fig. 3). In more conventional cases, the final grinding operations determine the final state of residual stress rather than the turning operation(s) that preceded them.

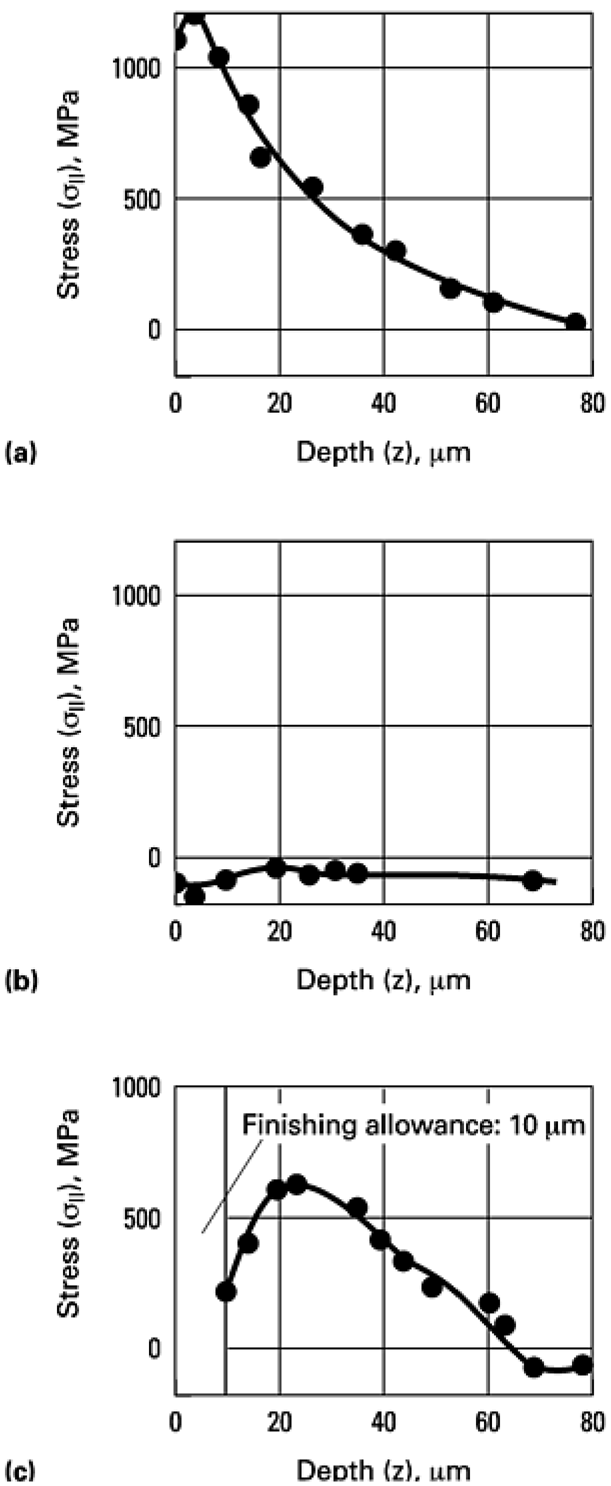


Fig. 3 Residual stress profiles in internal grinding cycles. Workpiece: 100Cr6; hardness, 62 HRC; diameter, 40 mm (1.6 in.). Table speed: 1 m/s. Corundum grinding wheel: A80K6V; diameter, 30 mm (1.2 in.); width, 8 mm (0.3 in.); speed, 40 m/s. Dressing: D 427 diamond cup wheel; speed ratio, 0.7; overlap, 40; infeed, 2 μm. Cooling: 4% emulsion. (a) Roughing. Relative metal removal rate (MRR), 6 mm^3/mm · s; relative volume of material removed, 18.8 mm^3/mm. (b) Finishing. Relative MRR, 1 mm^3/mm · s; relative volume of material removed, 1.6 mm^3/mm. (c) Roughing and finishing. Source: Ref 4

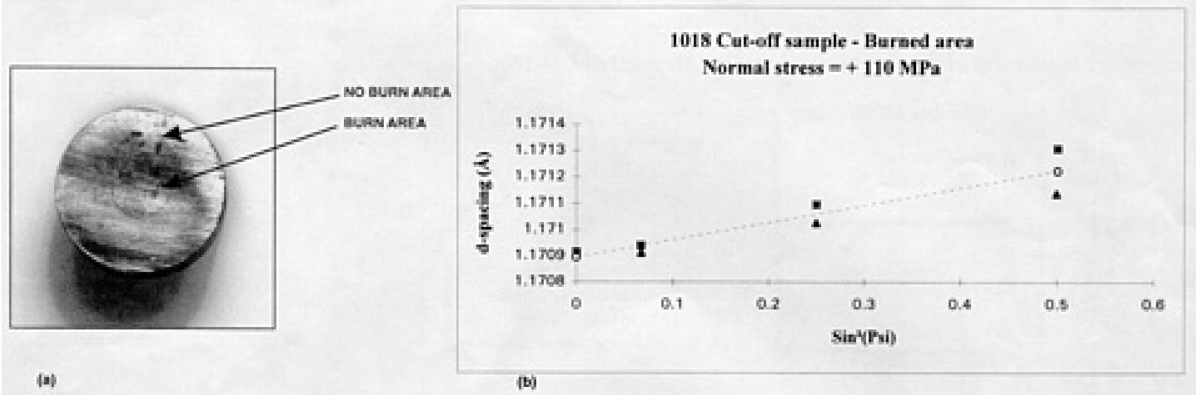
The residual stress effects of finishing processes can have a significant impact on the performance and viability of engineering components. Examples of possible negative effects are presented in Ref 5, which includes case histories of four finished parts that failed due to residual stresses.

Factors in Surface Integrity

When dealing with manufacturing issues, it is important to keep in mind that all the parameters involved in the finishing process have a direct influence on the surface integrity of the part. The six groups of key factors presented in Fig. 1 are not random, but are rather the deterministic outcome of the process chosen (Ref 2, 6). Basic understanding of the causal relationships between the mechanical, thermal, and chemical aspects of a finishing process and the six groups of key factors related to surface integrity is the key to successful improvement of a finishing process.

Visual Factors

Discoloration/Burn. In many manufacturing operations, surface damage can be detected with simple visual observations. See, for example, the 1018 steel cutoff sample shown in Fig. 4. Grinding burns are simply a discoloration due to the oxidation at high temperature. However, the absence of discoloration does not imply that the surface was not heated excessively. Work can be badly overheated in grinding without any trace of discoloration remaining on the finished surface if the conditions are such that the wheel cleans off the discoloration almost as soon as it appears. In cross-feed grinding, if the leading edge of the wheel takes a heavy cut so that the work is heated severely to a depth of several thousandths of an inch, the trailing portion subsequently may remove a layer a fraction of a thousandth inch deep, thus eliminating all evidence of the prior discoloration and leaving practically all of the heat-affected layer of metal (Ref 7).



Model: d = A + B sin²(Psi)

Regression:

	A	B
Value	1.17E+00	6.56E-04
Error	3.57E-05	1.19E-04

Statistics:

	R-Square	F-Test	p-value
Value	0.86	30.66	2.64E-03

Stress:

ksi	Value	CS Error	GOF
Normal	1.61E+01	1.16E+00	2.90E+00

Model: d = A + B sin²(Psi) + C sin(2Psi)

Regression:

	A	B	C
Value	1.17E+00	6.56E-04	6.06E-05
Error	1.66E-05	5.51E-05	1.39E-05

Statistics:

	R-Square	F-Test	p-value
Value	0.98	80.55	5.87E-04

Stress:

ksi	Value	CS Error	GOF
Normal	1.61E+01	N/A	1.35E+00
Shear	1.48E+00	N/A	3.39E-01

(c)

Fig. 4 Measurement and analysis of surface damage using x-ray diffraction. (a) 38 mm (1.5 in.) 1018 steel cutoff sample showing burn-related discoloration. Two residual stress measurements by x-ray diffraction were made on the sample at the locations marked by the four concentric markers. (b) Typical *d* versus sin ^{2} ψ curve (where *d* is the interatomic distance, which varies according to stress level, and ψ is the angle of the incoming x-ray beam relative to the surface) obtained from an x-ray diffractometer. Seven different ψ orientations (from -45° to +45°) were used. The *d*-spacing can be looked at as a natural strain gage in a material: a compressive stress tends to diminish the *d*-spacing value, whereas a tensile stress increases it by bringing two interatomic spaces farther apart. The x-ray diffractometer allows one to measure this value by providing a measurement for *d* from Bragg's law ($2d \sin \Theta = n\lambda$, where Θ is the angular distance between the incident and diffracted beams, *n* is the order of reflection, and λ is the wavelength of the x-rays). The slope of the curve, obtained by

linear regression, is directly proportional to the residual stress. (c) Two analyses of the curve shown in (b). The first is a simple linear regression that relates the lattice *d*-spacing to the $\sin^2\psi$ at various ψ angles, with the result σ_{11} = 110 MPa (16 ksi); it is assumed that σ_{13} = 0. The second model is a multiple linear regression with the result σ_{11} = 110 MPa (16 ksi) and σ_{13} = 10 MPa (1.5 ksi). Additional information about these measurement techniques is available in Ref 28.

As demonstrated in Fig. 4, measurement of residual stresses by x-ray diffraction now offers a practical way to quantify what used to be only a visual observation. A stress measurement in the burned area (darkest zone in Fig. 4a) indicated a tensile residual stress of 110 MPa (16 ksi), whereas the unburned area (clearest zone) indicated a compressive stress of -30 MPa (-4 ksi). The Eddy-current technique or careful microhardness measurements can also lead to meaningful information (Ref 8).

Micro- and Macrocracks. Cracks or even spalling may occur in finishing operations that have significant thermal and mechanical effects, such as grinding. For flat-surface grinding, cracks appear primarily perpendicular to the grinding direction, with typical depths from 0.010 to 0.020 in. (Ref 9). Interesting crack formations have been described (Ref 1) resulting from additional operations, including milling, reaming, drilling, electrodischarge machining, and laser beam machining.

Susceptibility to Corrosion / Stress-Corrosion Cracking. Finishing operations have a significant influence on the stress-corrosion resistance of a part, and it is well known that the introduction of some surface roughness may improve resistance in corrosive atmospheres. Crack propagation in a stressed material in a corrosive environment, termed *stress-corrosion cracking* (SCC), can occur in a finished part due only to residual stress, without any applied load.

Extensive research has been performed on the relationship between residual stress and SCC susceptibility for 304 and 316 austenitic stainless steel pipe weldments used in nuclear power plant boiling water reactors. In one study (Ref 10), intergranular SCC in a weld heat-affected zone (HAZ) was detected by ultrasonic testing long before any rupture occurred. Measurements of residual stress, by x-ray diffraction and stress relief techniques, were used in multipass gas-tungsten arc welding with reported accuracy of ±35 to 50 MPa (±5 to 7 ksi) and 135 MPa (15 ksi), respectively. It was found that the welding operations, along with the grinding operations used before and after welding, generated tensile stress. This stress contributed to the intergranular SCC in the weld microstructure, which was sensitized by the reactor water coolant containing small amounts of dissolved oxygen (200 to 300 ppb). A significant reduction in SCC was obtained by deliberately introducing compressive residual stress on the inside pipe surface. This was accomplished by creating a thermal gradient during the welding operation--the outside diameter of the pipe was maintained at a temperature between 500 and 550 °C (930 and 1020 °F), while the inner diameter was kept at 100 °C (212 °F) with circulating water.

Rough-turning operations studies have shown that tensile residual stresses at the surface of a part are quite detrimental to its corrosion resistance. Fluids used in finishing operations should also be considered when dealing with corrosion issues. For instance, based on hot-salt stress-corrosion tests (Ref 11), it has been shown that chemical milling can destroy the compressive stress layers that normally exist after machining, which gives a finished part reduced resistance to stress-corrosion cracking. Aluminum parts can show corrosion if they are machined for an extended period of time, due to galvanic action: current flow can occur between the machine tool base and the part if no special fluid is used (Ref 12). Even blowing off parts after machining can lead to rust if the compressed air used contains any moisture.

Aesthetic considerations are also important. When performance requirements are nearly equal, the finished component of choice is the one that has the better appearance. Cast iron sinks, brass plumbing equipment, hand levers, golf clubs, faucets, hammers, and silverware are examples of parts deburred, polished, or buffed by the thousands to improve their appearance. Even very large parts can be buffed to a bright finish. For example, Ref 13 describes the buffing of an entire aircraft fuselage (32.3 m, or 106 ft, long) using machines with 457 mm (18 in.) buffing wheels mounted on four computer numerically controlled floating heads on a movable gantry.

Dimensional Factors

Surface Finish / Waviness. Figure 5 indicates the surface finish (expressed as the roughness average, R_a) that can be achieved with a variety of manufacturing processes. Traditionally, the requirements for finishing processes have been compromises between achieving better surface finishes while at the same time reducing the total finishing time. Recent developments in microgrinding with fixed abrasives have enabled this process to compete with the slower lapping operation using loose abrasives (Ref 14).

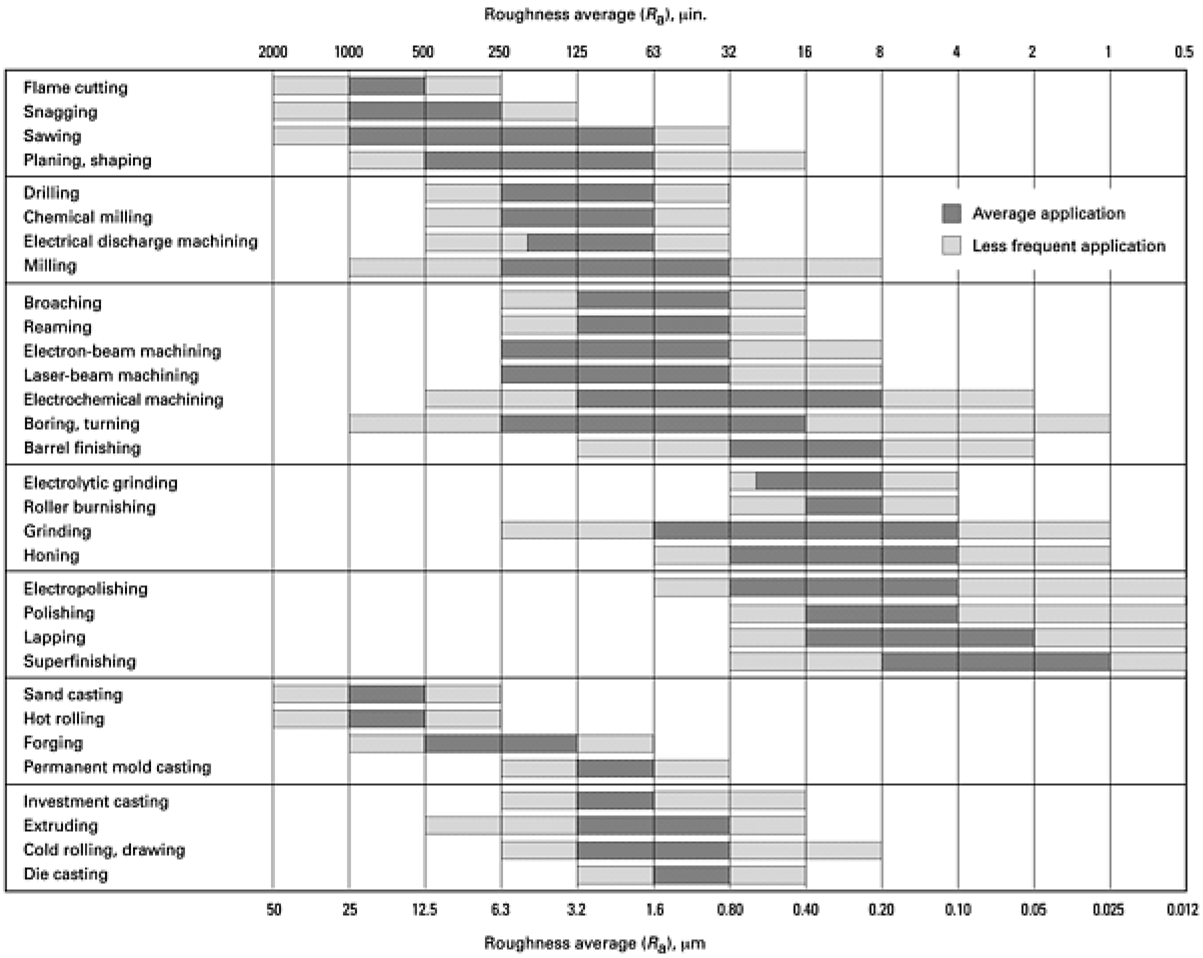


Fig. 5 Ranges of average surface roughness produced by various processing methods. Source: *Machinery's Handbook,* 24th ed., Industrial Press, 1992, p 672

Beyond their well-known importance for tribology (Ref 15, 16) and aesthetics, surface finish and waviness can have a significant impact on the surface integrity of a part, because wear behavior of surfaces is influenced by the surface roughness. Huang (Ref 17) has studied the fatigue life of turned and ground superalloys and has shown that the surface roughness, especially at high temperature, and residual stresses of the samples had more effect on fatigue resistance than surface hardening does.

Stress relaxation can be a finishing operation per se. Reference 18 describes a variety of thermal and/or mechanical operations can be applied for stress relieving. For example, 90 s in a salt bath at 345 °C (650 °F) relieved 80% of the residual stress of ground steel parts (Ref 19). Even if no stress relaxation technique is used, fatigue-related relaxation sometimes occurs due to microplastic deformation. The rate of relaxation is greatest when the finishing process produces the steepest residual stress gradient normal to the surface (Ref 20). Thus, sand-blasted or rolled parts could be expected to relieve their residual stress much faster than milled ones, for metallic components.

Residual Stress Factors

Sign of the Residual Stress. It has frequently been stated that a compressive state of residual stress enhances the fatigue behavior of a finished component. Crack initiation and propagation in ground components of aerospace or automotive engines are indeed slowed down tremendously when negative (compressive) residual stress values are present. In a few instances zero residual stress is the desired goal, as in the case of read/write heads of hard disks, because all residual stresses lead to magnetically inactive layers.

Magnitude and Direction of the Residual Stress. The loading conditions to which the finished part will be submitted are an important consideration. The total applied stress (mechanical, thermal, etc.) plus the residual stress

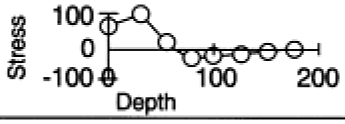
determine the mechanical behavior of a finished part, such as its fatigue resistance. Quantitative analysis of residual stress with both destructive techniques (e.g., hole drilling, deflection technique, indentation, etching) and nondestructive techniques (e.g., x-ray or neutron diffraction, Eddy current, Barkhausen noise analysis) are being used more often to help characterize the magnitude and direction (Ref 21). Applications have been reported in gear grinding assessment (Ref 22), bearings manufacturing (Ref 23), camshaft grinding monitoring (Ref 24), rotor shaft examination (Ref 25), welding (Ref 26), and even production of rail components for the French fast speed TGV train (Ref 27).

Residual Stress Field. When considering the type of residual stress field present in the part, it is important to know about the specific stress tensor component concerned. Many studies focus only on the principle stress component, σ_{11}, when the shear component, σ_{13}, should also be considered. Indeed, many experimental techniques assume a perfectly biaxial stress when the various characteristics of the finishing method being considered can lead to a highly triaxial residual stress field. X-ray or neutron diffraction techniques can be valuable nondestructive tools in quantifying such biaxial and/or triaxial stress fields (Ref 28).

Stress Below the Surface. X-ray techniques emphasize *surface* measurement of residual stress, because x-ray penetration depths are typically less than 20 μm in steels. However, the critical areas often appear much deeper in the part (150 to 200 μm being typical), emphasizing the need for careful plotting of residual stress versus depth, possibly with the help of electropolishing techniques.

The four residual stress factors are summarized in Table 1. Examples of residual stress introduced by grinding, milling, turning, planing, shaping, electrical discharge machining (Ref 29), abrasive tumbling, rolling, and shot peening can be found in Ref 2 and 19, as well as in the very good survey paper by Brinksmeier et al. (Ref 30).

Table 1 Parameters that characterize a state of residual stress in a finished component

Parameter	Comments	
Sign at the surface	Tensile or compressive	
Magnitude/Direction	Applied stress + Residual stress = Total loading conditions	
Stress field	Stress tensor components	$\begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{13} & \sigma_{23} & \sigma_{33} \end{bmatrix}$
Stress below the surface	Stress profile — Stress gradient Typically with electropolishing	

Example 1: Residual Stresses in Grinding.

The existence of residual stresses in a ground specimen is due to the combined action of mechanical and thermal effects.

Mechanical Effect. Mechanical forces during grinding expand the surface of a sample, so that the plastically deformed surface experiences a compressive residual stress state while the elastically deformed near-surface layer is left in a state of residual tension. The elevation of temperature in the surface of the sample as a result of the cutting action causes a reduction in local yield strength and, therefore, more plastic deformation. This mechanical aspect of grinding is somewhat comparable to shot peening, in which small-diameter beads plastically deform the surface of a sample, leaving the finished surface in a compressive state of residual stress.

The thermal effect is probably the more important of the two effects. During the grinding operation, the temperature dramatically increases in a thin surface layer of the specimen, while the bulk inner parts remain cool. It has been shown (Ref 31) that the maximum value of the tensile stress in a machined surface obtained by grinding or any other cutting technique is directly related to the maximum surface temperature reached during the process. As the plastically deformed surface layer cools, its thermal contraction is aided by the part's interior, generating tensile residual stresses at the surface.

As shown in Fig. 6, the resulting value of the residual stress induced during the grinding operation is the superimposition of these two phenomena. If the thermal effect is the more important, as in high-metal-removal-rate grinding where considerable heat is generated, the first layers of the specimen's surface show tensile residual stresses. In "low-stress grinding" (that is, grinding operations with low metal-removal rates), the mechanical effect overtakes the thermal aspects,

and the superimposition of the two results in a residual stress profile that is predominantly in the compressive zone. Of course, this distinction between mechanical and thermal aspects is a simplification--during grinding the two phenomena cannot be dissociated. The friction associated with the mechanical effect is the primary source of heat, while in turn the temperature generated can considerably reduce the yield strength of the material being ground. Consequently, if the material being ground has a higher thermal expansion coefficient, this will directly translate into higher stresses (Ref 32). A material with a low yield strength will experience the same effect.

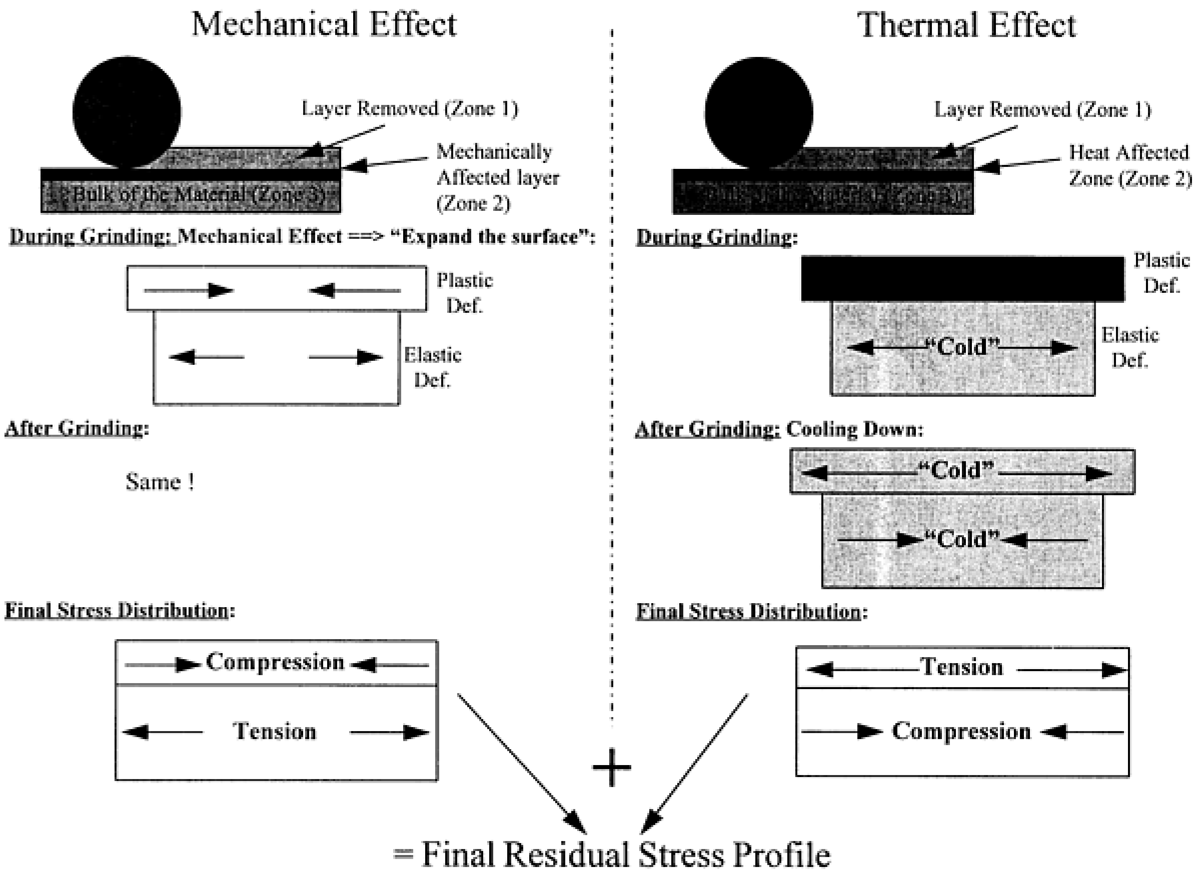


Fig. 6 Residual stress profile left in ground components by the superimposition of a mechanical (left) and a thermal (right) effect. For the process shown on the left, three distinct zones can be distinguished: zone 1 is the surface layer being ground, zone 2 is the "mechanically affected zone" immediately underneath zone 1, and zone 3 is the remaining bulk of the material. During grinding, zone 2 experiences an increase in length, which is constrained by the unaffected zone 3. The plastically deformed surface (zone 2) is therefore left in a state of compression, while the bulk of the material (zone 3) is in slight tension. For the process shown on the right, zone 2 is the "heat-affected zone" at the surface of the material. During grinding, the heated surface (zone 2) expands in length, but once again is constrained by the bulk of the material (zone 3), which remains at room temperature, leaving the surface in a state of compression. The workpiece begins to cool immediately after grinding, reversing the distribution and resulting in a surface layer in tension and the bulk of the part in slight compression. For most parts, the "real" stress distribution is the sum of these mechanical and thermal effects.

References 33 and 34 explain in depth how residual stresses are generated during a grinding operation. Reference 35 contains an interesting discussion of these mechanical and thermal effects and their influence on the fatigue life of a ground component. Numerous additional studies have been devoted to surface integrity in specific finishing operations, such as for grinding (Ref 30, 36, 37, 38), honing (Ref 39), and lapping (Ref 40). For all finishing operations, relative control of the residual stresses generated by the process can be achieved through a good understanding of the thermal and mechanical effects involved. Some operations, such as shot peening and rolling, are predominantly governed by the mechanical aspects, while others, such as electrical discharge machining, favor the thermal aspects. Most combine both aspects in a ratio that depends on the specific operating parameters of the process.

Example 2: Residual Stresses in Shot Peening.

Shot peening is a cold working process in which thousands of spherical shot (typically $\frac{1}{2}$ mm diam spheres of steel, glass, or ceramic) are propelled against the surface of a part. The overlap of the small craters formed by the impact of each sphere creates a compressive layer at the surface of the part. In this process, the intensity of the stresses generated typically exceeds half the yield strength of the material being peened. The depth of the residual stress layer obtained depends on the operating parameters of the process, including the intensity of the process as measured by Almen gages; the size, velocity, and impingement angle of the shot (Ref 41); and the characteristics of the material being shot peened.

Table 2 indicates the wide variation in fatigue life performance that can be obtained by varying the finishing process. These data clearly demonstrate the benefits of creating compressive residual stresses at the surface of a part by shot peening. In addition to improving the fatigue behavior of a part, controlled shot peening can also be used as a finishing process to generate three-dimensional surfaces such as those on aircraft wings and empennage skin. Additional examples of shot peening applications are listed in Ref 43. This process is described in detail in the article "Shot Peening" in this Volume.

Table 2 Fatigue life performance obtained by parts finished using various methods

Operation	Endurance limit in bending (10^7 cycles), MPa (ksi)	Relative endurance limit[(a)]
Surface grinding		
Gentle	414(60)	100
Conventional	165(24)	40
Turning		
Gentle	414(60)	100
Abusive	414(60)	100
Electrochemical machining		
Standard	269(39)	65
Off standard	269(39)	65
Standard plus peening	538(78)	130
Off standard plus peening	462(67)	112
Electrical discharge machining		
Finish	152(22)	37

Rough	152(22)	37
Finish plus peening	455(66)	110
Rough plus peening	517(75)	125
Electropolishing		
Standard	290(42)	110
Standard plus peening	538(78)	130

Note: Material for all parts was Inconel 718.

Source: Ref 42

(a) Expressed as a percentage of that obtained with gentle grinding.

Tribological Factors

A finished workpiece is often designed to be part of a moving mechanism where wear or friction might become an important issue. Finishing operations therefore should to be selected based on their consequences on the wear resistance of the parts, their friction coefficient, their hardness, and so on (Ref 15, 16).

Wear. The influence of finishing method on the run-in of AISI A10 and AISI 4140 steel cams has been demonstrated (Ref 44). The wear mechanisms involved were found to be strongly dependent on the surface finishing method used (milling, grinding, ion nitriding, or blasting) as well as the microstructure of the steel. Interestingly, this study also clearly demonstrated the advantage of computer-controlled finishing machines over their analog counterparts as far as wear is concerned.

Friction. A study of the break-in period of automotive components demonstrated that honing and lapping operations can reduce the initial friction of cylinder liners and cam shafts (Ref 45).

Hardness. As many studies have demonstrated (e.g., Ref 17), surface hardening resulting from a finishing operation can lead to significant improvement in the fatigue life of a component.

A good understanding of the micromechanisms associated with a finishing technique might bring some significant mechanical advantages. Of course, a tradeoff might have to be made. In Ref 44, for instance, the lower wear of nitrided and bead-blasted cams had to be judged against a decrease in their dynamic performance, compared with that of ground cams.

Metallurgical Factors

A wide variety of metallurgical effects can occur during a finishing process: formation of untempered or overtempered martensite, retained austenite, volume changes due to phase transformation, oxidation, and other effects can become important, depending on the mechanical and thermal aspects of the finishing operation. Reference 9 provides a good introduction to these phenomena in the case of grinding, while Ref 1 reviews various metallurgical alterations in the cases of milling, reaming, drilling, electrodischarge machining, and laser beam machining.

Most of these metallurgical characteristics can be qualitatively assessed through a wide variety of observation techniques, such as metallography, scanning electron microscopy, and chemical etching. New techniques have also been developed

for better quantification. For example, the percentage of retained austenite present at the surface of material can be measured by x-ray diffraction on the same diffractometer used for residual stress measurements. Reference 47 describes measurements of both residual stress and percentage of retained austenite on various heat-treated steels ground with cubic boron nitride. Acoustic microscopy has also been used to evaluate the thickness of the metallurgically damaged layer on a ground surface (Ref 48). Table 3 lists various testing techniques and references that provide additional information. Some of these metallurgical factors that may restrict a finishing operation can also be turned to advantage. For example, significant toughening of ceramic materials can be obtained by forcing phase transformations to occur at the surface through a grinding operation. Reference 21 gives an example of a controlled stress-induced phase transformation from the tetragonal to monoclinic phase of ZrO_2. The 3 to 5% volume expansion associated with this phase transformation resulted in highly compressive residual stresses with values exceeding 1 GPa at the surface, which strengthened the ceramic.

Table 3 Testing techniques for surface integrity evaluation

Surface integrity factor considered	Evaluation technique	References
Cracks	Acoustic emission	57
	Acoustic microscope	48
	Eddy current	
	Etching	9, 46
	Magnetic particle	9
	Metallography	9
	Optical microscope	58
	Penetrant	9
	Scanning electron microscopy	
	Transmission electron microscopy	
	Ultrasonic signal	4
	Visual observation	
Metallurgy	Magnetic particle	
	Metallography	1, 9, 58
	Scanning electron microscopy with microprobe analysis	4

	X-ray diffraction	47, 56
Hardness	Microhardness	58
	Superficial hardness	4
	Ultrasonic signal	4
Residual stresses	Barkhausen noise analysis	4, 24
	Eddy current	
	Hole drilling	59, 60, 61
	Interferometry	62
	Layer removal	27, 30, 42
	Neutron diffraction	26, 63
	Ultrasonic signal	4
	X-ray diffraction (XRD)	27, 28, 30, 42
	XRD with electropolishing	4

This table, by no means exhaustive, provides references that describe various techniques one can use to qualify or quantify key surface integrity factors and that present practical examples of applications for various finishing methods. Volume 9 *Metallography and Microstructures,* and Volume 17, *Nondestructive Evaluation and Quality Control,* of the *ASM Handbook* also provide specifics on most of these techniques.

Other Surface Integrity Considerations

In some applications, additional specific properties of the surface layers have to be considered. The chemical, magnetic, optical, or electrical properties of a finished part can sometimes be dramatically affected by a finishing process. For instance:

- Chemical glass strengthening by ion exchange can result in high compressive residual stress when large sodium ions replace smaller lithium ions in a salt bath rich in sodium ions (Ref 49).
- For manganese-zinc and nickel-zinc surfaces, the deformation and residual stress induced during a lapping operation can generate magnetically dead layers detrimental to the performance of a magnetic recording head system (Ref 50).
- Optical properties of infrared materials may be influenced by various processing techniques (Ref 51).
- The surface condition, particularly the presence of cracks due to brittle fracture during the finishing process, can affect the electrical behaviors of insulators (Ref 52).

In other cases (Ref 53), the finish surface might require special consideration due to the risks of hydrogen embrittlement (cracking without corrosion) or liquid metal embrittlement (as in the case of aluminum alloys with mercury). The breakdown of machining fluid, especially sulfurized ones, can result in high levels of hydrogen in ground steel samples (Ref 54). Other examples include a sanding technique that influences the wettability and shear strength of wood (Ref 55) and abrasive jet machining finishing techniques that are used where there is risk of explosion.

References cited in this section

1. M. Field and J.F. Kahles, Review of Surface Integrity of Machined Components, *Ann. CIRP,* Vol 20 (No. 2), 1971, p 153-163
2. K. Subramanian and R.P. Lindsay, A System Approach for the Use of Vitrified Bonded Superabrasive Wheels for Precision Production Grinding, *J. Eng. Ind.,* Vol 114, Feb 1992, p 41-52
3. B. Sholtes, Residual Stresses Introduced by Machining, *Advances in Surface Treatments--Technology--Applications--Effects,* Vol 4, *Residual Stresses,* A. Niku-lari, Ed., Pergamon Press, 1987, p 59-71
4. E. Brinksmeier, E. Schneider, W.A. Theiner, and H.K. Tonshoff, Nondestructive Testing for Evaluating Surface Integrity, *Ann. CIRP,* Vol 33 (No. 2), 1984, p 489-509
5. S.W. Shin and G.H. Walter, Case Histories of Residual Stress Related Component Failures, *Residual Stress for Designers and Metallurgists,* L.J. Vande Walle, Ed., American Society for Metals, 1980, p 1-20
6. J.B. Bryan, The Power of Deterministic Thinking in Machine Tool Accuracy, *Proc. 1st Int. Machine Tool Engineers Conf.* (Tokyo), 1984
7. E.R. Marshall and M.C. Shaw, Forces in Dry Surface Grinding, *Trans. ASME,* Jan 1952, p 51-59
8. H.K. Tonshoff and E. Brinksmeier, Determination of the Mechanical and Thermal Influences on Machined Surfaces by Micro-Hardness and Residual Stress Analysis, *Ann. CIRP,* Vol 29 (No. 2), 1980, p 519-530
9. L.P. Tarasov, Some Metallurgical Aspects of Grinding, *Machining--Theory and Practice,* H. Ernst et al., Ed., American Society for Metals, p 409-464
10. J.C. Danko, Effect of Residual Stresses on the Stress-Corrosion Cracking of Austenitic Stainless Steel Pipe Weldments, *Practical Applications of Residual Stress Technology,* Clayton Ruud, Ed., ASM International, 1991, p 27-37
11. J.W. Dini, Fundamentals of Chemical Milling, *Am. Mach.,* July 1984, p 113-128
12. C.A. Sluhan, Grinding with Water Miscible Fluids, *Grinding--Theory, Techniques and Troubleshooting,* C. Batheja and R.P. Lindsay, Ed., Society of Manufacturing Engineers, 1982, p 183-205
13. Harper Surface Finishing Systems, Inc., "Airliners in the Buff," reprint from *Manufacturing Engineering*
14. K. Subramanian, P.D. Redington, and S. Ramanath, A Systems Approach for Grinding of Ceramics, *Bulletin of the American Ceramics Society,* Vol 73 (No. 3), March 1994, p 61-66. Adapted from *Machining of Advanced Materials,* Proceedings of the International Conference on Machining of Advanced Materials, 20-22 July 1993, Gaithersburg, MD, NIST Special Publication 847, p 43-53
15. E. Rabinowicz, *Friction and Wear of Materials,* John Wiley and Sons, 1966
16. N.P. Suh, *Tribophysics,* Prentice-Hall, 1986
17. Q. Huang and J. Jing Xin, Surface Integrity and Its Effects on the Fatigue Life of the Nickel-Based Superalloy GH33A, *Int. J. Fatigue,* Vol 13 (No. 4), 1991, p 322-326
18. M.R. James, Relaxation of Residual Stresses--An Overview, *Advances in Surface Treatments--Technology--Applications--Effects,* Vol 4, *Residual Stresses,* A. Niku-Lari, Pergamon Press, 1987, p 349-365
19. H.R. Letner and A.B. Sauvageot, Relief of Residual Grinding Stress by Annealing, in *Grinding Stress--Cause, Effect and Control--Collected Papers,* Grinding Wheel Institute
20. M.R. James, The Relaxation of Residual Stresses during Fatigue, *Proc. 28th Sagamore Army Materials Research Conf.--Residual Stress and Stress Relaxation* (Lake Placid, NY), Plenum Press, 1981, p 297-314
21. M.R. James, Application of X-Ray Residual Stress Measurements in Industrial R&D, *Measurements of Residual and Applied Stress using Neutron Diffraction,* M.T. Hutchings and A.D. Krawitz, 1991, p 37-50
22. H.D. Dodd and K.V. Kumar, Technological Fundamentals of CBN Bevel Gear Finish Grinding, Technical

Paper MR85-273, *Superabrasives '85* (Chicago), Society of Manufacturing Engineers, 1985

23. G.R. Kuhlman and B.S. Pardue, Correlation of Residual Stress to Bearing Condition, *Residual Stress in Design, Process and Materials Selection,* ASM International, 1987, p 169-181
24. R.M. Fix, K. Tiitto, and S. Tiitto, Automated Control of Camshaft Grinding Process by Barkhausen Noise, *Mater. Eval.,* Vol 48 (No. 7), July 1990, p 904-908
25. J.F. Porter, D.O. Morehouse, M. Brauss, R.R. Hosbons, J.H. Root, and T. Holden, X-Ray Diffraction Determination of Metallurgical Damage in Turbo Blower Rotor Shafts, in *Nondestructive Monitoring of Materials Properties,* Vol 142, J. Holbrook and J. Bussiere, Ed., Materials Research Society, 1988, p 171-176
26. G.A. Webster, Role of Neutron Diffraction in Engineering Stress Analysis, *Measurement of Residual and Applied Stress using Neutron Diffraction,* M.T. Hutchings and A.D. Krawitz, 1991, p 21-35
27. B. Miege, P. Barbarin, and F. Convert, Applications Industrielles de la Mesure de Contraintes par Diffractometrie X, *Rev. Fr. Méc.,* Vol 3, 1987, p 187-195
28. I.C. Noyan and J.B. Cohen, *Residual Stress--Measurement by Diffraction and Interpretation,* Springer-Verlag, 1987
29. R.L. Bormann, Cut-Surface Quality--The Pluses and Minuses of EDM, *Tool. Prod.,* Jan 1985, p 37-41
30. E. Brinksmeier, J.T. Cammett, W. Konig, P. Leskovar, J. Peters, and H.K. Tonshoff, Residual Stresses--Measurement and Causes in Machining Processes, *Ann. CIRP,* Vol 31 (No. 2), 1982, p 491-510
31. R. Snoeys, Thermal Damage in Grinding, *Proc. Milton C. Shaw Grinding Symp.,* R. Komanduri and D. Maas, Ed. (Miami Beach, FL), The American Society of Mechanical Engineers, 1985, p 425-434
32. J. Peters, R. Snoeys, and M. Maris, Residual Stress in Grinding, *Advanced Fabrication Processes,* Conference Proceedings No. 256, Advisory Group for Aerospace Research and Development
33. S. Ramanath, "Residual Stresses in Grinding Hardened Steel," Ph.D. dissertation, Arizona State University, Dec 1986
34. E. Brinksmeier, A Model for the Development of Residual Stresses in Grinding, *Advances in Surface Treatments--Technology--Applications--Effects,* Vol 5, A. Niku-Lari, Ed., Pergamon, 1986, p 173-189
35. H.K. Tonshoff and F. Hetz, Influence of the Abrasive on Fatigue in Precision Grinding, *Proc. Milton C. Shaw Grinding Symp.,* R. Komanduri and D. Maas, Ed. (Miami Beach, FL), The American Society of Mechanical Engineers, 1985, p 191-197
36. J.A. Kovach and S. Malkin, Thermally Induced Grinding Damage in Superalloy Materials, *Ann. CIRP,* Vol 37 (No. 1), 1988, p 309-313
37. M. Yokogawa and K. Yokogawa, Improvements in Work Surface Integrity and Material Fatigue Strength by the CBN Wheel Process, *Int. J. Jpn. Soc. Prec. Eng.,* Vol 26 (No. 3), Sept 1992, p 201-206
38. R.S. Hahn and R.P. Lindsay, The Production of Fine Surface Finishes while Maintaining Good Surface Integrity at High Production Rates by Grinding, *Proc. 14th Int. Machine Tool Design and Res. Conf.,* F. Koenigsberger and S.A. Tobias (Manchester), Macmillan, 1973, p 645-652
39. D.M. Eastman, CBN Internal Honing of Hardened Gear and Pinion Bores, *1986 Proc.--24th Abrasive Engineering Society Conf., Grinding Technology: Today's Bridge to the Future* (Cincinnati), Abrasive Engineering Society/American Society for Metals, 1986, p 116-125
40. W. Pfeiffer and T. Hollstein, Damage Determination and Strength Prediction of Machined Ceramics by X-Ray Diffraction Techniques, *Machining of Advanced Materials,* S. Jahanmir, Ed., Special Publication 847, National Institute of Standards Technology, p 235-245
41. *Shot Peening Applications,* 7th ed., Metal Improvement Company, Inc.
42. M. Field, J.F. Kahles, and J.T. Cammett, A Review of Measuring Methods for Surface Integrity, *Annals of the CIRP,* Vol 21 (No. 2), 1972, p 219-238
43. J.S. Eckersley and T.J. Meister, Intelligent Design Takes Advantage of Residual Stresses, *Practical Applications of Residual Stress Technology,* Clayton Ruud, Ed., ASM International, 1991, p 175-181
44. C. Alamsyah, S.A. Dillich, and A.P. Femia, Effects of Initial Surface Finish on Cam Wear, *Wear,* Vol 134, 1989, p 29-47

45. M. Shimizu, Y. Morita, H. Matsumoto, and R. Nozawa, Study of Friction Loss during the Break-In Period in an Automotive Engine, *JSAE Rev.,* Vol 13 (No. 3), 1992, p 28-33
46. R.W. Messler, Jr., K.G. Hoffman, and R.R. Maller, A Non-Destructive Etching Technique for Detecting Grinding Damage in Chromium Plated Parts, *Materials and Processes for the 70's--Cost Effectiveness and Reliability, Proc. 5th Nat. Tech. Conf.* (Kiamesha Lake, NY), Society for the Advancement of Material and Process Engineering, 1973, p 51-62
47. R. Herzog, A. Sollich, and H. Wohlfahrt, Residual Stresses of Heat Treated Steels with Different Hardness after Grinding with Cubic Boron Nitride (CBN), *Int. Conf. Residual Stress (ICRS2) Conf. Proc.,* Elsevier Applied Science, 1988, p 740-746
48. T. Semba, K. Sakuma, Y. Tani, and H. Sato, Thickness Measurement of a Metallurgically Damaged Layer on a Ground Surface Using an Acoustic Microscope, *Ann. CIRP,* Vol 38 (No. 1), 1989, p 549-552
49. S. Ramanath and M.C. Shaw, Role of Abrasive and Workpiece Properties Relative to Surface Temperature and Residual Stress, *Proc. 14th North American Manufacturing Research Institute,* May 1986, p 636-642
50. R.R. Hebbar, Y. Ahn, S. Chandresekar, and T.N. Farris, Surface Damaged Layers in Lapped Surfaces of Magnetic Ceramics, *Proc. NSF Design and Manufacturing Grantees Conference* (Atlanta, GA), Jan 1992
51. K. Cerqua-Richardson, S. Schmidt, O. Czajkowski, J. Vakiner, and J. Platt, Automated Manufacturing Expands to the Infrared, *Laser Focus World,* Jan 1994, p 101-106
52. R.J. Stokes, B.G. Koepke, and R.G. Johnson, Effects of Surface Finishing on Magnetic and Electrical Properties of Ceramics, *Process. Kinet. Prop. Electron. Magn. Ceram. Proc. U.S.-Jpn. Semin. Basic Sci. Ceram.,* W. Komatsu, R.M. Fulrath, and Y. Oishi, Ed., Japan. Soc. Promot. Sci., 1976, p 201-205
53. N.E. Dowling, *Mechanical Behavior of Materials--Engineering Methods for Deformation, Fracture, and Fatigue,* Prentice-Hall, 1993
54. K. Das, B. Parrish, and P.A. Parrish, Influence of Grinding Fluids on the Introduction of Hydrogen in High Strength Steel, *Corrosion,* Vol 31 (No. 2), Feb 1975, p 72-74
55. J. Belfas, K.W. Groves, and P.D. Evans, Bonding Surface-Modified Karri and Jarrah with Resorcinal Formaldehyde I. The Effect of Sanding on Wettability and Shear Strength, *Holz als Roh-und Werkstoff,* Vol 51, 1993, p 253-259
56. B.D. Cullity, *Elements of X-Ray Diffraction,* 2nd ed., Addison-Wesley, 1978
57. H. Eda, Y. Kakino, A. Fujiwara, M. Nakajima, H. Ueno, and K. Kishi, In-Process Detection of Grinding Cracks by the Use of Acoustic Emissions, *Bull. Jpn. Soc. Prec. Eng.,* Vol 19 (No. 3), Sept 1985, p 181-186
58. M. Field, J.F. Kahles, and J.T. Cammett, A Review of Measuring Methods for Surface Integrity, *Ann. CIRP,* Vol 21 (No. 2), 1972, p 219-238
59. "Standard Test Method for Determining Residual Stresses by the Hole-Drilling Strain-Gage Method," E 837-92, *Annual Book of ASTM Standards,* ASTM, 1992
60. G.S. Schajer, Measurement of Non-Uniform Residual Stresses using the Hole Drilling Method--Part I: Stress Calculation Procedure, *Advances in Mechanical Behavior and Properties Evaluations,* ASME, 1988, p 85-91
61. G.S. Schajer, Measurement of Non-Uniform Residual Stresses using the Hole Drilling Method--Part II: Practical Application of the Integral Method, *Advances in Mechanical Behavior and Properties Evaluations,* ASME, 1988, p 93-99
62. D. Golini and S.D. Jacobs, Physics of Loose Abrasive Microgrinding, *Appl. Optics,* Vol 30 (No. 19), 1 July 1989, p 2761-2777
63. M.T. Hutchings, Neutron Diffraction Measurements of Residual Stress Field: Overview and Points for Discussion, *Measurement of Residual Stress and Applied Stress using Neutron Diffraction,* M.T. Hutchings and A.D. Krawitz, 1991, p 3-18

Thermal Aspects of Surface Finishing Processes

S. Chandrasekar, T.N. Farris, R.R. Hebbar, S.A. Hucker, and V.H. Bulsara, Purdue University

Introduction

THE FINISH MACHINING of materials is commonly accomplished by surface finishing processes such as grinding, lapping, and polishing. All of these processes typically use abrasive particles to carry out material removal. In grinding, the abrasive particles are usually bonded to a wheel using a vitrified or resin bond, whereas in lapping and polishing, the particles are usually present in a slurry that is between the workpiece and a lapping block. The material removal action in grinding resembles two-body abrasion, whereas in lapping and polishing, this action is akin to three-body wear. The surface finish (roughness average, or R_a) on ground surfaces is typically in the range of 0.2 to 1 μm, whereas lapped and polished surfaces can have R_a values of less than 0.05 μm. The material removal rates in lapping and polishing are usually an order of magnitude less than in grinding. At the fundamental level, material removal takes place in all of these processes due to the localized action of an abrasive particle on the workpiece surface. The local pressures prevalent in the abrasive-workpiece contact region are of the order of the hardness of the workpiece material (Ref 1), and the relative sliding speeds between the particle and the workpiece are in the range of a few centimeters per second to 150 m/s, with the higher speeds occurring for modern high-speed grinders (Ref 2). At the local level, the action of the abrasive particle resembles that of a sliding indenter applied to the workpiece surface.

The localized abrasive-workpiece contact pressures and high sliding speed cause high temperatures to be generated at the interface between the abrasive particle and the work surface, as well as in the work subsurface, due to frictional heating (Ref 3, 4). This is especially so in grinding, where sliding speeds are high (30 to 150 m/s). The high temperatures are an important source of several forms of damage on the machined surface. First, the transient temperatures contribute to residual stresses and microcracking on ground surfaces (Ref 5, 6, 7). Second, the localized temperatures can cause warping of the component being finished, especially when it is of small size, having a relatively large surface-to-volume ratio. This is a serious problem in the finishing of small electronic devices such as recording heads (Ref 8). Third, they can induce phase transformations in the materials being finished. For example, during the grinding of hardened steels, if the surface temperature of the workpiece is sufficiently high, the surface reaustenitizes; a consequence of the transformation is the formation of brittle, untempered martensite. This type of thermal damage is commonly referred to as *workpiece burn* and is highly undesirable (Ref 9, 10, 11, 12). Another type of phase transformation occurs during the grinding of transformation-toughened zirconia. Here, the phase transformation is due to the transient mechanical and thermal stresses generated during grinding. These forms of thermal damage alter the mechanical, magnetic, and electrical properties of finished materials.

Thus far, thermally induced damage in work materials produced by finishing processes has been highlighted. The local temperatures also play an important role in the degradation of abrasive particles and their bonding material. The transient temperatures prevailing at the abrasive particle tip during grinding contribute significantly to wheel wear. For example, during grinding with diamond wheels, wheel wear can occur by thermally induced degradation of the bond holding the diamond abrasives together on the wheel, by graphitization of the diamond particles when heated above 1200 °C (2200 °F) in air, by microfracture of the abrasive grain as a consequence of repeated heating and cooling, or by diffusion wear of diamond at high temperatures when grinding ferrous metals (Ref 9).

Thermal phenomena thus play a key role in the mechanics of surface finishing processes. The analysis and measurement of temperatures and associated thermal damage generated by finishing processes are essential to the production of engineered components with controlled surface properties. A discussion of these topics constitutes the bulk of this article. Focus is placed on kinematically simple configurations of finishing processes such as surface grinding and flat surface polishing and lapping. The discussion will be applicable with some modifications to kinematically more complex finishing configurations such as form grinding and polishing as well as honing.

References

1. R.R. Hebbar, S. Chandrasekar, and T.N. Farris, Ceramic Grinding Temperatures, *Journal of the American Ceramic Society,* Vol 75 (No. 10), 1992, p 2742-2748
2. K. Subramanian, *Superabrasives for Precision Production Grinding--A Case for Interdisciplinary Effort,* preprint, Norton Co., 1990
3. M.C. Shaw, Grinding Temperatures, *Proceedings of the 12th North American Manufacturing Research Conference,* Society of Manufacturing Engineers, 1984, p 304-308

4. M.C. Shaw, Fundamentals of Grinding, *New Developments in Grinding,* M.C. Shaw, Ed., Carnegie Press, 1972
5. D. Brinksmeier, J.T. Cammett, W. Koenig, P. Leskovar, J. Peters, and H.K. Tonshoff, Residual Stresses--Measurement and Causes in Machining Processes, *Annals of CIRP,* Vol 31 (No. 2), 1982, p 491-510
6. S. Chandrasekar, M.C. Shaw, and B. Bhushan, A Comparison of the Grinding and Lapping in of Ferrites and Metals, *Journal of Engineering for Industry,* Vol 109, 1987, p 76-83
7. R. Samuel, S. Chandrasekar, T.N. Farris, and R.H. Licht, The Effect of Residual Stresses on the Fracture of Ground Ceramics, *Journal of the American Ceramic Society,* Vol 72 (No. 10), 1989, p 1960-1966
8. S. Chandrasekar, T.N. Farris, M.C. Shaw, and B. Bhushan, Surface Finishing Processes for Magnetic Recording Head Ceramics, *ASME Advances in Information Storage Systems,* Vol 1 (No. 1), 1991, p 353-373
9. S. Malkin, *Grinding Technology: Theory and Application of Machining with Abrasives,* Ellis Horwood, 1989
10. A.A. Torrance, Metallurgical Effects Associated with Grinding, *Proceedings of the 12th International Machine Tool Design and Research Conference,* MacMillan, 1978, p 637
11. W.E. Littmann and J. Wulff, The Influence of the Grinding Process on the Structure of Hardened Steels, *Transactions ASM,* Vol 47, 1955, p 692
12. L.P. Tarasov, Some Metallurgical Aspects of Grinding, *Machining--Theory and Practice,* American Society for Metals, 1950, p 409

Grinding

Figure 1 shows a schematic of a surface grinding process that will serve as the framework for the discussion of the thermal aspects of grinding. In this operation, the workpiece is moved back and forth across a grinding wheel that is rotated at surface speeds typically exceeding 30 m/s.

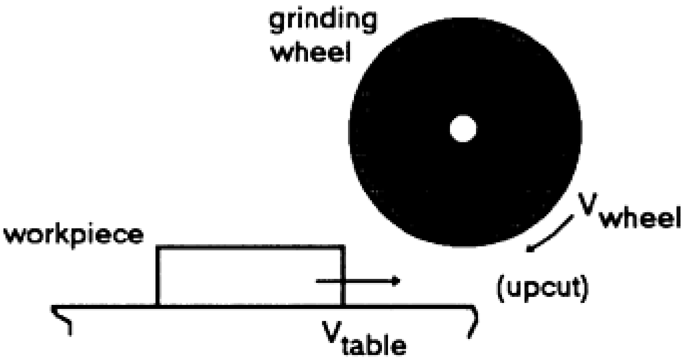


Fig. 1 Typical surface grinding configuration

The Moving Heat Source. In grinding, significant heat is generated at the localized contacts between the abrasive particle and the workpiece material. Moving heat source theory, with the heat generation being taken as the product of a frictional force (idealized to act tangentially at the particle-workpiece contact) and the relative sliding velocity between the abrasive and the workpiece, is applied to calculate the temperature field produced. The moving heat source model does not address the mechanism of heat generation, which is thought to be primarily due to plastic deformation of the workpiece very near the surface (Ref 13). However, this phrase *near the surface* begs the question of defining the workpiece-particle interface. This question is especially difficult in grinding, where material is being constantly removed from the workpiece.

The temperature field produced by a heat source moving over the surface of a semi-infinite solid (here, the workpiece) has been analyzed extensively (Ref 14, 15, 16, 17). One of the earliest analyses of such problems is that due to Blok (Ref 14); this was in the context of calculating sliding contact temperatures. He calculated the maximum surface temperature produced by frictional heating when a single asperity (attached to a semi-infinite solid) was slid against the surface of

another semi-infinite solid. Blok's main contribution was in the estimation of the partition of the frictional heat between the two bodies, which was based on the assumption that the maximum temperature in the contact region was the same in either of the two bodies. Subsequently, Jaeger (Ref 15) provided a detailed analytical solution of the temperature field in a semi-infinite solid due to an infinitely wide strip heat source, having finite length in the direction of motion, moving over it. The calculations of Blok and Jaeger showed that the maximum surface temperature produced by the moving heat source in the solid was reached at the trailing edge of the contact region. Shaw (Ref 3) combined the work of Blok and Jaeger and applied it to estimate wheel and work temperatures in dry surface grinding. In this analysis the frictional heat generated at the wheel-work interface was applied as a moving heat source to the surface of a semi-infinite solid. Partition of the heat into the wheel and workpiece was carried out based on Blok's procedure. The mean work-surface temperatures thus calculated were found to be in good agreement with measured surface temperatures in dry grinding. The application of this analysis to calculate the maximum temperature of the abrasive particle and the workpiece during grinding is described below. More details can be found in Ref 1.

Calculation of Abrasive Grain Temperatures. Figure 2 shows a schematic of the moving heat source model used in the following calculations. The moving heat source model approximates the workpiece as a semi-infinite solid whose boundary is insulated away from the heat source. The heat source has length 2*a* in the sliding direction and is of infinite extent perpendicular to the sliding direction. It is moving across the solid with a velocity *V* and is assumed to generate heat at a rate of *q* per unit area per unit time. This solution of the temperature distribution for this problem involves modified Bessel functions. If the Peclet number

$$L \cong \frac{2Va}{a} > 20 \qquad \textbf{(Eq 1)}$$

where α= *k*/(*c*) is the thermal diffusivity of the solid, *k* is the thermal conductivity, is the mass density, and *c* is the specific heat, then the flow of heat parallel to the surface can be neglected with respect to the velocity of the moving heat source. This approximation is appropriate for single-point (particle) grinding experiments where the abrasive particle is moving with a velocity of ≈30 m/s.

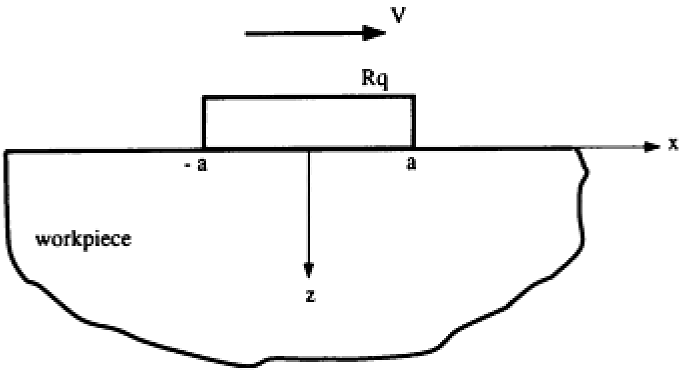


Fig. 2 Schematic of the moving heat source model used in the temperature calculations in text

The differential equation and the boundary conditions governing the one-dimensional transient temperature distribution are:

$$\alpha\frac{\partial^2 T}{\partial z^2} = \frac{\partial T}{\partial t} \qquad z \geq 0, t \geq 0$$
$$k\frac{\partial T}{\partial z}\Big|_{z=0} = -Rq \qquad \textbf{(Eq 2)}$$
$$\lim_{z \to \infty} T \to 0$$
$$T(z, 0) = 0$$

where $T \equiv T(z, t)$ is the temperature of the workpiece, t is time, and R is the fraction of the generated heat that flows into the workpiece. The solution to this boundary value problem is (Ref 17):

$$T(z, t) = \frac{Rq}{k}\left[2\sqrt{\frac{\alpha t}{\pi}}\exp\left(-\left[\frac{z}{2\sqrt{\alpha t}}\right]^2\right) - z\,\mathrm{erfc}\left(\frac{z}{2\sqrt{\alpha t}}\right)\right] \quad \text{(Eq 3)}$$

where erfc is the complementary error function. On the surface:

$$T(0, t) = 2\frac{Rq}{k}\frac{\sqrt{\alpha t}}{\sqrt{\pi}} \quad \text{(Eq 3a)}$$

Assuming that at a particular point on the surface the heat is applied beginning at $x = -a$, the time of heating for a point on the surface is $t = (a - x)/V$ and the temperature at a point on the surface is:

$$\bar{T}(x) = 2\frac{Rq}{k}\frac{\sqrt{\frac{\alpha(a-x)}{V}}}{\sqrt{\pi}}, \text{ for } -a < x < a \quad \text{(Eq 4)}$$

The average surface temperature is:

$$\bar{T}_{\text{avg}} \equiv \frac{1}{2a}\int_{-a}^{a}\bar{T}(x)\,\mathrm{d}x = \frac{4}{3\sqrt{\pi}}\frac{Rq2a}{k}\frac{1}{\sqrt{L}} \quad \text{(Eq 5)}$$

The form of this analysis is consistent with that of a similar analysis given by Ramanath and Shaw (Ref 18) for full wheel grinding.

Equations 2 and 5 can be written for the abrasive particle (or wheel) as well as the workpiece if R is replaced by $1 - R$ and the properties of the abrasive are used. Writing such an equation and setting the average temperature of the grain equal to the average temperature of the workpiece under conditions of thermal equilibrium gives (Ref 18):

$$R = \frac{1}{1 + \sqrt{\frac{(k\rho c)_A}{(k\rho c)_W}}} \quad \text{(Eq 6)}$$

where the subscripts A and W refer to the abrasive and the workpiece, respectively.

The concentrated contact between the abrasive and the workpiece is very similar to that occurring in a microhardness test. If we assume that the contact is a circular patch of radius a, the radius of contact can be obtained as:

$$a = \sqrt{\frac{N}{\pi H}} \quad \text{(Eq 7)}$$

where N is the normal grinding force and H is the Knoop hardness of the workpiece. (The workpiece generally has a smaller hardness than the abrasive.) The heat generated per unit area per unit time is:

$$q = \frac{FV}{\pi a^2} \qquad \textbf{(Eq 8)}$$

where *F* is the tangential grinding force. Note that this model of the moving heat source does not require any knowledge of the fundamental deformation mechanism (such as brittle fracture, plastic deformation, or plowing) leading to heat generation. Substituting Eq 1, 6, 7, and 8 in Eq 5, the average surface temperature ($\overline{T}_{avg}$) of the workpiece and the particle in single-point grinding is obtained as:

$$\overline{T}_{avg} = \frac{8\sqrt{V}}{3\pi^{3/2}\sqrt{2}} \frac{F}{a^{3/2}} \frac{1}{\sqrt{(k\rho c)_W}} \frac{1}{1+\sqrt{\frac{(k\rho c)_A}{(k\rho c)_W}}} \qquad \textbf{(Eq 9)}$$

When $\frac{(k\rho c)_A}{(k\rho c)_W} >> 1$, Eq 9 becomes:

$$\overline{T}_{avg} = \frac{8\sqrt{V}}{3\pi^{3/2}\sqrt{2}} \frac{F}{a^{3/2}} \frac{1}{\sqrt{(k\rho c)_A}} \qquad \textbf{(Eq 10)}$$

and ($\overline{T}_{avg}$) is independent of the thermal properties of the work material. Equation 9 or 10, along with Eq 7 and 8, can now be used to calculate $\overline{T}_{avg}$ if the normal and tangential grinding forces acting on an abrasive particle are known.

The normal and tangential forces on a single abrasive particle can be directly measured during single-point grinding or in single-grain fly cutting (Ref 1, 9, 19). When grinding is done with a full wheel, the statistical distribution of forces on individual grits can be estimated from a statistical analysis of grit sizes on the wheel surface. Such a calculation has recently been carried out for lapping and polishing (Ref 20). There has, however, been no direct measurement of forces on individual grits during full wheel grinding of metals and ceramics.

There are two important points to be noted in Eq 8 and 9. First, the work-surface (or particle-surface) temperature (Eq 9) is a function of the grinding specific energy (i.e., the energy required for a unit volume of material removal) and the heat partition coefficient, *R*. This implies that to achieve lower grinding temperatures, a lower specific energy and a smaller value of *R* are needed. The specific energy depends on the physics of deformation processes leading to material removal, but *R* is dependent on the thermal properties of the abrasive and the workpiece (Eq 6). The second point is that the main thermal property influencing *R* is not just the conductivity (*k*), but the product (*k c*) of the abrasive and workpiece materials, respectively. This fact has been highlighted by Shaw (Ref 3). Table 1 gives physical properties of various abrasive and work materials, including values of *k c*. From Table 1, it can be seen that both cubic boron nitride (CBN), and diamond have significantly higher values of *k c* than alumina (sapphire). Thus, Eq 6 and 9 imply that all other factors remaining the same, grinding temperatures would be lower with a system using CBN or diamond wheels than with one using aluminum oxide wheels. This is consistent with both direct and indirect experimental measurements of temperatures and its derived variables. Quantitative comparisons between measured and predicted temperatures (using Eq 9) are made in the next section.

Table 1 Properties of work materials and diamond abrasive

Property	Material						
	Zirconia (YZ-110)[(a)]	Si_3N_4	Sapphire	Ni-Zn ferrite	1070 steel	Diamond	CBN
E, GPa	210	300	390	191	203	1000	660

v	0.24	0.26	0.23	0.2	0.26	0.2	0.15
k, W/m/°C	2.2	33	35	8.7	47	1000	300-600
c, J/gm/°C	0.63	0.72	0.95	0.71	0.432	0.525	0.51
, gm/cc	6.1	3.22	3.90	5.3	7.84	3.5	3.48
k c	8.45	76.5	129.7	32.7	159.2	1837.5	532-1065
HK, GPa	12	16.7	19.6	7.3	. . .	88	40-70

(a) YZ-110 is a tetragonal zirconia polycrystal manufactured by Norton Co.

Measurement of Grinding Temperatures. The abrasive-tip and work-surface temperatures in grinding are highly localized spatially (~100 μm or less in spot size) and decay rapidly with time (within microseconds). Measurement of these temperatures is therefore a challenging task.

Some of the early measurements of grinding temperatures were carried out with thermocouples embedded into the workpiece (Ref 9, 21). The relatively large time constant and poor spatial resolution of thermocouples enable only an estimate of the average temperature to be obtained. In the grinding of steels, such measurements have reported values of ~800 °C (1475 °F) for the work-surface temperature (Ref 9). This is in the neighborhood of the austenitizing temperature for many low-carbon steels.

Another technique for measuring grinding temperatures, which is much more sensitive both spatially and in time, involves monitoring and analysis of infrared radiation being emitted by the abrasive particle and/or the workpiece (Ref 1, 6, 22, 23). Using such a technique, the authors recently measured full-wheel, single-particle, and work-surface temperatures during the dry grinding of metals and ceramics (Ref 1, 23). For more details about the technique, see Ref 1; Table 2 and Fig. 3, 4, 5, and 6 show some of the results. In Table 2, the measured temperatures in single-particle (diamond) grinding of ceramics are compared with the analytical estimates (Eq 9) for this temperature at different wheel velocities. There is good agreement between the measured and predicted values. It must be noted here that the measured particle temperatures are high, ~600 to 1600 °C. When grinding is done with a full wheel, different abrasive particles on the wheel surface are exposed to different depths of cut due to their varying amounts of protrusion from the wheel surface. Therefore, each of these particles cuts out a different volume of material, and their tip temperatures are likely to differ. Indeed, this is seen to be the case in Fig. 3, 4, 5, and 6, where the particle temperatures are plotted as histograms. The mean of the particle-surface temperatures on the wheel (and consequently work-surface hot-spot temperatures) are found to vary between 592 °C for zirconia and 721 °C for 1070 steel.

Table 2 Single-point grinding temperatures

Material	***R***	**Temperature, °C, at wheel velocity of:**					
		25 m/sec		**32 m/sec**		**37 m/sec**	
		E	**A**	**E**	**A**	**E**	**A**

Zirconia	0.064	1260±51	1320	1601±74	1494	. . .	. . .
Si_3N_4	0.17	1133±60	1110	1452±49	1255	. . .	. . .
Ni-Zn ferrite	0.12	570±30	537	620±35	607	690±30	653
Sapphire	0.21	920±65	. . .	1060±45	. . .	1270±80	. . .

(a) *R*, fraction of the generated heat that flows into the workpiece, as defined in Eq 6; E, experimentally measured value (including standard deviation; A, analytically measured value (depth of cut 10 μm, table velocity 23.4 mm/s, diamond indenter tip radius 15 μm)

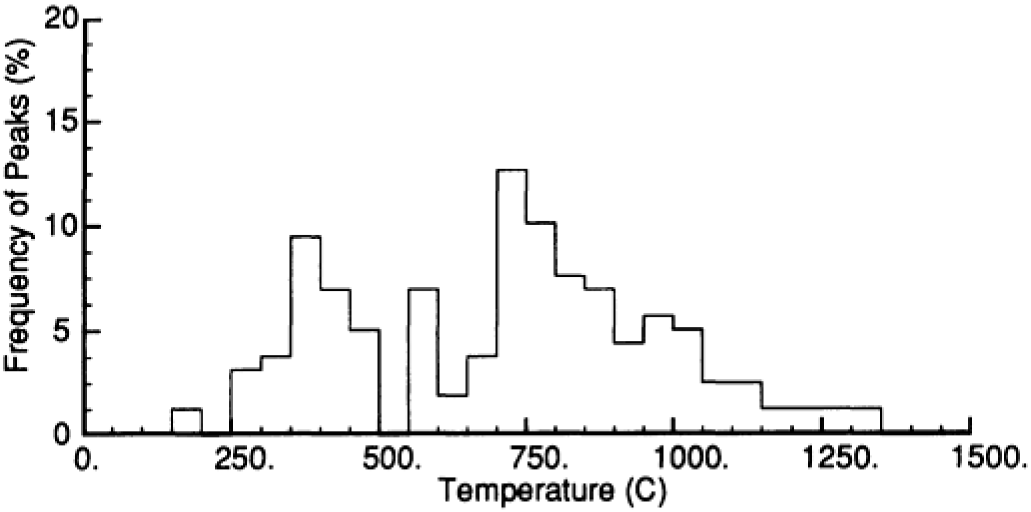


Fig. 3 Distribution of wheel temperatures in full wheel grinding of silicon nitride. Depth of cut, 12.5 μm; table velocity, 23.4 mm/s; wheel velocity, 32 m/s; 220-grit

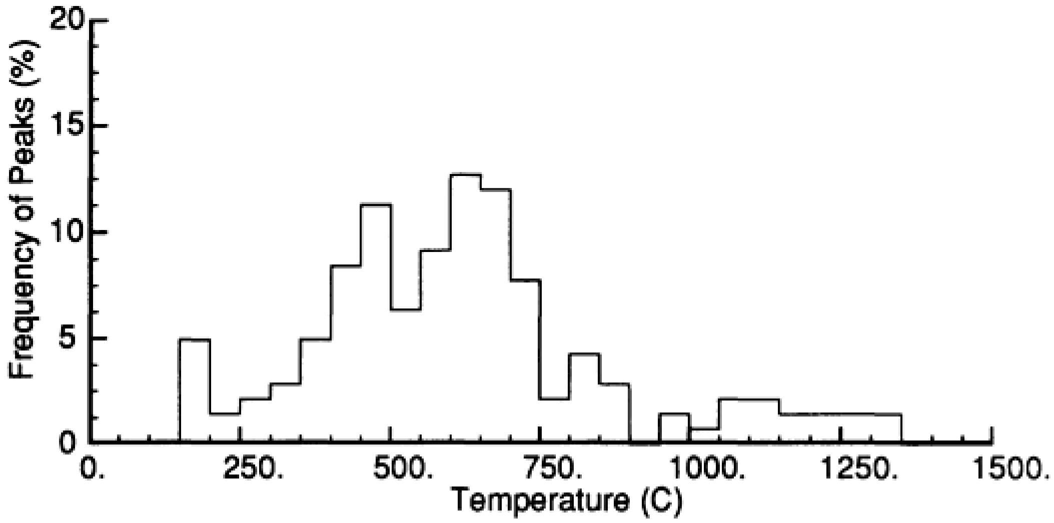


Fig. 4 Distribution of wheel temperatures in full wheel grinding of zirconia. Depth of cut, 12.5 μm; table velocity, 23.4 mm/s; wheel velocity, 32 m/s; 220-grit

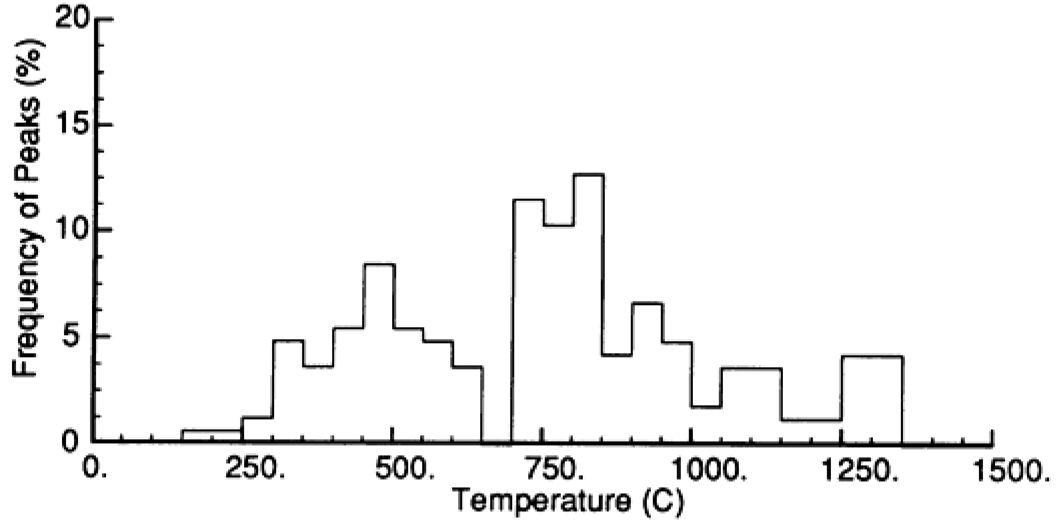


Fig. 5 Distribution of wheel temperatures in full wheel grinding of 1070 carbon steel. Depth of cut, 12.5 μm; table velocity, 23.4 mm/s; wheel velocity, 32 m/s; 220-grit

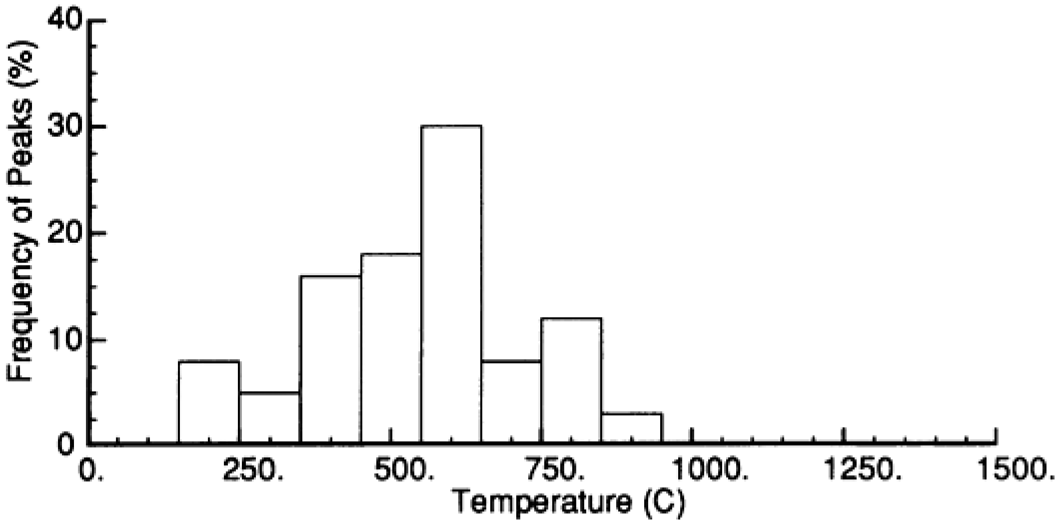


Fig. 6 Distribution of wheel temperatures in full wheel grinding of ferrite. Depth of cut, 20 μm; table velocity, 23.4 mm/s; wheel velocity, 32 m/s; 320-grit

Sometimes, abrasive-particle temperatures are observed to reach the melting point of steel during the grinding of hardened steels. It is possible that under such conditions, there is actually melting of the steel at some regions along the wheel-work contact. Such melting could cause the spherical swarf particles shown in Fig. 7. Indeed, there is compelling evidence in support of this hypothesis (Ref 24). Many investigators (Ref 9, 25), however, have attributed the formation of such spherical particles only to melting during exothermic oxidation of the chips in air; this is, no doubt, a parallel mechanism. Infrared temperature measurements have also shown that the subsurface temperature in a workpiece decays rapidly with depth (Fig. 8). The high temperature gradients are the primary source of the tensile residual stresses, microcracking, and phase transformations sometimes observed on ground surfaces. Another observation from temperature measurements is that an abrasive grain on the wheel surface cools down rapidly after leaving the grinding zone and almost reaches room temperature in one revolution of the wheel before it begins its next cut (Ref 1).

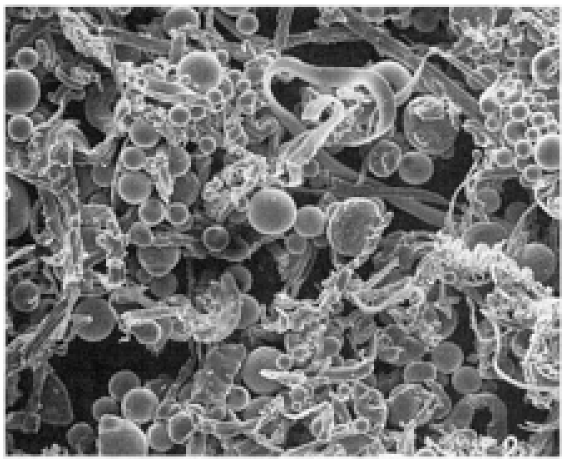


Fig. 7 Scanning electron micrograph of grinding swarf from 52100 steel showing spherical particles

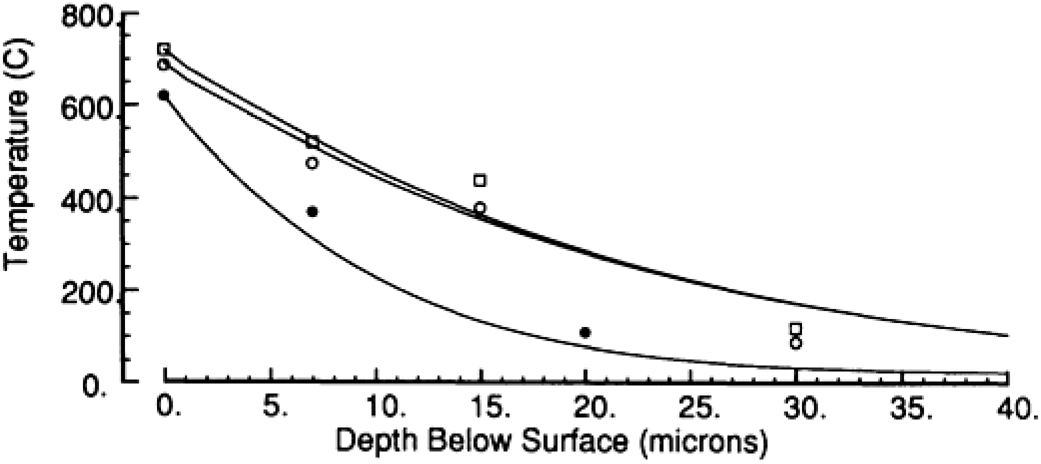


Fig. 8 Distribution of subsurface workpiece temperatures in full wheel grinding. Table velocity, 23.4 mm/s; wheel velocity, 32 m/s. d , silicon nitride (measured, 220-grit, 12.5 μm depth of cut); •, ferrite (measured, 320-grit, 20 μm depth of cut); ☐, 1070 steel (measured, 220-grit, 12.5 μm depth of cut). The solid lines are calculated values for the subsurface temperature obtained by matching the experimentally measured temperatures at the surface.

Coolant and Grinding Temperatures. Thus far, focus has been concentrated primarily on dry surface grinding. In practice, grinding operations on metals usually involve use of a coolant-lubricant fluid (Ref 4, 9). The purpose of this fluid is twofold: to provide lubrication and reduce frictional forces at the wheel-work interface and to cool the workpiece. No well-validated analysis of grinding temperatures takes into account heat transfer into the fluid, but the physical principles underlying such an analysis would not alter the broad nature of the temperature calculations given in Eq 9. It is generally accepted that the coolant has little influence on the peak abrasive tip temperature but does reduce the average bulk temperatures of the wheel and workpiece, thereby limiting thermally induced dimensional distortions. Although there is no experimental verification of the former hypothesis, the proper application of coolant is very beneficial in many grinding operations with metals due to its influence on the bulk temperature.

Surface Damage. The high surface temperatures and steep temperature gradients at the surface of the workpiece material during grinding are responsible for many forms of damage (Ref 26). During the grinding of ceramics, which are relatively brittle compared to metals, the high thermal stresses developed near the surface cause microcracking (Ref 27). Such microcracking is one of the main causes of strength degradation and strength anisotropy (with respect to grinding direction) commonly observed in ground ceramic components (Ref 28). Control of these thermal stresses is critical to the

development of better grinding methods for ceramics. In electronic ceramic materials, the high temperatures and temperature gradients cause the near-surface electromagnetic properties to be changed, which affects the performance of these materials when they are fabricated into devices. Examples in this category are the ferrites (Ni-Zn, Mn-Zn, etc.) used in recording heads in magnetic storage systems. Grinding residual stresses or heating of the material during grinding to above the Curie temperature (typically between 800 and 900 °C, or 1470 to 1650 °F, for these materials) usually leads to the formation of magnetically damaged surface layers that have an adverse effect on recording head performance during the read/write process (Ref 8).

During the grinding of plain carbon or hardened alloy steels, one of the most common types of thermally induced damage is workpiece burn (Ref 29). The burn is characterized visually by bluish temper colors on the work surfaces, which are usually attributed to oxide-layer formation. The temper colors can be removed by sparkout at the end of the grinding cycle. However, this does not mean that the effects of burn are removed. Microhardness measurements on workpieces show that visible burn is accompanied by reaustenitization of the work surface during grinding. When hardened steels are ground without any burning, there is generally some softening due to tempering of the material close to the surface. This is seen in the "no burn" curve in Fig. 9 (Ref 29). Here, the material near the surface is seen to have a smaller microhardness value than the material in the bulk. However, under burn conditions in hardened steels, quite the opposite effect is seen at the surface; the "burn" curve in Fig. 9 shows that the surface layer has been hardened by grinding. This occurs as a consequence of reaustenitization of the work material near the surface during grinding, followed by the formation of hard, untempered martensite as a result of quenching. The martensitic layer can be identified upon etching of the surface as a white phase, usually occurring in patches (Ref 11, 12, 29). When grinding of soft steels is done, however, workpiece burn is not seen to cause any surface hardening. In such instances, burn is best detected by metallographic techniques (Ref 11, 12). The occurrence of workpiece burn in steels has been shown to be virtually coincident with the work-surface temperature exceeding the austenizing temperature (~800 °C, or 1470 °F, for low- to medium-carbon steels) during grinding. This observation has provided a basis for analytically deriving "burn limit" conditions for steels through calculations of grinding temperature from power or force measurements (Ref 29).

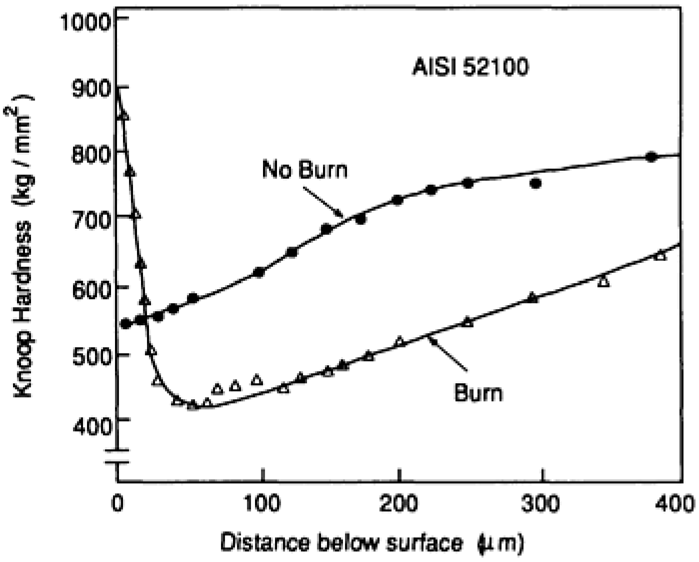


Fig. 9 Variation of microhardness with depth in a hardened bearing steel ground under "burn" and "no burn" conditions. Source: Ref 9

The avoidance of workpiece burn during the grinding of hardened steels is critical for better tribological performance. For example, workpiece burn in bearing steels is found to affect their fatigue life adversely (Ref 30). Figure 10 shows the L_{10} fatigue life of hardened bearing rings finished under various grinding conditions (L_{10} is the fatigue life exceeded by 90% of the specimens). The fatigue life decreases dramatically when the grinding specific energy, *u*, exceeds the threshold limit for burn, u^* (i.e., $u/u^* > 1$).

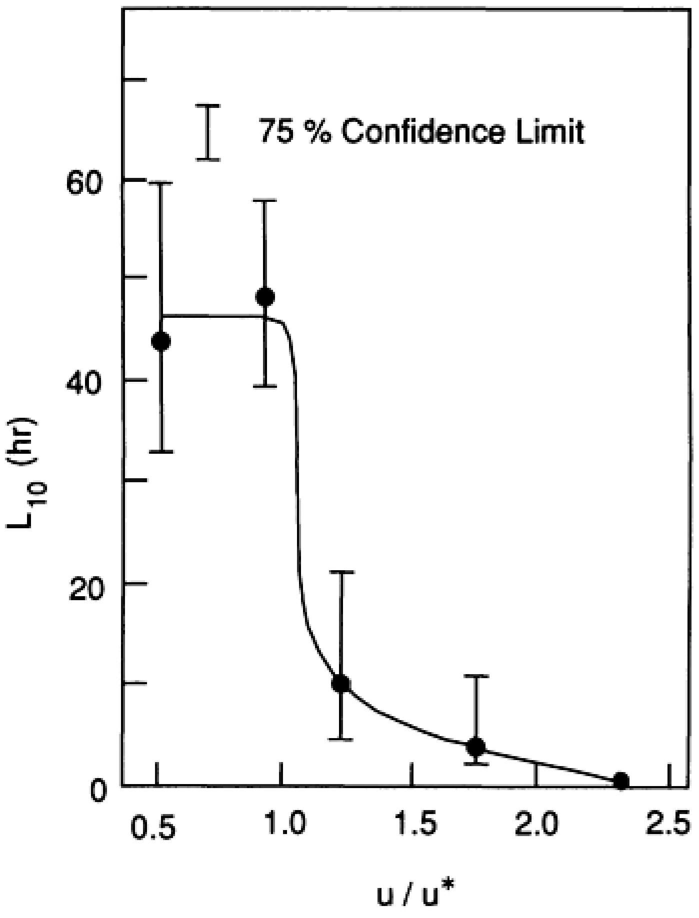
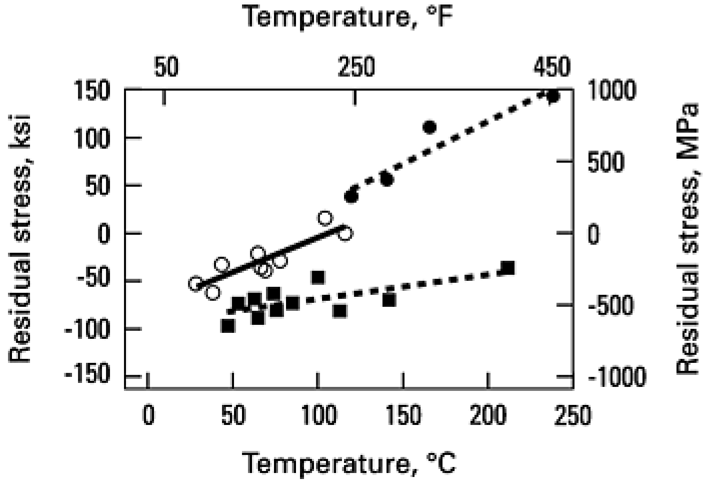
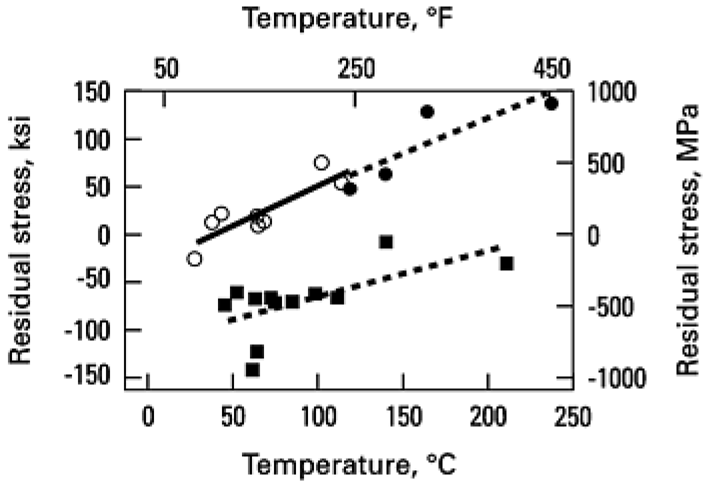


Fig. 10 Variation of L_{10} fatigue life with specific energy ratio (*u*/*u) for a ground bearing steel. The critical value is *u*/*u** = 1, beyond which burn is observed to occur typically. Source: Ref 9**

Besides workpiece burn in steels, the occurrence of high temperatures usually leads to tensile residual stresses on ground steel surfaces. This is again undesirable for enhanced tribological performance. However, control of the residual stress distribution on ground surfaces of steels is possible by ensuring that surface temperatures are kept low during grinding. Figure 11 shows the variation of measured surface residual stress with calculated grinding temperature for 52100 bearing steel ground with Al_2O_3 and CBN wheels. Under most conditions reported in Fig. 11, CBN grinding is found to produce compressive residual stresses on the surface, in contrast to Al_2O_3 grinding. This is due to the lower temperatures at the ground surface in CBN grinding. It has been suggested that lower grinding temperatures lead to reduced tensile stresses on ground surfaces, and Fig. 11 provides perhaps the most striking experimental illustration in support of this speculation.



(a)



(b)

Fig. 11 Variation of surface residual stresses with grinding temperature in ground surfaces of 52100 steel. d , aluminum oxide 60 J6; •, aluminum oxide 100 H6; ■cubic boron nitride. (a) Residual stress perpendicular to grinding. (b) Residual stress parallel to grinding

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References cited in this section

1. R.R. Hebbar, S. Chandrasekar, and T.N. Farris, Ceramic Grinding Temperatures, *Journal of the American Ceramic Society,* Vol 75 (No. 10), 1992, p 2742-2748
3. M.C. Shaw, Grinding Temperatures, *Proceedings of the 12th North American Manufacturing Research Conference,* Society of Manufacturing Engineers, 1984, p 304-308
4. M.C. Shaw, Fundamentals of Grinding, *New Developments in Grinding,* M.C. Shaw, Ed., Carnegie Press, 1972
6. S. Chandrasekar, M.C. Shaw, and B. Bhushan, A Comparison of the Grinding and Lapping in of Ferrites and Metals, *Journal of Engineering for Industry,* Vol 109, 1987, p 76-83
8. S. Chandrasekar, T.N. Farris, M.C. Shaw, and B. Bhushan, Surface Finishing Processes for Magnetic Recording Head Ceramics, *ASME Advances in Information Storage Systems,* Vol 1 (No. 1), 1991, p 353-373

9. S. Malkin, *Grinding Technology: Theory and Application of Machining with Abrasives,* Ellis Horwood, 1989

11. W.E. Littmann and J. Wulff, The Influence of the Grinding Process on the Structure of Hardened Steels, *Transactions ASM,* Vol 47, 1955, p 692

12. L.P. Tarasov, Some Metallurgical Aspects of Grinding, *Machining--Theory and Practice,* American Society for Metals, 1950, p 409

13. F.F. Ling, *Surface Mechanics,* Wiley, 1973

14. H. Blok, Theoretical Study of Temperature Rise at Surfaces of Actual Contact under Oiliness Lubricating Conditions, *Institution of Mechanical Engineers Discussion Meeting on Lubrication,* Vol 2, 1937, p 222-235

15. J.C. Jaeger, Moving Sources of Heat and the Temperature at Sliding Contacts, *Proceedings of the Royal Society of New South Wales,* Vol 76, 1942, p 203-224

16. D. Rosenthal, The Theory of Moving Sources of Heat and Its Application to Metal Treatments, *Transactions ASME,* 1946, p 849

17. H.S. Carslaw and J.C. Jaeger, *Conduction of Heat in Solids,* 2nd ed., Section 2.9, Oxford University Press, 15-18

18. S. Ramanath and M.C. Shaw, Abrasive Grain Temperature at the Beginning of a Cut in Fine Grinding, *Journal of Engineering for Industry,* Vol 110 (No. 1), 1988, p 18

19. T.N. Farris and S. Chandrasekar, High Speed Sliding Indentation of Ceramics: Thermal Effects, *Journal of Materials Science,* Vol 25, 1990, p 4047-4053

20. R. Chauhan, Y. Ahn, S. Chandrasekar, and T.N. Farris, Role of Indentation Fracture in Free Abrasive Machining of Ceramics, *Wear,* Vol 162, 1993, p 246-257

21. J.O. Outwater and M.C. Shaw, Surface Temperatures in Grinding, *Transactions ASME,* Vol 74, 1952, p 73

22. T. Ueda, A. Hosokawa, and A. Yamamoto, Studies of Temperature of Abrasive Grains in Grinding--Application of Infrared Pyrometer, *Journal of Engineering for Industry,* Vol 107, 1985, p 127-133

23. S. Chandrasekar, T.N. Farris, and B. Bhushan, Grinding Temperatures for Magnetic Ceramics and Steel, *Journal of Tribology,* Vol 112, 1990, p 535-541

24. L. Lu, T.N. Farris, and S. Chandrasekar, Sliding Microindentation Wear Particles: Spheres in Grinding Swarf, *Wear Particles: From the Cradle to the Grave,* D. Dowson, C.M. Taylor, T.H.C. Childs, M. Godet, and G. Dalmaz, Ed., Elsevier, 1992, p 257-263

25. S. Ramanath, T.C. Ramaraj, and M.C. Shaw, What Grinding Swarf Reveals, *Annals of CIRP,* Vol 36 (No. 1), 1987, p 245-247

26. R. Snoeys, M. Maris, and J. Peters, Thermally Induced Damage in Grinding, *Annals of CIRP,* Vol 27 (No. 2), 1978, p 571-581

27. K. Subramanian, Precision Finishing of Ceramic Components with Diamond Abrasives, *American Ceramic Society Bulletin,* Vol 67 (No. 6), 1988, p 1026-1029

28. S. Jahanmir, Ed., *Machining of Advanced Materials,* SP 847, National Institute of Standards and Technology, 1993

29. S. Malkin, Thermal Aspects of Grinding, Part 2--Surface Temperatures and Workpiece Burn, *Journal of Engineering for Industry,* Vol 96, 1974, p 484

30. A.A. Torrance, R.J. Stokes, and T.D. Howes, The Effect of Grinding Conditions on the Rolling Contact Fatigue Life of Bearing Steel, *Mechanical Engineering,* 1983, p 63

Lapping and Polishing

Lapping and polishing are used to produce smooth or ultrasmooth surfaces (i.e., surfaces with an R_a of a few nanometers). They are carried out by placing a slurry of abrasive particles in a liquid vehicle between the specimen and a hard metallic block (lapping) or a soft, flexible pad (polishing). While the block is loaded against the workpiece (specimen) either hydraulically or mechanically, the abrasive particles roll or slide across the specimen so that the wear process is one of three-body abrasion (Ref 20). As in grinding, the abrasive particles have a wide range of sizes, with an average value

typically between of 0.05 to 70 μm. The mean sliding velocity between the abrasive and the specimen in lapping or polishing is typically no greater than 0.5 m/s, which is two orders of magnitude less than that in grinding.

At present there are no reliable calculations of lapping and polishing temperatures. The maximum temperature rise at the abrasive-work interface is thought to be small due to the relatively low sliding velocity between the contacting surfaces, and several arguments support this hypothesis. Recent calculations of the distribution of forces on diamond abrasive particles during the lapping and polishing of ceramics show that the average load applied to a particle is no greater than 1 N under typical conditions (Ref 20). If this load is assumed to act on a particle sliding at a velocity less than 0.5 m/s, a heat partition and heat-transfer analysis carried out along the lines of the grinding calculations described earlier shows that the maximum temperature rise at the work surface is no greater than 100 °C (212 °F) for a friction coefficient of μ= 0.1 between the abrasive and work surface. Even though such an analysis might not be completely rigorous for lapping and polishing, the error in the calculation of the temperature rise is not expected to be significant. Further evidence to support the low temperature rises comes from observations pertaining to residual stresses and microcracking. Lapped or polished surfaces of metals and ceramics are generally found to contain compressive residual stresses due to localized plastic deformation resulting from an indentation/microcutting action of the abrasive particles (Ref 6, 8). Thermally induced residual stresses, in contrast, are tensile in nature; see the previous discussion pertaining to grinding. Metallurgical studies of the structure of lapped or polished steel surfaces show little evidence of structural changes commonly associated with localized high temperatures (e.g., no indication of phase transformations or burn in lapped surfaces of hardened steels). Also, there is very little microcracking to be seen on lapped or polished surfaces of ceramics (Ref 6, 8). Such microcracking, if present, is usually a strong indicator of the occurrence of steep temperature gradients near the surface that cause high, transient stresses.

References cited in this section

6. S. Chandrasekar, M.C. Shaw, and B. Bhushan, A Comparison of the Grinding and Lapping in of Ferrites and Metals, *Journal of Engineering for Industry,* Vol 109, 1987, p 76-83
8. S. Chandrasekar, T.N. Farris, M.C. Shaw, and B. Bhushan, Surface Finishing Processes for Magnetic Recording Head Ceramics, *ASME Advances in Information Storage Systems,* Vol 1 (No. 1), 1991, p 353-373
20. R. Chauhan, Y. Ahn, S. Chandrasekar, and T.N. Farris, Role of Indentation Fracture in Free Abrasive Machining of Ceramics, *Wear,* Vol 162, 1993, p 246-257

Selection, Application, and Disposal of Finishing Fluids

Cynthia K. Cordell, Master Chemical Corporation

Introduction

FINISHING METHODS can include a wide variety of processes such as lapping, polishing, tumbling, and loose media. However, in keeping with metalworking tradition and for the purposes of this discussion, the term *finishing methods* will largely be confined to what are commonly called grinding operations. It should be kept in mind, however, that rapid advances in ceramic, cubic boron nitride, and diamond tools, machine rigidity, high-speed spindles, and machine control systems are providing metal workers with many alternatives traditional grinding operations in generating smooth, close-tolerance surfaces. By the same token, the creep-feed grinding process, especially the "continuous dress" version, can effect extremely high rates of stock removal while generating very close size control and good surface finish *without* causing thermal damage to the workpiece, and it is allowing a grinding process to be substituted for more traditional chipmaking material removal processes.

This article discusses environment issues and regulations related to surface finishing processes. Additional information is a available in the article "Environmental Regulation of Surface Engineering" in this Volume.

The Grinding Zone Environment

The grinding process is extremely complex, and a number of elements in it must be reviewed in order to make a reasonably adroit initial selection of a fluid or fluids for a manufacturing plant. At a minimum one must catalog the grinding operations, the work materials and their hardnesses, the wheels and/or belts in use and their bond systems, the amount of material to be removed and the finish desired in each operation, and the relative need for in-process corrosion protection. A number of these elements can impose conflicting requirements on fluids and force compromises in fluid selection. For example, lubricating and cooling ability are conflicting properties in grinding fluids, very much as hardness and toughness are conflicting properties in cutting tools.

Grinding fluids can be composed of petroleum oil, extreme-pressure lubricants, emulsifiers, soaps, wetting agents, coupling agents, corrosion inhibitors, biocides, antifoams, and water. Depending on composition, fluids are generally categorized as:

- *Synthetic or chemical fluids* contain no petroleum oil and generally have very high cooling but low lubricating properties.
- *Semisynthetic or semichemical fluids* contain a small to moderate amount of oil and generally have high cooling and moderate lubricating properties.
- *Emulsions or soluble oils* are largely composed of oil and emulsifiers and generally have good cooling an moderate to high lubricating properties.
- *Straight or "neat" oils* are used without dilution in water and generally have poor cooling but the highest lubricating properties.

In general, one will never be able to select a single fluid that will be optimum for all types of grinding operations, all types of work materials, and all types of abrasives. The object then becomes finding a reasonable number of fluids, perhaps two or three, that will work well for the vast majority of grinding operations in the plant and have the desirable characteristics of being safe for the machine operators, being "kind" to the machine tools, providing good in-process corrosion protection, and providing long sump life and the potential for recycling. With the proper selection of fluids, total manufacturing costs will decrease because of improved wheel life, decreased dressing, higher throughput, and decreased machine maintenance and fluid disposal.

Fluid Selection. The use of the metalworking fluid itself should be appropriate for the intended operation. However, one has to take into consideration the other operations in the shop, because to keep the management of the fluid easier it is sometimes best to use one fluid that can do the majority of the work. In a grinding operation it is important for the fluid to provide cooling and not foam, so synthetic fluids or soluble oils are generally recommended. The synthetic fluids are commonly used in surface grinders or when diamond wheels are involved, whereas the soluble oils are used in centerless or creep-feed grinding. Straight oils are used in thread grinding or crush grinding where more lubricity is required.

The semisynthetic fluids are somewhere in the middle where cooling is important but lubricity is required. In an electrical discharge machining operation, it is important that the dielectric oil provide good resistivity at the point of initial forming of the part and not smoke. Table 1 lists suggested fluids for a variety of metals on specific operations.

Table 1 Selection guide for metalworking fluids for finishing operations

Work materials	Thread gear, form	Centerless cylindrical	Internal	Surface	Abrasive cutoff
Free-machining steel (low-medium carbon)	MD oil, HD water	LD oil, MD-HD water (miscible)	GP water (miscible)	LD-GP water (miscible)	Water (miscible)
Low-alloy structural steel (martensitic)	HD oil, HD water (miscible)	HD oil, HD water (miscible)	LD oil, GP water (miscible)	GP water (miscible)	Water (miscible)
Hot-work die steels (martensitic), stainless steels (austenitic, martensitic, precipitation-hardened), maraging steels, nickel and cobalt alloys	HD oil, HD water (miscible)	HD water (miscible)	GP oil, GP water (miscible)	HD water (miscible)	Water (miscible)
Cast iron	HD water (miscible)	GP water (miscible)	GP water (miscible)	GP water (miscible)	Water (miscible)
Magnesium and alloys	LD oil, SP fluids	LD oil, SP fluids	LD oil, SP fluids	LD oil, SP fluids	LD oil, SP fluids
Aluminum and alloys	HD water (miscible)	HD water (miscible)	HD water (miscible)	HD water (miscible)	HD water (miscible)
Copper and alloys	HD water (miscible)	LD oil, HD water (miscible)	LD oil, HD water (miscible)	LD oil, HD water (miscible)	HD water (miscible)
Titanium and alloys	HD water (miscible)	HD water (miscible)	HD water (miscible)	HD water (miscible)	HD water (miscible)
Beryllium and alloys	HD water (miscible)	HD water (miscible), SP fluids	HD water (miscible), SP fluids	HD water (miscible), SP fluids	Water (miscible)
Refractories	HD oil	HD oil, HD water (miscible)	HD oil, HD water (miscible)	HD oil, HD water (miscible)	HD oil, HD water (miscible)

MD, medium duty; HD, heavy duty; LD, light duty; GP, general purpose; SP, special.

Source: Ref 1

The fluid recommendation and correct dilution should be supplied by the manufacturer. The proper dilution is important because a lean solution increases rust and bacteria growth, whereas a rich solution can produce residues and dermatitis. Another area of concern is the water used for the dilution, which may contain contaminants that can cause the concentrate to separate and produce residues and rust. The use of a deionizer will remove the minerals from hard water and form a better dilution.

Once the metalworking fluid is in the machine it needs to be maintained to ensure chemical stability and operator safety. The metalworking fluid can be contaminated with oils, rust preventives, cleaners, and solubilized metals that can degrade the fluid. The fluid manufacturer will be able to determine the problem and make the necessary corrections. All additives and biocides should be used only as recommended by the manufacturer.

Fluid Application. Proper fluid application (volume and pressure) is essential to make the grinding wheel run cooler, decrease its tendency to grab and hold particles of metal removed from the work, and reduce the cut and therefore create a smoother, finer finish. In a grinding operation, it is most important that chips not interfere with the operation, so the application of the selected fluid is vital to provide the appropriate amount of cooling at the point of cut and still flush the chips from the machining area.

To deliver cutting fluid efficiently into the arc of cut, the velocity of the cutting fluid must be at least equal to or 10 to 15% faster than the peripheral speed of the grinding wheel. The optimum flow rate and pressure need to be developed for each application; however, in creep-feed grinding it is recommended that the flow rate should be of the order of 60 to 80 gal/min (225 to 300 L/min) and the nozzle pressure around 80 to 100 psi (550 to 700 kPa). The nozzle should be adjusted to direct the fluid stream on the work at or above the point of cut, and the incorporation of a cutting fluid guideway behind the workpiece will maintain the flow of fluid through the arc of cut, eliminating the burn at the end of a cut. Specially designed nozzles or slotted and grooved wheels will help the metalworking fluid penetrate to the point of cut. Methods of applying the fluid range from flooding to misting, depending on the type of fluid selected, the operation itself, and the amount of heat being transferred to the tool and workpiece.

The effect of the fluid on the cutting temperature may be due either to direct cooling or the reduction of the energy required in performing the operation. At low speeds, the fluid has time to penetrate to reduce friction and decrease the temperature. At high speeds the fluid has little effect on the temperature at the point of cut, but it removes heat from the tool and workpiece, preventing heat accumulation and temperature buildup in the vicinity of the active cutting edge of the tool. Application of the correct fluid can also cut down the number of passes required to finish the part. Another way to shorten the cycle time is to increase the speeds and feeds.

Reference cited in this section

1. T.J. Drozda and C. Wick, Ed., *Machining,* Vol 1, *Tool and Manufacturing Engineers Handbook,* 4th ed., Society of Manufacturing Engineers, 1983

Disposal Issues

When the time comes to dispose of spent fluids, consideration must be given to the myriad of regulations that protect the environment and the people from improper dumping of hazardous materials. All municipalities and states have the authority to promulgate their own specific set of waste disposal regulations, and many have done so. It is important that before any waste is disposed of, the appropriate local, state, and federal regulations be consulted. This discussion, however, is limited to the federal Environmental Protection Agency (EPA) Resource Conservation and Recovery Act (RCRA) regulations. This federal law establishes the minimum requirements for waste disposal and is the basis for local regulation of wastes. All industrial waste, including spent metalworking fluids, must be evaluated against RCRA criteria to determine if it is hazardous or not.

Hazard Determination. RCRA gives the EPA the authority to regulate industrial waste from generation through transportation to treatment and ultimate disposal, the so-called "cradle-to-grave" approach. Currently the major thrust of RCRA is directed toward the management of hazardous waste. EPA has indicated in its regulatory agenda that designated waste oil (i.e., engine, hydraulic, lubricating, and cutting oils) is not classified as a hazardous waste. Although this designation does encompass all types of cutting and grinding fluids, the fact that they are not generically listed as a hazardous waste does not mean specific spent fluids are not hazardous or subject to regulation. For example, a spent fluid might be classified as a hazardous waste due to the presence of certain metals. Any fluid used in the machining process tends to dissolve some of the metals being machined. If the part being worked contains any metals considered to be hazardous by RCRA definition and the fluid solubilizes enough of that metal to exceed the regulatory limit, the fluid as a whole is considered to be a hazardous waste. For many possible metallic contaminants, a few parts per million is sufficient to exceed the regulatory limit. The only way to be certain is to run a toxicity characterization test to determine whether any of the contaminants on the list are present in the fluid at levels that would trigger treatment of the waste as hazardous. Table 2 is a listing of the contaminants and their trigger levels.

Table 2 Maximum concentration of contaminants for the toxicity characteristic

EPA HW No.[(a)]	Contaminant	CAS No.[(b)]	Regulatory level, mg/L
D004	Arsenic	7440-38-2	5.0
D005	Barium	7440-39-3	100.0
D018	Benzene	71-43-2	0.5
D006	Cadmium	7440-43-9	1.0
D019	Carbon tetrachloride	56-23-5	0.5
D021	Chlorbenzene	108-90-7	100.0
D020	Chlordane	57-74-9	0.03
D022	Chloroform	67-66-3	6.0
D007	Chromium	7440-47-3	5.0
D024	m-Cresol	108-39-4	200.0[(c)]
D023	o-Cresol	95-48-7	200.0[(c)]
D025	p-Cresol	106-44-5	200.0[(c)]
D026	Cresol	. . .	200.0[(c)]
D016	2,4-D	94-75-7	10.0
D027	1, 4-Dichlorobenzene	106-46-7	7.5
D028	1,2-Dichloroethane	107-06-2	0.5
D029	1,1-Dichloroethylene	75-35-4	0.7
D030	2,4-Dinitrotoluene	121-14-2	0.13[(d)]
D012	Endrin	72-20-8	0.02

D031	Heptachlor (and its epoxide)	76-44-8	0.008
D032	Hexachlorobenzene	118-74-1	0.13[(d)]
D033	Hexachlorobutadiene	87-68-3	0.5
D034	Hexachloroethane	67-72-1	3.0
D008	Lead	7439-92-1	5.0
D013	Lindane	58-89-9	0.4
D009	Mercury	7439-97-6	0.2
D014	Methoxychlor	72-43-5	10.0
D035	Methyl ethyl ketone	78-93-3	200.0
D036	Nitrobenzene	98-95-3	2.0
D037	Pentrachlorophenol	87-86-5	100.0
D038	Pyridine	110-86-1	5.0[(d)]
D010	Selenium	7782-49-2	1.0
D011	Silver	7440-22-4	5.0
D039	Tetrachloroethylene	127-18-4	0.7
D015	Toxaphene	8001-35-2	0.5
D017	2, 4,5-TP (Silvex)	93-72-1	1.0
D040	Trichloroethylene	79-01-6	0.5
D041	2, 4,5-Trichlorophenol	95-95-4	400.0
D042	2, 4,6-Trichlorophenol	88-06-2	2.0
D043	Vinyl chloride	75-01-4	0.2

Source: Ref 2

(a) HW, hazardous waste.

(b) CAS, Chemical Abstracts Service.

(c) If o-, m-, and p-cresol concentrations cannot be differentiated, the total cresol (D0026) concentration is used. The regulatory level of total cresol is 200 mg/L.

(d) The quantitation limit is greater than the calculated regulatory level and therefore becomes the regulatory level.

Another factor in determining whether the spent fluid is hazardous is chlorine content. According to the federal regulations, if the waste contains over 1000 ppm Cl it is assumed to be hazardous. However, if the chlorine present is due to chlorinated paraffins, which are used in industry as an extreme-pressure additive, then the classification as "hazardous" can be rebutted. That is, if the generator of the waste can demonstrate that the only source of chlorine present in the spent fluid is from a nonhazardous and nonregulated component and/or contaminant, then the waste need not be handled as hazardous. An important point to note is that several states have promulgated their own state laws that define all waste oils that contain any chlorine or petroleum oil as hazardous.

Reducing Disposal Frequency. If a spent fluid is determined to be a hazardous waste, the effects include increases in disposal, administrative, labor, and insurance expenses. The amount of paperwork increases, due to requirements for use of a manifest system, labeling, reporting, and recordkeeping, and the liability exposure of the waste generator increases. One solution that helps minimize the impact of all these costs is to set up a recycling program that extends the life of the fluid, therefore decreasing the amount of environmental pollution and eliminating some of the cost, paperwork, and liability. The fluid is periodically removed from the machine, and the tramp oil and metal fines are removed from the dirty fluid. Fresh fluid is then added as makeup to the recycled fluid, and the clean mixture goes back into the machine. The recycling process reduces the frequency with which the fluid, which can be as much as 98% water, must be hauled away. This can save a substantial amount, as the costs for haulaway have increased considerably (Table 3). It is therefore very advantageous for the metalworking fluid user to consider some form of recycling to extend the life of the fluid.

Table 3 Trends in haulaway costs for spent coolant

Region	Dollar cost per gallon			
	1983	1985	1988	1991
Northeast	0.20-2.00	0.20-3.00	0.24-3.00	0.50-5.00
Southeast	0.20-1.00	0.20-1.25	0.30-2.00	0.20-2.75
Midwest	0.12-1.00	0.18-1.00	0.17-1.75	0.22-3.00
Northwest	0.30-1.00	0.50-1.75	0.70-2.25	2.00-4.00
Southwest	0.07-1.50	0.16-1.75	0.60-2.00	0.75-5.00

Note: These costs do not include transportation, lab fees, or surcharges for waste. Source: Ref 3

Disposal Methods. Eventually the fluid will reach a point where it can no longer be recycled and must be disposed of. Currently there are three methods: haul everything away; evaporate the water and haul the residual away; or perform chemical/mechanical pretreatment.

Hauling. When selecting a company that hauls away the spent fluid and treats it, it is important to ensure that it is licensed and reputable. If the fluid is disposed of illegally the law will hold the waste generator responsible.

Evaporating. The use of an evaporator to reduce the volume of water can eliminate some of the cost. A problem area can be created if oil floats to the top, where it has a tendency to cover the fluid and prevent the evaporation process from taking place. Some types of agitation, such as the introduction of small air bubbles to dissipate the oil layer, will aid the evaporation process. The use of heat to increase the evaporation rate is effective but needs to be controlled so that the fluid does not boil, creating a potential for air pollution and the need for air permits.

Pretreating involves breaking the fluid down by separating the water from the fluid concentrate and contaminants. The reduced volume of oil and organic material can then be hauled away at a lower cost. The waste generator treats the water phase so it can be released to the sanitary sewer for further treatment by the local wastewater treatment company. The water phase should not go into a waterway. The oil that is discarded of can be rerefined or used in the supplemental fuels program.

The disposal of grinding fines is another concern, so one needs to select the correct type of chip wringer to squeeze out as much fluid as possible. The drier the chip, the lower the cost. There are several methods to dry chips, including evaporators, filters, and wringers. As with fluid, the waste generator of the chips is responsible for them forever, making it very important to use a reputable chip hauler and disposal firm. Some of these chips can be remelted, although others will have to be scrapped.

References cited in this section

2. 40 CFR 261.24, Table 1, 1 July 1992

3. Survey by Master Chemical Corp., 1992

Regulatory Trends

The 1970s saw the passage of numerous legislative efforts to improve worker health and safety and protect the environment. The Occupational Safety and Health Act, National Environmental Protection Act, Clean Water Act, Clean Drinking Water Act, Clean Air Act, Toxic Substances Control Act, Comprehensive Environmental Response, Compensation and Liability Act ("Superfund"), and Resource Conservation and Recovery Act are just a few.

This regulatory trend has carried on into the 1990s, but with a slightly different emphasis. Initially, the greatest impact was felt by chemical producing companies. Now, chemical user industries, including the metalworking industry, are being more directly affected by the regulation of chemicals. Regulations such as the OSHA Hazard Communication Standard (worker right-to-know) and the EPA rules for the Emergency Response and Community Right-To-Know Act place considerable responsibilities on all manufacturing sectors that use chemicals in their processes, not just on the chemical makers. These responsibilities include education and training of workers, use of proper labels and material safety data sheets, written plans, maintenance of inventory records, and submission of inventory and release data. All metalworking fluids will be covered by many of the regulations to some degree or another, so users of cutting and grinding fluids will find themselves subjected to many of these regulations. To determine which regulations apply and to what degree takes a considerable amount of time, but the consequences of not complying can include fines and jail sentences.

Future regulations which the metalworking industry should carefully watch are OSHA reform, EPA management standards, the Great Lakes Initiative, the Clean Air Act, and the Oil Pollution Act.

Influence of Work Material Properties on Finishing Methods

K. Subramanian, World Grinding Technology Center, Norton Company

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Introduction

FINISHING METHODS used to generate surfaces of work materials range from rough finishing to precision finishing to ultraprecision finishing, depending on the surface features or quality desired. For instance, stone is quarried by cutting processes, which are primarily rough finishing methods. The stone may then be precision finished to achieve the smooth surfaces used in tiles or furniture. If the stone is to be used for a machine tool bed or gaging plate, extreme control of tolerances and surface finish will be required, and an ultraprecision finishing method will probably be used to achieve the desired results. The ability to finish a work material through all these processes largely depends on the work material properties.

Work Material Properties and Their Role in Finishing

Hardness is the resistance to indentation. Because every surface finishing method involves creation of new surfaces, higher hardness always implies greater machining forces (e.g., it is more difficult to machine harder steel than softer steel). Higher hardness also implies greater wear of the cutting tool or abrasive product. This may be due to the wear caused by direct contact between the tool and the work, or it may be due to the wear caused by the hard and abrasive chip after it is released from the work material.

Toughness is the resistance to fracture. It is easier to propagate cracks or fracture through material of lower toughness. Hence, it is easier to machine high-hardness, low-toughness alloy steels than high-toughness stainless steel of equal hardness. However, extremely low toughness is not desirable, as is readily evident from the difficulty in machining glass or ceramics. In these materials it is desirable to use finishing methods or finishing process conditions that prevent the generation of cracks rather than minimizing or controlling crack propagation.

Stiffness is the resistance to deformation. It is often measured as the elastic modulus, or the slope of the stress-strain curve. Because most finishing methods require application of force for surface generation, it is desirable to have minimum deflection or distortion under the applied force to achieve close dimensional tolerances. In this regard, it is easier to achieve complex contours, closer geometry, and closer surface finish in higher-stiffness material. For instance, extremely thin sections can be machined in ceramics, and closer tolerances and surface finishes can be achieved in ceramics than in metals, because ceramics have about twice the stiffness (elastic modulus) of most metals or alloys.

Ductility is the ability of the material to deform plastically before fracture is initiated or propagated. This is generally measured in terms of percentage elongation. Ductile materials are generally more difficult to machine; they require considerably more energy to generate the chips. For instance, the specific energy required to machine soft steel is generally higher than that required to machine cast iron of equal hardness. This energy requirement is minimized by close control of the geometry of the cutting tool. Hence, positive-rake tools of small nose radius are required for machining aluminum, brass, and so forth.

The long, stringy chips produced in ductile materials often lead to extensive sliding that results in erosion or wear of the cutting tool or bond matrix (in the case of abrasive finishing methods). Hence, it is essential to have a means to control the shape (or curl) of the chip, as well as a means to dispose of the chip away from the cutting zone (chip clearance) in the finishing of ductile materials such as aluminum and copper and their alloys, as well as thermoplastic materials.

Ductility is also used to advantage in ultraprecision processes such as lapping or buffing, where mirror finish surfaces are achieved by extensive deformation of surface layers without affecting bulk material structure or properties. This is the technique used in the preparation of hard disks for computers and the machining of printing rolls.

Thermal Properties. Because most finishing methods are mechanical processes in the presence of a thermal front, the thermal properties of work materials play a key role in their response to finishing. For example, the conduction of heat away from the machining zone and the rate of heat buildup determine the maximum temperature at the surface, which influences tool life as well as the quality of the work surface after finishing. As a rule, poor thermal conductors are difficult to machine. Typical examples are polymers, stainless steel, and titanium. Any external effort to reduce surface sliding and heat conduction are very beneficial in the finishing of these materials.

Thermal cracks are generated when the thermal stress exceeds the strength of the material. Materials with high thermal conductivity, a low thermal expansion coefficient, and low stiffness (elastic modulus) are less susceptible to thermal cracks.

Thermal stability is resistance to decomposition. For example, in the presence of high temperatures, titanium readily reacts with carbon to form carbides. This is an inherent limitation for tool life in the finishing of titanium using diamond or silicon carbide tools.

The mechanical properties described earlier (hardness, toughness, ductility, and so on) need to be considered at room temperature as well as at elevated temperatures corresponding to the maximum "cutting" temperature. The conventional wisdom is that the strength of a work material decreases with temperature and increases with strain rate, and that these two opposing effects have a minimal net effect on machining processes. However, this may not always be the case.

Thermal properties are also of interest to the nonmechanical finishing processes such as electrical discharge machining and laser machining. These processes depend primarily on thermal energy and its use for material removal and surface generation.

Thermal effects are inherently unstable and should be carefully controlled in any finishing process. For instance, excessive heat buildup at the grinding zone increases the maximum temperature, which accelerates tool wear. This results in inefficient cutting action, which in turn leads to further increase in heat input to the grinding zone. These effects can proceed until severe damage is caused to the part, the abrasive tool, or both. Thermal effects also depend on the geometry of the work material and the nature of the applied forces. Thin cross sections of work materials are more susceptible to thermal damage than large cross sections, and heat distribution that minimizes thermal inputs to he cross section (e.g., up grinding vs. down grinding) also improves part quality and minimizes thermal damage.

Electrical and Magnetic Properties. Electrical conduction and resistivity are properties of importance, particularly in finishing methods such as electrical discharge machining. Magnetic materials such as ferrous alloys are readily clamped by electromagnetic chucks during their finishing, whereas paramagnetic and nonmagnetic materials require mechanical clamping.

Microstructure Effects. As a general rule, a uniform and predictable microstructure of the work material is preferable for reliable finishing processes and their automation. Inclusions, surface defects, and hard surface layers always impair performance. This is true for castings, forged components, rolled steels, densified ceramics, and so on.

The size, shape, content, and uniformity of hard second-phase material and second-phase particles also influence finishing results. As a general rule, the smaller the hard second-phase particles, the more efficient the finishing.

Grain size of the work material plays a key role in finishing results. Finer grain size is usually associated with higher strength and toughness and greater machining difficulty. Grain size modifications due to processing, such as by heat treatment and shot peening, yield results such as residual stresses, anisotropic properties, and work hardening, all of which pose difficulty in the finishing processes and hence should be carefully controlled or monitored. Changes in the morphology in one finishing process may influence the next finishing step. For example, brass is frequently work hardened during drawing or forming, which may contribute to a nonuniform finish. Polishing prior to buffing is desirable to reduce this nonuniformity.

Material Properties and Their Relationship to Grindability

This section addresses the relative response of work materials such as metals, ceramics, and composites to grinding.

Relative Grindability of Metals. Table 1 gives the relative grindability of seven metallic alloys. As used in the table, *grindability* is a calculated value that represents the efficiency of the grinding process. Grindability can be calculated using the the following relationships:

$$\text{Specific energy} = \frac{\text{Grinding power (W)}}{\text{Material removal rate (mm}^3\text{/s)}}$$

$$\text{G-ratio} = \frac{\text{Volume of material removed (mm}^3\text{)}}{\text{Volume of wheel used (mm}^3\text{)}}$$

$$\text{Grindability} = \frac{\text{G-ratio (mm}^3\text{)}}{\text{Specific energy (J)}}$$

Grindability is then a measure of the volume of material removed per unit of energy consumed, normalized by the volume of wheel material consumed during the process. It takes into account the ease of difficulty of removing the material along with the process economics influenced by the rate of material removed and the breakdown of the grinding tool. Absolute values of grindability are useful specific situations. However, comparisons of grindability among work materials under identical conditions, as shown in Table 1, are more relevant for the purposes of the present discussion. Table 1 shows that grindability is dramatically affected by the type of work material and by the use of oil coolant.

Table 1 Relative grindability of work materials in wet outside diameter grinding

Work material	Hardness HRC	Relative grindability	
		Water-soluble coolant	Oil coolant
512100 bearing steel	60	60-80	500-1000
4340 structural steel	60	50-100	500-700
1020 low-carbon steel	23	10-40	100-150
M7, D2 tool steel	60	1-2	100-150
440 stainless steel	47	1-10	200-500
304 stainless steel	4	1-5	100-200
Inco 718 aerospace alloy	30	1	30-60

Notes: (1) A set of outside-diameter grinding tests were conducted using the same grinding wheel specifications and identical grinding process conditions. The tests were conducted using water-soluble coolant and oil coolant. From these tests, data were analyzed to compute grindability (defined in text). The individual grindability measures for each alloy and each coolant were normalized to the grindability of Inco 718 using water-soluble coolant to determine the relative grindability. (2) The above data are based on limited data sets and should be used only as a guideline.

Grindability of Ceramics versus Grindability of Metals. The strength of ceramic material varies widely, depending on the material chosen. Even for a given material such as silicon nitride, the strength depends on the sintering aids used and the sintering methods applied (pressureless sintering, hot pressing, hot isostatic pressing, etc.). Ceramic materials are analogous to metals in that their composition, microstructure, and strength influence grindability. Table 2 compares the typical properties of selected ceramic materials with those of metals and those of a typical polymer.

Table 2 Physical and mechanical properties of selected ceramics, metals, and a polymer

Material	Physical properties				Mechanical properties		
	Density	Melting/ decomposition	Thermal	Coefficient of thermal	Tensile	Modulus of	Fracture

			temperature		conductivity, *k*		expansion, 10^{-6}/K	strength		elasticity, *E*		toughness	
	g/cm^3	**lb/in.^{3}**	**°C**	**°F**	**W/m · K**	**Btu · in./ft^2 · h · °F**		**MPa**	**ksi**	**GPa**	**10^6 psi**	**MPa $\sqrt{m}$**	**ksi $\sqrt{in}$**
Ceramics													
Aluminum oxide	3.4-4.0	0.12-0.14	2050	3720	27	190	8	205-550	30-80	385	55	2.0-3.0	1.8-2.7
Silicon carbide	3.0-3.2	0.11-0.12	2500	4530	63-155	435-1075	4-5	415-550	60-80	420	60	2.5-3.5	2.3-3.2
Silicon nitride	3.2-3.5	0.12-0.13	1900	3450	9-30	60-210	3	620-1100	90-160	305	44	3.5-5.0	3.2-4.6
Zirconium oxide	5.8	0.21	2500	4530	2	14	9-10	965-1380	140-200	140	20	6.0-8.0	5.5-7.3
Ferrite	5.0-6.0	0.18-0.22	2000	3630	8	55	7.5	140-170	20-25	205	29	1.0-1.3	0.9-1.2
Fused quartz	2.2	0.079	1670	3040	1.4	9.7	0.55	110	16	77	11	1.0	0.9
Metals													
Inconel 718	8.1	0.29	1400	2550	12.4	86.0	7	1240-1405	180-204	215	31	24	22
Tool steel	7.84	0.283	1500	2730	52	360	7	1405-2000	180-290	210	30	98	89
52100 bearing steel	7.85	0.284	1500	2730	30-40	210-280	11	415-550	60-80	210	30	56	51
Aluminum	2.2	0.079	660	1220	204	1420	13	275-550	40-80	70	10	36	33
Polymer													
Polyethylene	1.1	0.040	120	250	0.32	2.2	167	7-20	1-3	3.5	0.5	0.25	0.23

In general, ceramic materials have higher stiffness (Young's modulus) than metals. The elastic deformation of ceramic materials during grinding is therefore less than that for metals, given the same grinding forces, so ceramic materials can be machined to closer tolerances, more precise geometries, superior finishes, and better flatness and parallelism than is

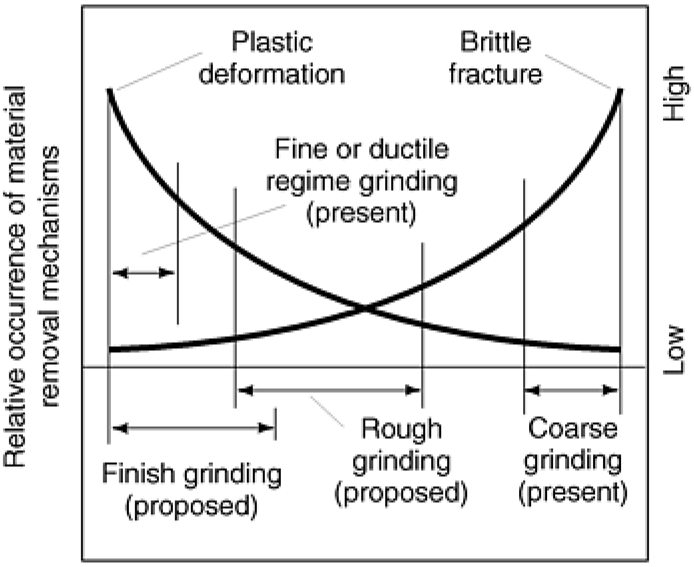
possible for metals. This is the basis for choosing ceramic materials over metals in precision-made instrument parts, machine tool beds or ways, and gage blocks.

Ceramic materials are generally more chemically stable than metals, so the burn sometimes observed on metals during grinding is rarely observed on ceramics. On the other hand, the hot hardness and recovery hardness of ceramics are much higher than those of metals, and the large-scale thermal softening that often aids in the grinding of metals can rarely be counted on in the grinding of ceramics.

Thermal conductivity (the property that determines the ability to conduct heat away from the grinding zone) varies widely in ceramic materials. Just as poor thermal conductivity in metals such as titanium and Inconel can lead to high temperatures and great difficulty in grinding, it is more difficult to grind ceramic materials that have poor thermal conductivity. The problem becomes worse when the ceramics are also poor in thermal shock resistance.

One characteristic that significantly distinguishes ceramics from metals is their low fracture toughness. Considering all the similarities between metals and ceramics, it should be possible to achieve successful grinding of ceramics if the generation and propagation of cracks during the grinding process can be minimized.

From Fig. 1, it appears that the mechanisms of material removal in the grinding of ceramic material are associated with both plastic deformation and brittle fracture. It may be nearly impossible to isolate one mechanism or the other unless extreme grinding conditions are chosen. These are identified as *coarse grinding* (where brittle fracture dominates) and *fine* or *ductile regime grinding* (where plastic deformation dominates). The consequences of such choices are low strength and poor reliability, in the case of coarse grinding, and an extremely small material removal rate, high forces, and high specific energy, in the case of fine or ductile regime grinding. Referring to the process interactions described in Fig. 1, it may be envisioned that plastic deformation is desirable in order to increase the cutting component. However, excessive deformation may produce an inefficient cutting process accompanied by excessive ploughing and rubbing and/or sliding. Although brittle fracture is a means of generating surfaces at the lowest forces and energy, it is certainly not desirable where highest strength and reliability are required.



Input		
Machine tool		
Low	Vibration	Large
Processing tool		
Small	Grain size	Large
Small	Grain tip radius	Large
Work material		
Small	Grain size	Large
High	Fracture toughness	Low
Operational factors		
Large	Cutting velocity	Small
Small	Depth of cut	Large
Small	Chip thickness	Large
Process variables		
Small	Force per grain	Large
Large	Specific energy	Small
Large	Grinding force	Small
Output		
High	Part strength	Low
Fine	Surface finish	Poor
Good	Edge chippage	Poor
Low	Material removal rate	High

Fig. 1 Governing mechanisms and control variables for grinding of ceramics

Thus, optimizing the ceramic grinding system becomes a process of maximizing the cutting component through plastic deformation while minimizing the grinding forces and energy input. This can be accomplished through a careful and simultaneous selection of the input parameters identified in Fig. 1 and Fig. 2. Although this approach is common with metals grinding, the additional factor in ceramics grinding is the control of force per grain. Under such process interactions, selection of a suitable grinding cycle, including rough and finish grinding steps, is a tradeoff between process economics and the surface characteristics desired.

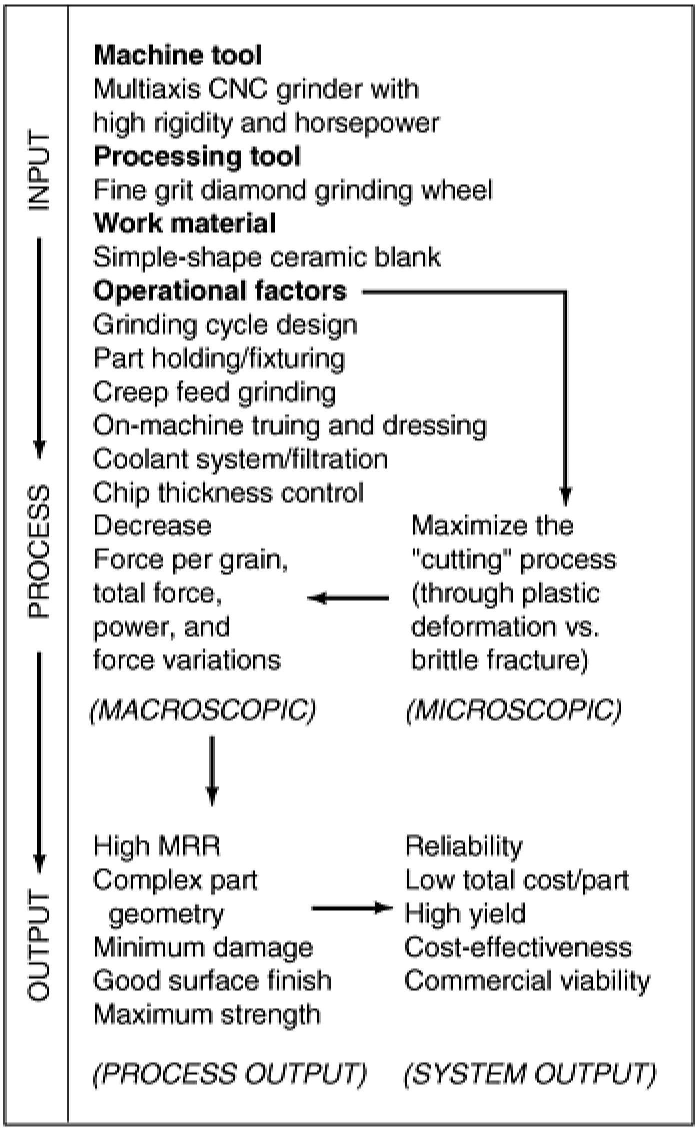


Fig. 2 Systems description of the precision grinding of ceramics. CNC, computer numerically controlled; MRR, material removal rate

Finishing of Composites. There are a wide variety of materials in which more than one family of materials has been brought together to achieve unique performance requirements. Typical examples are shown in Fig. 3. Successful finishing of such composites depends on understanding each of the components of the composite, its properties, and its response to finishing. It is also important to understand whether a composite is dominated by a "hard" or "soft" matrix, as outlined in Table 3. This distinction is crucial in developing rational and economical finishing methods.

Table 3 Matrix material that influences the finishing difficulty of typical composites

Composite	"Hard" matrix	"Soft" matrix
Castings	Sand	Cast iron
High-silicon aluminum alloys	Silicon	Aluminum
Polycrystalline diamond tools	Diamond	Carbide substrate

Reinforced concrete	Steel reinforcement	Concrete
Carbide-tipped tools	Carbide	Steel
Fiber-reinforced composites	Glass-carbon fiber	Polymer
Ceramic coatings for thermal barriers	Alloy steel	Ceramic coating

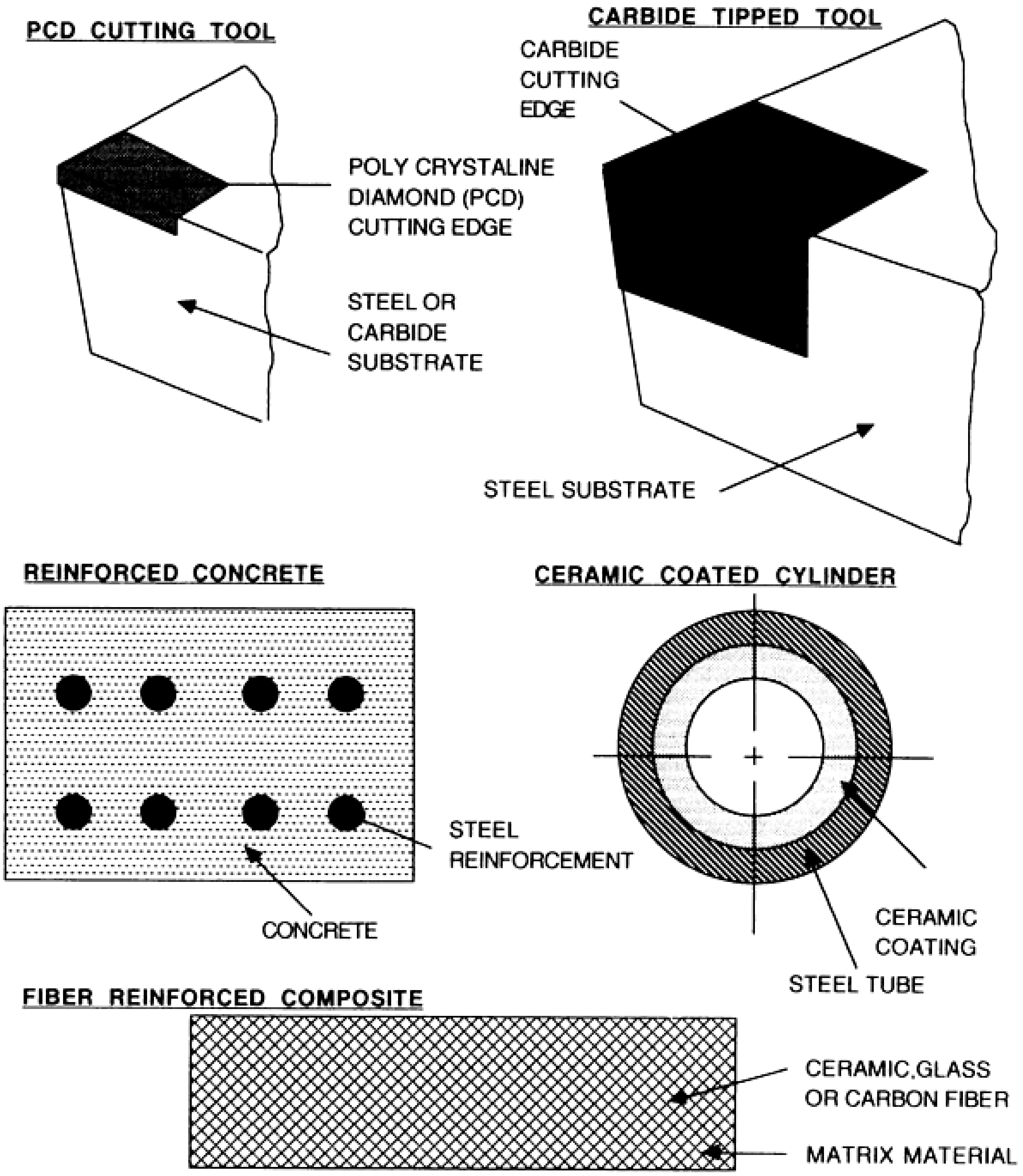


Fig. 3 Typical composites that require surface generation

Copper Plating

Revised by L.M. Weisenberger and B.J. Durkin, MacDermid, Inc.

Introduction

COPPER PLATING DEPOSITS are used for both functional and decorative applications. They are used widely as underplates in multiplate systems, as barrier coatings, as stopoffs in heat treatment, and for heat transfer (e.g., as heat sinks). They also find use in electroforming, in electromagnetic shielding, and in plating of electronic circuitry. The smoothness and brightness of copper deposits can be improved through buffing techniques because copper is a relatively soft metal. Copper deposits also act as thermal expansion barriers, especially in multiplate systems, due to their ability to absorb the stress produced when metals with different thermal expansion properties undergo temperature changes or if the deposit is thermally shocked. Similarly, corrosion failures from cracking caused by physical deformation of a part can be reduced by incorporation of a soft metal such as copper in the composite plate. Copper plating is also used as a final finish in some decorative applications and is sometimes used alone in applications where a durable and attractive surface is required. However, copper tarnishes and stains rapidly when exposed to the atmosphere and must be protected against this by an overcoating of clear lacquer or another suitable type of corrosion-resistant finish.

Copper can be deposited from both electrolytic and autocatalytic (electroless) electrolytes that are alkaline or acid.

Cyanide and noncyanide, pyrophosphate alkalines plus sulfate and fluoborate acid baths are the electrolytes used in the electrolytic deposition of copper deposits. For additional information, see the article "Electroless Copper Plating" in this Volume.

Alkaline Plating Baths

Alkaline cyanide copper solutions are used to plate the initial deposits (as a strike) on a variety of substrates. These baths can be easily controlled to produce thin deposits of relatively uniform thicknesses on all surfaces. They have the best macro throwing power, which describes the relative plating thickness distribution over all current densities. They also have traditionally been the most widely used strike and plating baths. However, with a greater emphasis on hazards and waste management, more recently developed alkaline, noncyanide systems are being examined and used as replacements for the copper cyanide systems in many applications. The deposits from the noncyanide copper processes compare favorably with those from the cyanide processes. These noncyanide processes require more precise control and more thorough cleaning and surface preparation compared to cyanide systems; however, their use does allow the elimination of cyanide in many plating facilities. Pyrophosphate alkaline copper solutions are seldom used because they are difficult to control and have limited operating ranges. They are used primarily to produce thick deposits because they exhibit good plating rates. They also find some use in through-hole printed wiring board applications.

Dilute cyanide and Rochelle cyanide baths are primarily used to deposit a strike coating of 1.0 to 3.0 μm (0.05 to 0.1 mil) of copper prior to further copper plating or electrodeposition of other metals. Often the coverage during this step is the most important in the overall performance and appearance of the final plated part. The high-concentration Rochelle cyanide bath can be used efficiently for plating up to about 8 μm (0.3 mil) thickness. With a modification in composition, the Rochelle electrolyte may be used for barrel plating. The Rochelle cyanide bath can be used for still-tank plating, with mechanical agitation, or more efficiently with air agitation. These baths can also be used with pulsed-current or periodic-reverse plating.

The cyanide copper plating baths listed in Table 1 are characterized by low-copper metal and high free-cyanide contents. This type of chemistry helps to clean the surface of parts during the plating operation. This results because of the tendency to produce gassing at the work due to the low cathode efficiencies. Although plating baths should not be used intentionally for cleaning purposes, the cleaning action of these cyanide baths can be an advantage, because difficult-to-clean parts can be given a copper strike in one of these baths with a high degree of success. Plating in other baths without the use of an alkaline cyanide copper strike could result in poor adhesion and incomplete coverage.

Table 1 Compositions and operating conditions of cyanide copper plating baths

Constituent or condition	Rochelle cyanide				High-efficiency	
	Dilute cyanide (strike)	Standard barrel	Low concentration[a]	High concentration[a]	Sodium cyanide[b]	Potassium cyanide[b]
Bath composition, g/L (oz/gal)						
Copper cyanide	22 (3)	45 (6)	26 (4)	60 (8)	80 (11)	80 (11)
Sodium cyanide	33 (4)	68 (9)	35 (5)	80 (11)	105 (14)	105 (14)
Sodium carbonate	15 (2)	. . .	30 (4)	30 (4)	. . .	. . .
Sodium hydroxide	To pH	. . .	To pH	To pH	30 (4)	. . .
Rochelle salt	15 (2)[c]	45-75 (6-10)	45 (6)	90 (12)	. . .	. . .
Potassium hydroxide	. . .	8-15 (1-2)	. . .	. . .	. . .	35 (5)
Bath analysis, g/L (oz/gal)						
Copper	16 (2)	32 (4)	18 (2)	43 (6)	56 (7)	56 (7)
Free cyanide	9 (1)	27 (3.6)	7 (0.8)	15 (2)	18 (2)	18 (2)
Operating conditions						
Temperature, °C (°F)	30-50 (86-120)	55-70 (130-160)	55-70 (130-160)[d]	60-75 (140-170)	60-75 (140-170)	60-75 (140-170)
Cathode current density, A/dm^2 (A/ft^2)	1.0-1.5 (10-15)	. . .	1.0-4.0 (10-40)	2.0-5.0 (20-50)	2.0-6.0 (20-60)	2.0-6.0 (20-60)
Cathode efficiency, %	30-50	. . .	40-60	60-90	70-100	70-100
Voltage, V	6	6[e]	6	6	6	6
pH	12.0-12.6	. . .	12.0-12.6[d]	13	>13	>13
Anodes	Copper, steel	Copper	Copper	Copper	Copper	Copper

(a) Low concentration typical for strike; high concentration typical for plating.

(b) Used with addition agents, as proprietary or patented processes.

(c) Optional

(d) For zinc-base die castings, maintain temperature at 60-71 °C (140-160 °F)and a pH between 11.6 and 12.3.

(e) At 6 V, the bath draws approximately 0.3 A/L (2 A/gal) through the solution. At 12 V, the bath draws 0.4 A/L (3 A/gal).

High-Efficiency Sodium and Potassium Cyanide Baths. With proprietary additives, the high-concentration baths are used to produce deposits of various degrees of brightness and leveling, in thicknesses ranging from 8 to 50 μm (0.3 to 2.0 mils). Thick deposits that are ductile and bright can be produced in routine operations. Under most plating conditions, the high throwing power of the electrolyte produces adequate coverage of sufficient thickness in recessed areas. Antipitting additives are generally used in these baths to promote pore-free (nonpitted) deposits.

Before being plated in the high-efficiency baths, parts must first receive a strike coating of copper, about 1.3 μm (0.05 mil) thick from a dilute cyanide copper electrolyte.

The high-efficiency baths are characterized by relatively high operating temperature, high copper content, and rapid operation. Deposition rates are three to five times faster than the rates for the dilute cyanide and Rochelle cyanide baths. Parts to be plated in the high-efficiency electrolytes must be cleaned thoroughly, or the plate will be of inferior quality and the bath will require frequent purification for the removal of organic contaminants.

The potassium complexes formed by the combination of potassium cyanide and copper cyanide are more soluble than those formed when sodium cyanide is used; therefore, a higher metal content and higher rates of deposition are possible than with the sodium cyanide high-concentration bath. The potassium bath has more operating flexibility than the sodium bath and is favored because it raises the resistance to deposit burning and accordingly permits the use of higher current densities (faster plating rates).

Pulsed-current techniques are used frequently for operating high-efficiency electrolytes to produce greater leveling and uniform distribution of copper on complex shapes and to reduce plating time and the amount of metal required for plating complex shapes to a specified minimum thickness. Periodic reversal may be used to provide even higher leveling and better metal distribution than can be obtained with current interruption. Periodic reversal also improves the pore-filling characteristics of the high-efficiency electrolytes. Compositions and operating conditions of cyanide copper plating baths are given in Table 1.

The operation of high-efficiency electrolytes can be improved by the use of proprietary additives, which improve anodic and cathodic bath efficiency and anode corrosion. These additives produce matte to full-bright, fine-grain deposits. Proprietary additives are also used to control the effects of organic and inorganic contaminants.

Alkaline noncyanide copper plating is the subject of recent interest due primarily to environmental pressures on the use and disposal of cyanide-containing processes. These systems are being used in many of the same applications where cyanide systems have traditionally found success. In applications where copper is plated as a heat-treat masking barrier prior to carburizing, nitriding, or through hardening, the noncyanide processes have been shown to perform equally well or better than cyanide systems (Ref 1). These systems produce fine-grain, smooth, dense deposits that are nonporous and exhibit good bonding properties that can be deposited in rack, barrel, and continuous operations. These systems have also found use as strikes prior to the additional plating of metals and in EMI shielding applications. Their proprietary formulations are based on a variety of chelating ligands, most commonly carboxylic acids, amines, and phosphonates (Ref 2). Metallurgical analysis of these deposits shows a crystalline structure and surface morphology comparable to that produced by copper cyanide plating baths, except that the cyanide-free deposit is more compact (Ref 3). Concentration limits and operating conditions of these baths are given in Table 2.

Table 2 Concentration limits and operating conditions of alkaline noncyanide copper plating baths

Constituent or condition	Typical
Copper metal (from copper sulfate) concentration limit, g/L (oz/gal)	6-13.5 (0.8-1.8)
pH, electrometric	9.0-10.5
Temperature, °C (°F)	38-65 (100-150)
Cathode current density, A/dm^2 (A/ft^2)	0.5-3.0 (5-30)
Tank voltage	2-12
Anode:cathode ratio	1.5:1
Copper anodes	OFHC or EPT 110 copper

Note: The systems currently commercially available are proprietary but typically contain an organic complexing agent, buffer salts, anode depolarizer, and proprietary addition agents.

Alkaline copper pyrophosphate baths are used for decorative multiplate applications including plating on plastic, plating through-holes of printed circuit boards, and as a stopoff in selective case hardening of steels. Concentration limits and operating conditions are given in Table 3.

Table 3 Concentration limits and operating conditions of copper pyrophosphate plating baths

Constituent or condition	Strike	Typical
Concentration limits, g/L (oz/gal)		
Copper metal	9-11 (1.2-1.5)	19-30 (2.5-4.0)
Potassium pyrophosphate	112-205 (15-27)	235-405 (31-54)
Copper pyrophosphate	25-30 (3.3-4.0)	52-84 (7.0-11.0)
Ammonium hydroxide (conc. mL/L)	0.5-1.0	3.75-11.0
Potassium nitrate	1.5-3.0 (0.2-0.4)	3.0-12.0 (0.4-1.6)
Weight ratio (pyrophosphate:copper)	7.0-8.0:1	7.0-7.5:1
Operating conditions		

Temperature, °C (°F)	22-30 (72-86)	43-60 (110-140)
Current density, A/dm^2 (A/ft^2)	1.0-3.0 (10-30)	1.0-7.0 (10-70)
Cathode efficiency	. . .	95-100%
Voltage at tank, V	2-5	2-6
pH, electrometric[(a)]	8.0-8.5	8.0-8.7
Anodes[(b)]	Copper	Copper
Anode:cathode ratio	2:1	2:1

(a) May be maintained with pyrophosphoric acid and potassium hydroxide.

(b) OFHC anodes

Copper pyrophosphate bath characteristics are intermediate between those of cyanide and acid baths and are very similar to those of the high-efficiency cyanide bath. Electrode efficiencies are 100%; throwing power and plating rates are good. The bath also operates at an almost neutral pH. Deposits from pyrophosphate baths are fine-grain and semibright. For pyrophosphate plating on steel, zinc die castings, magnesium, or aluminum, a preliminary strike should be used. For striking, a dilute cyanide or pyrophosphate copper, nickel, or other solution may be used.

References cited in this section

1. B. Smith, W. Rapacki, and T. Davidson, Heat Treatment Maskant Materials--Evaluation of Non-cyanide Containing Electrolytes, *Plating and Surface Finishing,* Vol 79 (No. 8), 1992, p 11
2. U.S. Patent No. 3,475,293, 1969
3. L.C. Tomaszewski and R.A. Tremmel, *Proc. of the 72nd AES Annual Tech. Conf.,* American Electroplating Society, 1985

Acid Plating Baths

Electrodeposition of copper from acid baths is used extensively for electroforming, electrorefining, and decorative electroplating. Acid copper plating baths contain copper in the bivalent form and are more tolerant of ionic impurities than alkaline baths. They also have less macro throwing power and poorer metal distribution. Acid baths have excellent micro throwing power, resulting in the ability to fill or level scratches, grooves, or other substrate conditions, and additionally they are effective in sealing porous substrates. In most instances the smooth deposits produced by these solutions reduce or eliminate the need for mechanical smoothing for various substrates. A cyanide, noncyanide copper, or nickel strike must be applied to steel or zinc-alloy die castings before they are plated in acid copper solutions. Acid copper solutions cannot be used directly over substrates that are attacked by the high acidity or those where the copper forms an immersion deposit. Immersion deposits usually have poor adhesion to the substrate. Concentration limits and operating conditions of acid copper plating baths are given in Table 4.

Table 4 Compositions and operating conditions of acid copper plating baths

Constituent or condition	Copper sulfate bath		Copper fluoborate bath	
	General	**Printed circuit through-hole**	**Low copper**	**High copper**
Bath composition, g/L (oz/gal)				
Copper sulfate, $CuSO_4 \cdot 5H_2O$	200-240 (27-32)	60-110 (8-15)	. . .	. . .
Sulfuric acid, H_2SO_4	45-75 (6-10)	180-260 (24-35)	. . .	. . .
Copper fluoborate, $Cu(BF_4)_2$	. . .	. . .	225 (30)	450 (60)
Fluoboric acid, HBF_4	. . .	. . .	To pH	40 (5)
Bath analysis, g/L (oz/gal)				
Copper	50-60 (7-8)	15-28 (2-4)	8 (1)	16 (2)
Sulfuric acid	45-75 (6-10)	180-260 (24-35)	. . .	. . .
Specific gravity at 25 °C (77 °F)	. . .	. . .	1.17-1.18	1.35-1.37
Operating conditions				
Temperature, °C (°F)	20-50 (68-120)	20-40 (68-105)	20-70 (68-160)	20-70 (68-160)
Current density, A/dm^2 (A/ft^2)	2.0-10.0 (20-100)	0.1-6.0 (1-6)	7.0-13.0 (70-130)	12-35 (120-350)
Cathode efficiency, %	95-100	95-100	95-100	95-100
Voltage, V	6	6	6	6-12
pH	. . .	. . .	0.8-1.7	<0.6
Anodes	Copper[a]	Copper[a]	Copper[b]	Copper[b]

(a) Phosphorized copper (0.02-0.08% P) is recommended.

(b) High-purity, oxygen-free, nonphosphorized copper is recommended.

The copper sulfate bath is the most frequently used of the acid copper electrolytes and has its primary use in electroforming. In this application, the advantages of acid copper lie in its strength and ductility. Acid copper sulfate is used to plate thick deposits over 150 μm (6 mils) on large nickel-plated rolls; it is then engraved to electroform textile printing screens. It is also used extensively for the application of copper as an undercoating for bright nickel-chromium plating, especially for automotive components. Plates and rolls have been plated with acid copper sulfate for graphic arts and rotogravure printing where thicknesses of 500 μm (20 mils) or more are not uncommon. Bright acid copper sulfate baths are used extensively as an underlayer in decorative plating of the plastic trim found on automobiles, appliances, and various housewares. By altering the composition of the copper sulfate bath, it can be used in through-hole plating of printed circuit boards where a deposit ratio of 1 to 1 in the hole-to-board surface is desired. In some applications, acid copper sulfate solutions are used to plate over electroless deposited copper or nickel. With additives, the bath produces a bright deposit with good leveling characteristics or a semibright deposit that is easily buffed. Where copper is used as an undercoating, deposit thicknesses will generally range up to about 50 μm (2 mils).

The copper fluoborate bath produces high-speed plating and dense deposits up to any required thickness, usually 500 μm (20 mils). This bath is simple to prepare, stable, and easy to control. Operating efficiency approaches 100%. Deposits are smooth and attractive. Deposits from the low-copper bath operated at 49 °C (120 °F) are soft and are easily buffed to a high luster. The addition of molasses to either the high copper or the low copper bath operated at 49 °C (120 °F) results in deposits that are harder and stronger. Good smoothness of coatings up to 500 μm (20 mils) thick can be obtained without addition agents. For greater thicknesses, addition agents must be used to avoid excessive porosity.

Surface Preparation Considerations

Careful cleaning and preparation of the substrate material being plated is required for the effective electrodeposition of copper. Surface oils and greases, buffing compounds, rust, scale, and oxides, especially around weld or solder areas must be thoroughly removed before copper plating to ensure adhesion and to minimize contamination of the plating bath. However, before considering any preparation, it is important to know the type of substrate being used as well as any substrate surface conditions that may be present. This information is important because the preparation cycles used prior to copper plating can vary considerably, depending on the alloy or type of substrate. Also, substrate heat treatment variations can contribute to complications in surface preparation. Because there are also variations in organic and inorganic soil conditions on the work to be plated, preparation cycles should include adequate cleaning, rinsing, and activation steps to ensure quality deposits. Some of the cleaning methods used to prepare substrate surfaces prior to copper plating include soak or electrolytic alkaline cleaning, alkaline derusting, vapor degreasing, and solvent cleaning.

Good rinsing between preparation steps is a very important and often-overlooked step in the preparation cycle. Time, temperature, and concentration considerations should be applied to rinsing techniques as well as to the cleaning processing solutions. Often, rinse times are too short, immersion temperatures are too cold, and the water flow rate is too low to adequately rinse cleaner films from the surfaces.

The activation step is usually carried out with the use of an acid to remove inorganic soils, oxides, or cleaner films from the surfaces. The acid used depends on the type of substrate to be plated. The most commonly used acids in preplate processes are hydrochloric acid and sulfuric acid. More information about the techniques used in these preparation processes is found in the Section "Surface Cleaning" in this Volume. Specifications and practices for copper electroplating are given in Table 5.

Table 5 Specifications and standards for copper electroplating

Specification	Uses
Copper plating	
AMS 2418	Copper plating
MIL-C-14550 (Ord)	Copper plating

ASTM B 503	Recommended practice for use of copper and nickel electroplating solution for electroforming
Copper plating in multiplate systems	
ASTM B 456	Specification for electrodeposited coatings of copper plus nickel plus chromium and nickel plus chromium
ASTM B 200	Specification for electrodeposited coatings of lead and lead-tin alloys on steel and ferrous alloys
AMS 2412	Plating silver, copper strike, low bake
AMS 2413	Silver and rhodium plating
AMS 2420	Plating, aluminum for solderability, zincate process
AMS 2421	Plating, magnesium for solderability, zincate process
QQ-N-290	Nickel plating (electrodeposited)
Surface preparation	
ASTM A 380	Practice for cleaning and descaling stainless steel parts, equipment, and systems
ASTM B 183	Practice for preparation of low-carbon steel for electroplating
ASTM B 242	Practice for preparation of high-carbon steel for electroplating
ASTM B 252	Recommended practice for preparation of zinc alloy die castings for electroplating
ASTM B 253	Practice for preparation of aluminum alloys for electroplating
ASTM B 254	Practice for preparation of and electroplating on stainless steel
ASTM B 281	Practice for preparation of copper and copper-base alloys for electroplating and conversion coatings
ASTM B 319	Guide for preparation of lead and lead alloys for electroplating
ASTM B 322	Practice for cleaning metals prior to electroplating
ASTM B 480	Practice for preparation of magnesium and magnesium alloys for electroplating
ASTM B 481	Practice for preparation of titanium and titanium alloys for electroplating

MIL-HDBK-132 (Ord)	Military handbook, protective finishes

Cyanide Baths. Although the dilute cyanide and Rochelle cyanide baths exert a significant cleaning action on the surface of the parts during the plating operation, thorough cleaning of parts to be plated in these baths is still necessary.

The high-efficiency sodium cyanide and potassium cyanide electrolytes have virtually no surface-cleaning ability during plating because of the absence of hydrogen evolution. Parts to be plated in these electrolytes must be thoroughly cleaned. Parts also must receive first a dilute cyanide copper strike about 1.3 μm (0.05 mil) thick.

Noncyanide Alkaline Baths. Unlike cyanide baths, noncyanide alkaline baths do not offer any cleaning, and parts plated in these electrolytes must first be thoroughly cleaned, rinsed, and activated. If being used as a strike prior to acid copper or other similar deposit, a minimum thickness of 5.2 μm (0.2 mil) is desired. These systems can be plated directly on properly prepared steel, brass, stainless steel, zincated aluminum, lead-tin, and most high-quality, properly prepared zinc-base die castings (Ref 4, 5). One advantage of the noncyanide electrolyte is the fact that accidental drag-in of acids poses no hazard of the evolution of poisonous cyanide gas, which could occur with cyanide copper electrolytes.

Pyrophosphate Baths. If pyrophosphate electrolytes are to be used, conventional cleaning cycles are generally satisfactory. A preliminary strike should be applied to steel, zinc-base die castings, magnesium, and aluminum. The strike solution may be a dilute cyanide copper, dilute pyrophosphate copper, or nickel. If a cyanide copper strike is used, adequate rinsing or, preferably, a mild acid dip following the strike is recommended before final pyrophosphate copper plating.

Acid Baths. When sulfate or fluoborate copper is to be deposited, steel or zinc must first receive a cyanide or noncyanide alkaline copper or nickel strike. With complete coverage, the strike may be as thin as 2 μm (0.08 mil). After the strike, the parts should be dipped in a dilute solution of sulfuric acid to neutralize solution retained from the alkaline strike bath. The parts should be rinsed thoroughly before acid copper plating. Nickel or nickel alloy parts, when surface activated by reverse-current etching in sulfuric acid, can be plated directly, provided contact is made to the work with the current or power on before immersion into the acid copper solution.

References cited in this section

4. "Cupral Alkaline Non-cyanide Copper," Operating Technical Data Sheet, Enthone/OMI, Warren, MI
5. "E-Brite 30/30 Alkaline Non-cyanide Copper," Operating Technical Data Sheet, Electrochemical Products, Inc., New Berlin, WI

Bath Composition and Operating Variables

The compositions and analyses given in Tables 1, 2, 3, and 4 for cyanide, noncyanide alkaline, pyrophosphate, and acid copper plating baths may be varied within the control limits to satisfy requirements for specific applications.

Current density can be altered to effect more efficient control and to increase the deposition rate of copper. The data in Table 6 can be used as a guide to the selection of current density.

Table 6 Estimated time required for plating copper (valence 1) to a given thickness at 100% cathode efficiency

Cyanide baths contain copper with a valence of 1. For baths containing copper with a valence of 2, such as noncyanide alkaline, sulfate, pyrophosphate, and fluoborate baths, double the time values given in this table. Values must be corrected for losses in cathode efficiency by adding the difference between the actual cathode efficiency and 100%; for example, for 70% cathode efficiency, add 30% to values in table to determine estimated time.

Thickness of plate	Plating time, min[(a)] at current density, A/dm^2 (A/ft^2)

µm	mils	1.0 (10)	1.5 (15)	2.0 (20)	2.5 (25)	3.0 (30)	3.5 (35)	4.0 (40)	4.5 (45)
2	0.08	4	3	2	2	2	1	1	1
5	0.2	11	8	6	5	4	3	3	2
10	0.4	23	15	11	9	8	6	6	5
20	0.8	45	30	23	18	15	13	11	9
30	1.2	68	45	34	27	23	19	17	14
40	1.6	90	60	45	36	30	26	23	18
50	2.0	113	75	57	45	38	32	28	23
60	2.4	136	90	68	54	45	39	34	27
70	2.8	158	106	79	63	53	45	40	32
80	3.1	181	120	90	72	60	52	45	36

(a) To nearest whole value

Impurities. The degree of control required to protect copper plating baths from impurities varies with the type of bath and the method of processing used. Known causes of roughness in copper deposits are:

- Dragover from cleaners, which results in the formation of insoluble silicates in the electrolyte
- Poor anode corrosion
- Insoluble metallic sulfides because of sulfide impurities
- Organic matter in the water used for composition, especially in rinse tanks
- Insoluble carbonates because of calcium and magnesium in hard water
- Oil from overhead conveyors
- Airborne dust or particles

If the level of impurities reaches a critical point, causing poor results, a batch carbon treatment or circulation through a carbon-packed filter may be required. For the noncyanide processes, a sulfur-free carbon pack must be maintained on the bath and changed weekly. Lead and cyanide are contaminants to these systems and tend to cause a black smutted deposit. When converting a plating line from a cyanide system to a noncyanide electrolyte, all associated equipment must be cleaned and thoroughly washed to ensure no cyanide contamination.

Caution: Cyanide remains in the system. Acids can be used only after all traces of cyanide have been eliminated.

Purity of Water Used in Composition. The purity of the water used in the composition of the baths is important for all plating operations. Iron in the water causes roughness in the deposit if the pH of the electrolyte is above 3.5 where iron

can be precipitated. Chlorides in concentrations greater than about 0.44 g/L (0.05 oz/gal) promote the formation of nodular deposits. Calcium, magnesium, and iron precipitate in the bath. Organic matter may cause pitting of deposits.

When plating in sodium or potassium, high-efficiency electrolytes and distilled, deionized, softened, or good quality tap water may be used for solution composition and for replenishment. Tap water with high contents of calcium and/or iron should not be used, because it may cause roughness of the deposit. Softened water should be used with care, especially in plating baths where chloride contents are critical, such as bright copper sulfate baths.

Agitation during plating permits the use of higher current densities, which create rapid deposition of copper. The amount of increase permissible in current density varies for the different baths. Preferred methods of agitation for the types of baths are:

Cyanide baths	Cathode movement, air agitation, or both
Pyrophosphate baths	Air agitation
Acid baths	Cathode movement, air agitation, or both
Noncyanide baths	Vigorous air agitation

When air agitation is used, all airline pipes should be made of inert material or coated with an inert material to prevent attack by the electrolytes. The air used for agitation must be clean to avoid bath contamination. Filtered air from a low-pressure blower is required.

Ultrasonic vibration also has been used for the agitation of copper plating baths. This method does not largely improve the properties or appearance of electroplates, but it can improve plating speed by permitting an increase in the current density without the hazard of burning the parts. Increased plating speed does not necessarily justify the increased cost and complexity of ultrasonic operation, because the high-speed baths can usually be operated with a fairly high current density at nearly 100% efficiency.

Plating in Dilute Cyanide Baths

In the dilute cyanide bath, corrosion of the anodes increases with increasing concentration of free cyanide. Low free-cyanide content may cause rough deposits due to anode polarization; however, excessive free cyanide lowers cathode efficiency, resulting in thinner deposits per unit of time. Modifications of the pH, or alkalinity, of the strike compositions are used for striking various substrates. For use on steel, additional NaOH or KOH improves the conductivity of the solution and aids in protecting steel anode baskets, tanks, and other steel fixtures from corrosion. For use on zinc-base die castings, the hydroxide concentration is kept in the range of 1.3 to 3.8 g/L (0.2 to 0.5 oz/gal). For use on zincated aluminum alloys, the pH should be reduced to approximately 9.7 to 10.0 with sodium bicarbonate. The operator should keep adding tartaric acid or sodium bicarbonate to the solution to maintain the desired pH range (e.g., 10.0 to 10.5 for plating on aluminum alloys.

The dilute copper cyanide bath can be operated at room temperature, but the general practice is to operate the bath between 32 and 49 °C (90 and 120 °F) to increase the rate of deposition and to improve anode dissolution. This electrolyte is usually operated with a cathode current density of 1 to 1.5 A/dm^2 (10 to 15 A/ft^2). The tank voltage is normally between 4 and 6 V.

Agitation of the bath produces more uniform composition throughout the electrolyte, more uniform anode corrosion, and an increase in current densities where the brightest deposits are obtained. Current densities in excess of 5 A/dm^2 (50 A/ft^2) have been applied successfully by using air agitation of the solution and agitating the work.

Continuous filtration is preferred for dilute cyanide baths. Organic contamination or suspended matter in the strike is frequently responsible for roughness of copper plate subsequently deposited in the cyanide copper plating bath. Hexavalent chromium in the strike causes blistering of the deposit. Proprietary additives can be used to improve the bath operation, as well as aid in the control of organic and inorganic contaminants. These proprietary additives consist of organic complexing agents, such as tartrate salts. Organic reducing agents are used to control impurities such as hexavalent chromium. Wetting agents (surfactants) are used to control organic contaminants and to lower the surface tension of the plating solution, to allow better throwing power of copper over substrate irregularities, and to aid drainage and rinsing.

Plating in Rochelle Cyanide Baths

Rochelle electrolytes with lower metal concentrations can be used both for striking applications and, with higher metal concentrations, for plating applications. Rochelle salts produce some grain refinement, reduce the effects of some metallic contaminants, and aid in anode corrosion by increasing the anode current density range before anode polarization occurs. The Rochelle electrolyte can also be used for periodic-reverse plating with good results. Barrel plating with a Rochelle bath requires a variation in the chemistry. When plating parts that tend to nest or stick together during the barrel rotation, it is necessary to increase the free cyanide to 25 to 30 g/L (3 to 4 oz/gal) or slightly higher to obtain adequate coverage on the nested parts.

Rochelle baths usually are operated at a current density between 2 and 5 A/dm^2 (20 and 50 A/ft^2). Substituting potassium salts for sodium salts in the baths with higher metal concentration, up to 38 g/L (5 oz/gal) copper, can increase the allowable current density to 6 A/dm^2 (60 A/ft ^{2}), with the penalty of lowering the cathode efficiency. The Rochelle baths are usually operated at between 54 and 71 °C (130 and 160 °F) for best efficiency. The rate of deposition is higher at the higher temperatures. A high-efficiency electrolyte having a higher metal concentration can be operated at up to 77 °C (170 °F). For copper plating zinc-base die castings, the electrolyte is best operated at 60 to 71 °C (140 to 160 °F), provided the pH of the bath is maintained between 11.6 and 12.3. An increase in the operating temperature of Rochelle cyanide baths increases the efficiency of the anode and cathode; however, free cyanide decomposes more rapidly, which increases carbonate formation. An increase in agitation causes an increase in anode efficiency, but this also increases carbonate formation. Carbonates are always present in cyanide copper solutions from oxidation of the cyanide and, also, from adsorption of carbon dioxide from the air that reacts with the alkali in solution. Carbonates from a sodium copper cyanide plating solution can be removed by cooling the solution, which precipitates the less soluble sodium carbonate. High carbonate concentrations lower the anode efficiency, which accelerates additional carbonate formation in addition to producing rough or porous plated deposits (Ref 6).

Rochelle copper baths should be maintained at a pH between 12.2 and 13.0. Anode efficiency may be prohibitively low if the pH is too high. Raising the pH also decreases the voltage drop across the anode film. Figure 1 shows a buffer curve for adjusting the pH of Rochelle electrolytes.

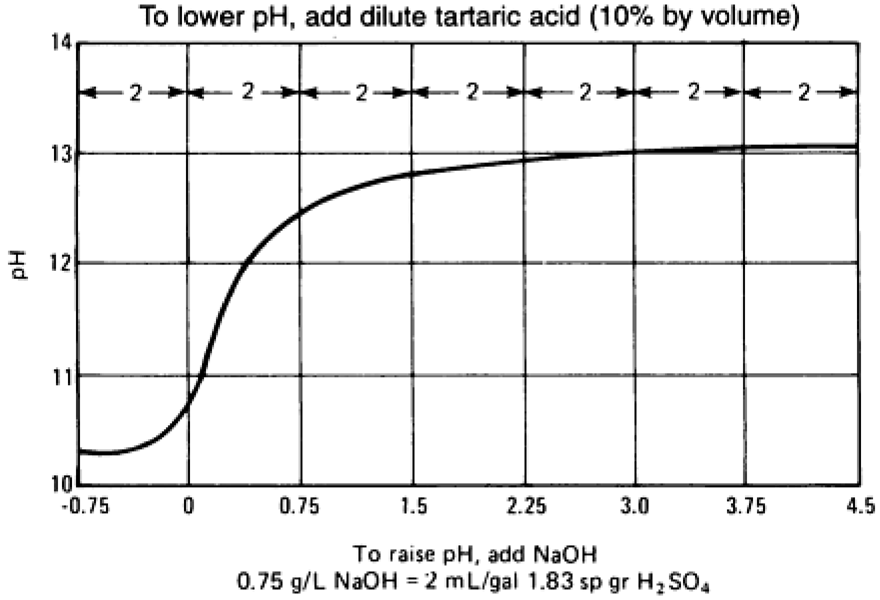


Fig. 1 Buffer curve for adjusting the pH of Rochelle electrolytes. Source: Ref 7

Conductivity of the bath is improved by raising the free alkali cyanide and the concentration of the copper complexes. When depositing copper directly on steel, brass, or copper, conductivity can be improved by the addition of 2 to 15 g/L ($\frac{1}{4}$ to 2 oz/gal) of sodium hydroxide. Sodium hydroxide concentrations should be reduced if the electrolyte is used to deposit copper onto zinc-base die castings, aluminum, or magnesium.

Rochelle baths can become contaminated during plating of zinc-base die castings. Zinc contamination can be removed by electrolysis of the bath at room temperature, at the current density that produces the most brassy or off-color deposit, usually 0.2 to 0.3 A/dm^2 (2 to 3 A/ft^2). Iron, which forms complexes with cyanide, cannot be removed readily from the bath and causes a reduction in current efficiency. Drag-in of chloride ion from acid dips must be kept very low to prevent iron buildup due to dissolution of steel equipment. Bipolarity of steel tanks or heat exchangers should be avoided.

The Rochelle bath is susceptible to organic contamination, which can be controlled by the use of wetting agents. Organic contaminants should be removed by periodic batch treatment of the electrolyte with activated carbon, followed by filtration. Organic contamination is especially high in barrel plating. A low-foaming, free-rinsing surfactant or a dispersion agent must be used in barrel plating baths to prevent organic contamination from adversely affecting the quality of the plated deposit. Organic contamination can be controlled with carbon treatment methods. Continuous filtration of cyanide electrolytes is recommended to eliminate particulate matter or salts, which can result in rough deposits.

Increase in the current density or the presence of lead in the Rochelle cyanide bath causes an increase in the stresses of copper plate. These stresses can be reduced by increasing the concentration of copper in Rochelle baths. The addition of 15 g/L (2 oz/gal) of potassium thiocyanate produces an expansion stress instead of the usual contraction stress. Figure 2 shows stress in thin copper electrodeposits plated from a cyanide solution onto stainless steel.

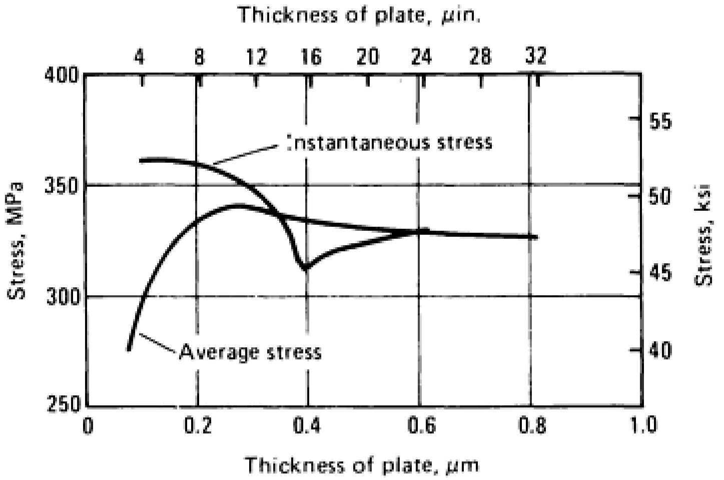


Fig. 2 Stress in thin copper plate deposited on stainless steel spirals. Stainless steel spirals are 0.127 mm (0.005 in.) thick. Source: Ref 8

References cited in this section

6. J. Horner, A Study of the Effects on Some Variables of the Speed and Distribution of Deposits from Cyanide Copper Plating Solutions, *Proc. of the 51st AES Annual Tech. Conf.,* American Electroplating Society, 1964
7. *Modern Electroplating,* Wiley, 1974, p 173
8. *J. Electrochemical Soc.,* Nov 1961

Plating in High-Efficiency Sodium and Potassium Cyanide Baths

High-efficiency sodium and potassium cyanide baths allow the use of higher current densities. Cyanide plating baths typically decrease in cathode efficiency, or speed of deposition, with increasing current, which accounts for the good plate distribution (throwing power). The cathode efficiency approaches 100% only at low current densities, often 10A/dm^2 or less. With more practical current densities of 2.0 to 3.0 A/dm^2, the cathode efficiency may drop 20%, especially with lower agitation rates. The sodium or potassium constituent improves the conductivity of the bath.

Operation of the sodium cyanide and potassium cyanide electrolytes at 66 to 74 °C (150 to 165 °F) produces quality deposits. Temperatures in excess of 74 °C (165 °F) allow the use of higher current densities, but breakdown of the cyanide becomes excessive at elevated temperatures. The anode current densities are limited by polarization, resulting in poor anode efficiency and higher voltage requirements. The cathode current densities are limited by burning of the deposit, resulting in reduced efficiency, loss of brightness, and roughness. These limits are higher in the potassium cyanide electrolyte.

Agitation of sodium cyanide and potassium cyanide high-efficiency baths is important for achieving maximum plating speed. Agitation can be accomplished by solution movement, cathode-rod movement, or use of air. Each type of agitation improves the maximum allowable current densities, with air agitation providing the greatest improvement. However, it should be noted that carbonate levels in air-agitated baths tend to increase at a greater rate than baths using mechanical agitation. All three types of agitation may be used within a single bath. Solution movement can be accomplished by mixing or by the flow of solution through filtration equipment. Cathode-rod movement of about 1 to 2 m/min (3 to 7 ft/min) allows increased plating rates. Gentle air agitation should be supplied by the use of a low-pressure blower that has a clean, filtered air source. Care must be taken to use clean, oil-free air for agitation to avoid contamination of the plating solution.

Filtration is also essential when operating high-efficiency cyanide copper electrolytes, especially for plating deposits thicker than 13 μm (0.5 mil). Filtration equipment should have the capability of one to two complete turnovers of the solution each hour while removing particulate matter from the electrolyte. Roughness of the copper deposits from particulate matter is often caused by faulty cleaning or by the formation of metallic copper or cuprous oxide particles at the anodes. Suspended dirt or solid matter in the cyanide copper electrolyte also causes surface roughness. Anode bags of proper size, material, weight, and weave are beneficial in retaining particulate matter formed at the anode. Other foreign particles introduced into the cyanide copper electrolyte are removed by the filtration equipment.

Carbonate buildup in high-efficiency copper cyanide baths can adversely affect the bath operation. High concentrations of carbonate reduce plating efficiency and speed. Excessive carbonates also affect the smoothness of the deposits. Carbonate contents of 120 to 150 g/L (16 to 20 oz/gal) or more may result in lower plating efficiency and plating speed. Excessive carbonates can also lower and reduce the acceptable plating range. These effects are more pronounced in a sodium cyanide bath than in a potassium cyanide bath.

The primary source of carbonate formation is the breakdown of cyanide as a result of poor anode efficiency. Operating cyanide electrolytes at temperatures above the recommended levels can also result in carbonate formation. Operating temperatures above about 74 °C (165 °F) cause decomposition of the cyanide ion. Air containing high levels of carbon dioxide should not be used in air-agitated systems, because the carbon dioxide is dissolved by the alkaline plating solution, also forming carbonate. The air source for air-agitated systems should be placed where it provides a clean, fresh supply.

Excessive carbonates can be removed by freezing or precipitation with lime or proprietary additives. Sodium cyanide baths can be treated either by precipitation or freezing. Potassium cyanide baths can only be treated by precipitation. Freezing is not effective for potassium cyanide baths because of the high solubility of the carbonate salts.

Current interruption cycles frequently improve the operating range of high-efficiency sodium or potassium copper cyanide plating solutions. Current interruption cycles generally allow the use of higher current densities while maintaining bath efficiency. Current interruption cycles also improve the brightness of the copper deposits, and in some cases they give excellent deposit brightness from bright plating baths that are so contaminated that acceptable deposits cannot be produced when using continuous direct current.

Current interruption cycles in the range of 8 to 15 s plating time followed by 1 to 3 s current interruption are generally used. Plating times of less than 8 s and current interruptions of more than 3 s lower the net plating rate. Plating times of more than 15 s and current interruption of less than 1 s reduce the benefits obtained by using a current interruption cycle.

The use of periodic current reversal can also be used to great advantage in high-efficiency copper cyanide plating solutions. This technique involves plating parts in the conventional manner for a selected time and then deplating for a shorter period by reversing the current. Shorter periodic reversal cycles, such as 2 to 40 s of plating followed by 1 to 10 s of deplating (reversal), result in improved deposit brightness similar to that obtained with current interruption. A major advantage in using periodic reversal is the degree of leveling that can be achieved, particularly when relatively long reversal cycles are used. These longer cycles, in excess of 45 s direct with reverse cycles in excess of 10 s, can provide leveling characteristics in excess of 50%. The use of periodic reversal permits the use of higher plating and deplating current densities.

The leveling characteristics of the deposit are improved by increasing the reversal current, whereas cycle efficiency is increased by lowering the reversal current. Figure 3 shows cycle efficiency for periodic-reverse plating. Figure 4 indicates thickness of deposit as a function of cycle efficiency.

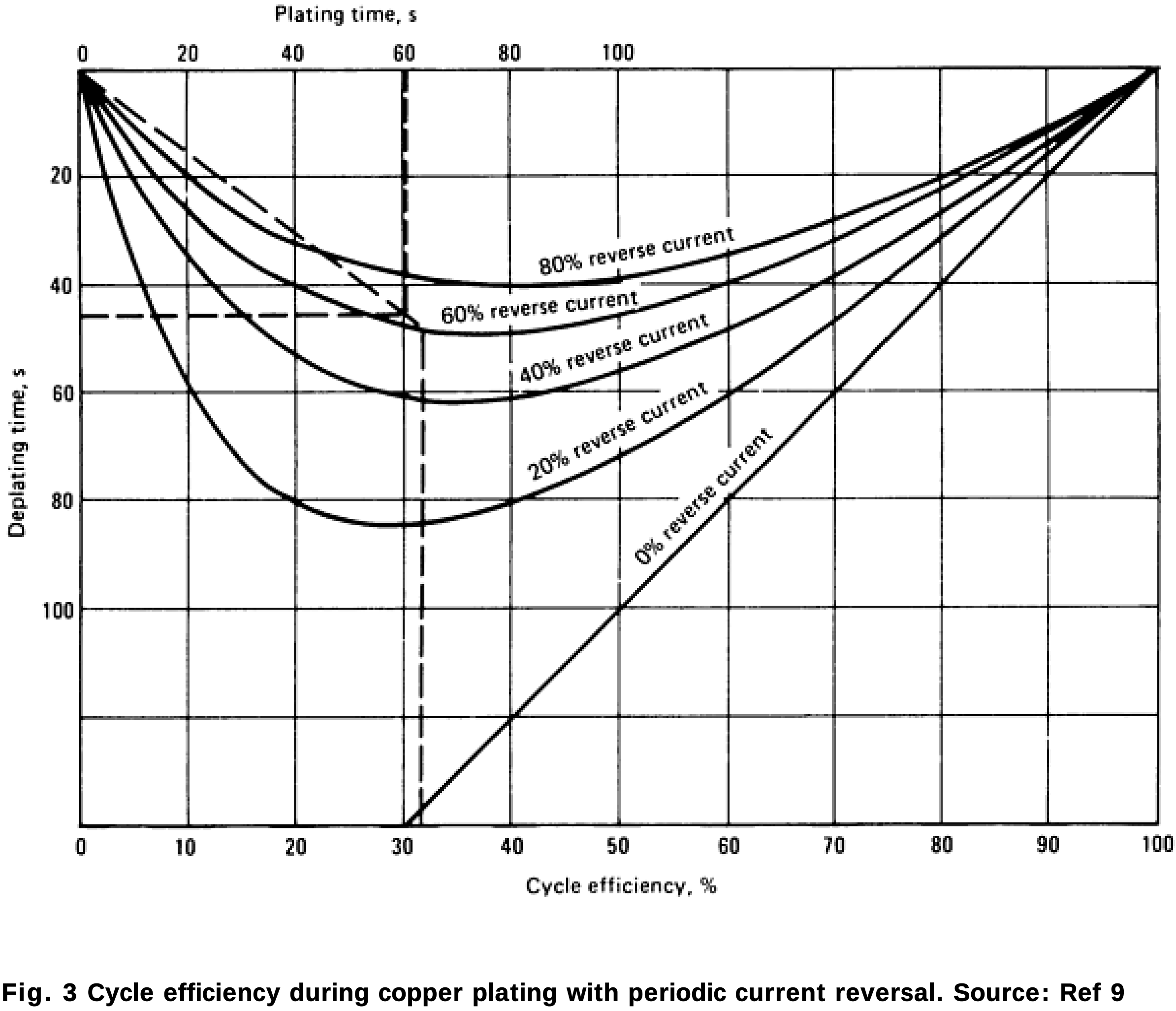


Fig. 3 Cycle efficiency during copper plating with periodic current reversal. Source: Ref 9

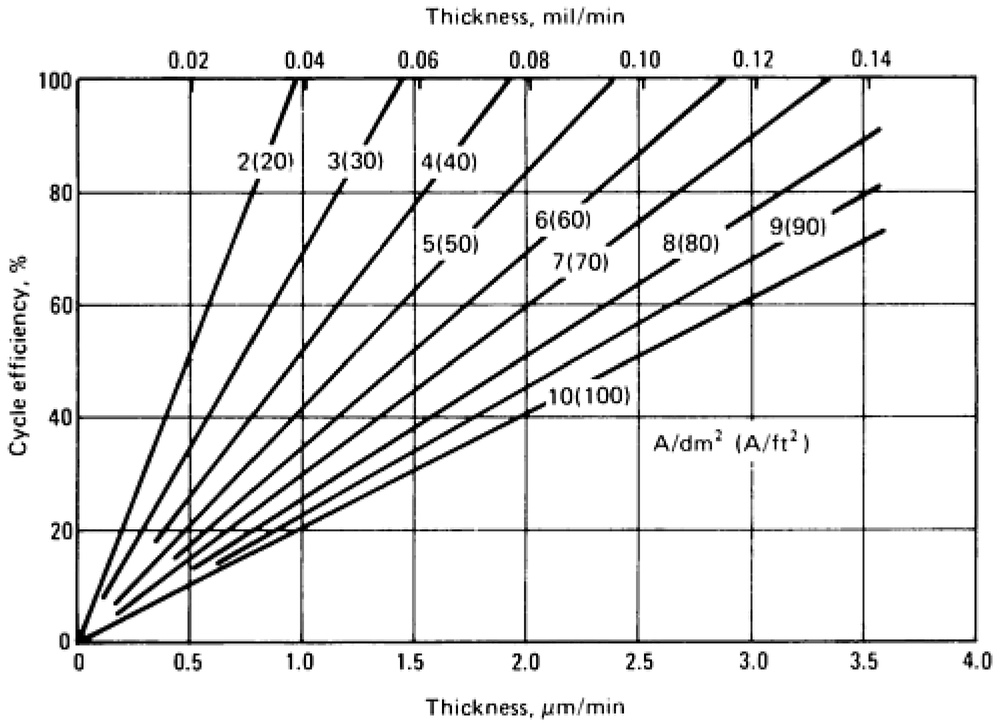


Fig. 4 Thickness of copper deposits as a function of cycle efficiency and current density during plating with periodic current reversal. Source: Ref 9

Another current-interrupting scheme being used for this and other copper plating systems is pulse plating. This normally involves a pulse power source (rectifier) that produces square-wave current pulses. *Square wave* conventionally suggests a pulse with a rise-and-fall time of approximately 10 to 85 μs and a standard frequency of 150 and 10,000 cycles. The periodic interruption of the current with proper time sequences allows much faster plating without surface burning, produces finer grain deposits, and increases throwing power and distribution.

Proprietary additives are used in high-efficiency copper cyanide baths to improve anode corrosion, increase both anode and cathode efficiencies, and control contamination. Organic and metallic additives are also used to improve deposit characteristics and brightness. These additives produce deposits ranging from matte to full-bright.

Reference cited in this section

9. *Electroplating Engineering Handbook*, Reinhold, 1971, p 748, 750

Plating in Noncyanide Copper Baths

The development and refinement of proprietary noncyanide copper baths continues today. The copper deposit from these systems is a fine-grain, dense deposit (Ref 3). The noncyanide copper systems exhibit excellent throwing and covering power, even in deeply recessed areas. In addition to eliminating the cyanide, these processes operate at much lower copper metal concentrations of 7.5 to 13.5 g/L (1 to 2 oz/gal). As a result, they offer additional savings in lowering waste treatment costs. Copper sulfate is the source of copper ions for these systems. The plating electrolytes producing these deposits are very stable compared to those of cyanide copper processes, because there is no decomposition of cyanide resulting in carbonate buildup.

Over the typical current density range of 0.5 to 3.5 A/dm^2 (5 to 35 A/ft^2), the cathode efficiency of noncyanide systems approaches 100%. The good efficiency tends to offset the lower deposition rate of divalent copper electrolysis compared to that of monovalent copper systems. Agitation has a dramatic effect on deposit appearance and cathode efficiency. To obtain a uniform, fine-grain deposit over a wide current density range, air agitation is required for these systems. Lack of agitation produces dull, burned deposits at average current densities of 1.5 to 2.0 A/dm^2 (15 to 20 A/ft^2).

Of the commercially available systems, one process is affected by the buildup of cuprous ions in the cupric phosphonate system, which results in rough, nonadherent copper deposits (Ref 10). To overcome this effect, the process uses continuous electrolysis carried out in an auxiliary tank with special ceramic or platinized anodes to oxidize the cuprous to cupric.

Because the operating pH of these systems is in the range of 9 to 10, these baths can be used as both strikes and plates. There are no special adjustments required for processing zinc diecast and zincated aluminum, as there are in cyanide copper plating. At pH values below 9, the deposits are brighter but adhesion is adversely affected. Values greater than 10 cause high-current-density dullness and can reduce the limiting current density.

These systems, unlike the cyanide systems, are more susceptible to metallic and organic contaminants. Iron, lead, and silver are critical impurities that should be removed by low-current-density electrolytic treatments. Organic impurities are treated using hydrogen peroxide and carbon treatments on a regular basis. Continuous filtration through a 10 μm retention-size cartridge is beneficial for the noncyanide systems. Occasional carbon filtration using a sulfur-free carbon can be used to control organic contamination. Noncyanide systems have very little tolerance to cyanide contamination. When converting cyanide plating lines to noncyanide processes, it is essential to clean and leach out all the cyanide from the tank linings, racks, filters, heaters, plating barrels, and any associated equipment.

References cited in this section

3. L.C. Tomaszewski and R.A. Tremmel, *Proc. of the 72nd AES Annual Tech. Conf.,* American Electroplating Society, 1985
10. D. Maule and B. Srinivasan, Alkaline Non-cyanide Plating, *Proc. of the 80th AESF Tech. Conf.,* American Electroplating and Surface Finishers, 1993

Plating in Pyrophosphate Baths

Copper pyrophosphate plating baths offer a number of desirable features. Copper pyrophosphate forms a highly soluble and conductive complex when dissolved in potassium pyrophosphate solution. Potassium salts are preferred because of their higher solubilities. Copper pyrophosphate plating baths operate at nearly 100% cathode efficiency and provide good throwing power. They are noncorrosive because the operating pH is near neutral. Concentration limits and operating conditions for copper pyrophosphate baths are given in Table 3.

Pyrophosphate forms a highly soluble complex with copper. Excess pyrophosphate is necessary to increase the conductivity of the bath and to effect proper corrosion of the anodes. Ammonia assists anode corrosion, helps enhance the luster of the deposit, and aids pH control. Nitrate allows the use of higher operating current densities by inhibiting the reduction of hydrogen at the upper end of the current density range. The pH of the pyrophosphate bath is maintained between 8.0 and 8.8. A high pH reduces anode efficiency, and a low pH reduces the throwing power of the solution and the stability of the complex compound in solution with the formation of orthophosphate. The pH of the bath can be lowered with pyrophosphoric acid and raised with potassium hydroxide. Good agitation is also essential for consistent operation. Air agitation provides for good performance of the anodes and cathodes and is preferred to cathode agitation.

Pyrophosphate electrolytes can be operated at current densities up to 7.0 A/dm^2 (70 A/ft^2) or higher. The operating current density can be increased by agitating the solution or by increasing the temperature of the bath. The anode current density should be maintained between 2 and 4 A/dm^2 (20 and 40 A/ft^2).

High bath temperatures should be avoided, because excessive formation of orthophosphate occurs. Orthophosphate formed by the hydrolysis of pyrophosphate is beneficial up to about 90 g/L (12 oz/gal), because it promotes anode corrosion and acts as a buffer. Above this concentration, conductivity and bright plating range are decreased and banded deposits are obtained. Orthophosphate cannot be removed chemically from the solution. The concentration can be reduced only by discarding the bath or diluting and rebuilding the pyrophosphate plating solution.

Copper pyrophosphate plating baths are susceptible to organic contamination, including oil and excess or decomposed addition agents. These are removed by treatment with activated carbon and filtration. Cyanide and lead also contaminate the bath. Cyanide is removed by treatment with hydrogen peroxide and lead by electrolysis. Precautionary methods, such as proper cleaning, adequate rinsing, and good solution control and maintenance, prevent these contaminants from

entering or building up in the bath, avoiding the need for frequent purification. Copper pyrophosphate solutions are tolerant of other metallic contamination.

Proprietary brighteners are available that refine the grain structure, impart leveling characteristics, and act as brighteners. However, decomposition products from an excessive additive concentration cause stress and brittle deposits. Thus, for quality deposits, additives should be added to the bath on an as-consumed basis.

Plating in Acid Sulfate Baths

The chemical composition of acid sulfate baths is simple. Copper sulfate pentahydrate and sulfuric acid are the primary constituents of the copper sulfate electrolyte. The metal ions are furnished by the copper sulfate. Sulfuric acid increases solution conductivity and helps prevent the formation of basic cuprous or cupric crystals on the anodes and the tank, which causes poor anode corrosion and roughness. Low sulfuric acid contents produce more high-current-density burn, poorer leveling, more low-current-density dullness, and more nodular deposits. High sulfuric acid has less effect on the deposit but increases the anode dissolution. With cathode efficiencies of 95 to 100%, the copper sulfate bath is easy to operate and control.

Many copper sulfate plating solutions require the use of additives to produce smooth, fine-grain, bright, leveled, and ductile deposits. Most of the addition agents used in copper sulfate plating solutions are proprietary formulations. These proprietary additives are capable of producing the desired characteristics in the copper deposit, and deposit hardness can be increased where necessary.

In copper sulfate systems that produce bright deposits, a catalyst must be added in addition to the primary constituents to avoid streaky deposits. This catalyst is chloride, which is maintained between 0.02 to 0.1 g/L (0.003 to 0.01 oz/gal), or 20 to 100 ppm. The chloride, usually added as hydrochloric acid, inhibits rough nodular plate from forming. Low chloride can cause dark deposits on the edges and high-current-density areas of the work, loss of leveling, loss of brightness, pitting, and poor anode corrosion. High chloride causes streaks, increased brightener usage, and loss of leveling and brightness in the bright bath formulations. High chloride can be reduced with zinc dust treatments or precipitation with silver.

If solution agitation or work movement is minimal, current densities should not exceed about 4.5 A/dm^2 (45 A/ft^2), because excessive anode polarization may occur and the deposits can be spongy. Where higher current densities are desired, such as for electrotypes or wire plating, air agitation is used. Air agitation is necessary to accelerate ionic diffusion and produce high-quality, fine-grain deposits where current densities are in excess of 10 A/dm^2 (100 A/ft^2).

The effect of temperature changes on the grain structure and surface smoothness of deposits plated from the copper sulfate bath is less significant than the effect of changes in cathode current densities. An increase in temperature results in higher conductivity and reduced anode and cathode polarization. Increased temperature also reduces the tensile strength of deposits and increases grain size. Excessive temperatures should be avoided in copper sulfate baths where proprietary brightener formulations are used, because reduced plating ranges, excessive additive use, and solution contamination from additive breakdown result.

Care must be taken to avoid accelerated buildup of copper metal, as in cases where dragout rates are low or improper anode-to-cathode ratios are maintained. An increase in the concentration of the copper sulfate increases the solution resistivity and slightly reduces the anode and cathode polarization. Copper sulfate concentrations in excess of 248 g/L (33 oz/gal) may result in salt crystallization in the plating solution. Normal bath composition is restored by discarding a portion of the bath and adding water and sulfuric acid.

To improve the throwing power of some bright copper sulfate baths used for plating printed circuit boards, a low copper sulfate and high sulfuric acid electrolyte is used. The use of this electrolyte allows a nearly equal deposit distribution when plating the through-holes of the printed circuit board.

In sulfate electrolytes, impurities such as silver, gold, arsenic, and antimony can codeposit with copper. Arsenic and antimony cause copper deposits to be brittle and rough, and silver may cause roughness. Nickel and iron impurities reduce the conductivity of the plating bath. Lead impurities do not codeposit with copper; however, they precipitate in the electrolyte. Soluble silicates may precipitate onto the work. Organic contamination from decomposition products of addition agents, tank linings, and anode bags can cause brittle or discolored deposits. These organics can be removed from the electrolyte by treating it with activated carbon.

Plating in Fluoborate Baths

Copper fluoborate and fluoboric acid are the primary constituents of the copper fluoborate electrolyte. The metal ions are furnished by the copper fluoborate, which is more soluble than copper sulfate used in the sulfate bath, and the anode current density is not critical. Therefore, the metal-ion concentration in the fluoborate bath can be more than twice that in the copper sulfate solution, and this permits higher cathode current densities. The cupric salts in the fluoborate bath are highly ionized, except for small amounts of less ionized complex salts formed with certain addition agents.

In the copper fluoborate bath, the anode current density can be as high as 40 A/dm^2 (400 A/ft^2) without excessive anode polarization. The effect of temperature changes on the grain structure and surface smoothness of deposits plated from the copper fluoborate bath is less significant than the effect of changes in cathode current density.

Agitation is preferred for the fluoborate bath, although acceptable deposits 25 μm (1 mil) thick have been produced in a high-concentration bath without agitation and with current density maintained at 35 A/dm^2 (350 A/ft^2). When agitation is used, a low-concentration bath operated at a current density of 4 to 5 A/dm^2 (40 to 50 A/ft^2) is preferred.

Although fluoborate baths containing no additives can produce dense and smooth deposits up to 500 μm (20 mils) thick, additives may be used to aid in the deposition of brighter or more uniform coatings or to assist in control of plating conditions. Although deposits from fluoborate baths are easily buffed to a high luster, brighteners of acetyl thiourea can be added to the electrolyte to produce bright coatings. The addition of free acid to the bath increases solution conductivity, reduces anode and cathode polarization, and prevents the precipitation of basic salts. Hard deposits and minimum edge effects result when molasses (1 mL/L, or 0.1 fluid oz/gal) is added to the electrolyte. If the pH of these baths exceeds 1.7, deposits become dull, dark, and brittle.

The resistivity of fluoborate electrolytes is reduced if the concentration of fluoboric acid exceeds 15 g/L (2 oz/gal) or if the concentration of copper fluoborate exceeds 220 g/L (29 oz/gal). In the fluoborate bath, the metal-ion concentration can be more than double that in a copper sulfate solution containing 50 to 75 g/L (6.7 to 10 oz/gal) of sulfuric acid.

In the fluoborate electrolytes, silver, gold, arsenic, and antimony may co-deposit with copper, but the effects of such impurities in this electrolyte have not been reported. Lead is the only metallic impurity known to interfere with the deposition of ductile copper deposits. Additions of sulfuric acid precipitate the lead. As with the sulfate electrolytes, organic impurities sometimes cause deposits to be brittle or discolored. They can be removed by treating the bath with activated carbon

Wastewater Control and Treatment

Increasing regulations governing discharge water have led to improved techniques for reducing the quantities of wastes that must be treated. These techniques have not only reduced the quantity of wastewater to be treated, but have also reduced the quantity of chemicals used and have lowered water consumption. These methods can be applied to any plating operation. Many references are available, including Ref 11, that cover waste treatment technologies.

The use of counterflow rinses has reduced water consumption and wastewaters while maintaining adequate rinsing between plating operations. Reduced dragout of plating electrolytes can be accomplished by allowing processed parts leaving the plating solution to drain into the plating solution. Drip pans also reduce the amount of electrolyte dragout.

Closed-loop systems have dramatically reduced wastewater, lowered water consumption, and diminished chemical usage. Closed-loop systems allow recovery of rinse waters and chemicals by evaporative, reverse osmosis, or ion exchange recovery methods. Care must be exercised when using closed-loop systems, especially with copper plating, to keep impurities and contaminants from preplate operations out of the copper plating bath where they will be trapped by the closed-loop operation.

In any plating operation, wastewaters must be treated to reduce the hazardous materials to meet regulations. The general procedures for treating copper plating electrolytes and rinse waters resulting from copper plating systems are:

- Cyanide-bearing solutions require oxidation of the cyanide with an oxidizing agent such as chlorine or hypochlorite, followed by precipitation of the heavy metals.
- Noncyanide alkaline solutions are pH-adjusted and have calcium chloride added to precipitate the

copper.

- Pyrophosphate wastes require low pH hydrolysis to orthophosphate, followed by precipitation of the heavy metals.
- Acid sulfate and fluoborate wastes are pH-adjusted to precipitate the copper.

Reference cited in this section

11. J.W. Patterson, *Industrial Waste Water Treatment Technology,* 2nd ed., Butterworth Publishers, 1985

Copper Plating Equipment

Construction materials for equipment are indicated in Table 7. Construction materials for racks and anodes are given in Table 8.

Table 7 Materials of construction for equipment basic to copper plating

Tank linings are of rubber or plastic[a], or Koroseal.

Plating bath	Heating coils	Filters	Filter aids
Dilute cyanide	Low-carbon steel Teflon[b]	Low-carbon or stainless steel; cast iron	Diatomite Cellulose
Rochelle cyanide	Low-carbon steel Teflon[b]	Low-carbon or stainless steel; cast iron	Diatomite Cellulose
High-efficiency cyanide	Low-carbon steel Teflon[b]	Low-carbon or stainless steel; cast iron	Diatomite Cellulose
Pyrophosphate	Stainless steel Teflon[b]	Stainless steel Rubber- or vinyl-lined steel	Diatomite Cellulose
Noncyanide alkaline[c]	Stainless steel Titanium	Stainless steel Rubber- or vinyl-lined steel	Diatomite Cellulose
Acid copper sulfate	Titanium[d] Teflon[b]	Rubber- or vinyl-lined steel	Diatomite Cellulose
Fluoborate	Carbon[d] Teflon[b]	Rubber- or vinyl-lined steel	Diatomite Cellulose

(a) Of approved compositions; in the absence of data on bath contamination and effects on deposits, compatibility tests are required.

(b) Dupont trademark.

(c) Polypropylene filter cartridges may be used.

(d) Also for cooling coils, if bath is used below 32 °C (90 °F)

Table 8 Materials for anodes and racks for use in copper plating

Racks are made of copper[a].

Plating bath	Anodes
Dilute cyanide	Copper; steel
Rochelle cyanide	Copper[b][c][d]
High-efficiency cyanide	Copper[b][c][d]
Noncyanide alkaline	Copper[d]
Pyrophosphate	Copper[b][c][d]
Acid copper sulfate	Copper[e]
Fluoborate	Copper[d]

(a) Racks are generally coated with an inert plastic coating to prevent plating.

(b) Cast copper, high purity.

(c) Rolled copper, high purity.

(d) Oxygen-free high-purity copper.

(e) Phosphorized copper

Tanks. For cyanide copper solutions, low-carbon steel tanks are suitable. Polypropylene tanks with adequate reinforcing may also be used, provided that the operating temperature is not excessive. Low-carbon steel tanks should be lined with rubber, polyvinylchloride, or another synthetic material that is not susceptible to attack by the cyanide plating solution. This will prevent bipolar effects, which may rob current from significant areas of the work. Tanks for alkaline noncyanide copper, copper pyrophosphate, acid copper sulfate, and copper fluoborate solutions should be of similar construction. Low-carbon steel tanks used for these solutions must be lined with the above materials to prevent the solutions from attacking the low-carbon steel, resulting in short tank life and immersion deposits. New tanks, as well as all other equipment coming in contact with the plating solution, should be leached before use to remove any materials that may leach into the plating solution and cause poor quality deposits. Leaching solutions should be similar to the plating solution to be used, such as a 15 to 30 g/L (2 to 4 oz/gal) caustic solution for copper cyanide or noncyanide copper equipment, or a 5 to 10% sulfuric acid solution for acid copper sulfate. When converting a tank or line that contained cyanide to a noncyanide electrolyte, it is essential to leach out all residual cyanide from the tank lining and any associated equipment.

Barrels. High-speed copper plating solutions for barrel plating are being used in product operations. Polypropylene barrels have been used successfully for prolonged periods.

Anodes. The types of copper anodes used in each of the copper plating solutions are indicated in Table 8. High-purity copper anodes are recommended. Anodes with a lesser purity may form heavy sludges during electrolysis and contribute appreciably to roughness of the deposit. Anodes used for acid copper plating solutions should be phosphorized. These contain a small percentage of phosphorus, which helps to control chemical dissolution and limits the buildup rate of copper in the acid solution. These types should not be used in alkaline cyanide or noncyanide electrolytes, because anode polarization will develop and cause deposit roughness and more difficult copper metal control.

Copper anodes are available in many forms, such as bars, balls, or chips. Bars are suspended from the anode bar. Balls or chips are placed in titanium baskets.

The anode area in a copper plating solution should be controlled and maintained. If the anode area is not maintained, it decreases as the copper is dissolved and the anode current density rises, resulting in increased polarization and formation of undesirable films. These films can restrict current flow or sluff from the anode and cause roughness in the plating solution.

Anode Bags. Bags made of cotton, Dynel, or polypropylene are used in copper plating solutions. Cotton bags are preferred for cyanide copper solutions, and Dynel or polypropylene are used in the acid copper solutions. Bags are used to keep the fine particles formed at the anode from migrating to the cathode, resulting in roughness. The weave and weight of the anode bag are most important. The bag material must be capable of retaining the particles formed at the anode and at the same time allow the plating solution to flow freely around the anode. Anode bags are not generally used in pyrophosphate baths, because they interfere with dissolution of the anode by decreasing the circulation of the solution around the anode.

Characteristics of Copper Plate

Variations in processing during surface preparation or during plating have significant effects on the quality of the copper electrodeposit. Certain variations can adversely affect the adhesion of copper to the substrate metal. Variations also can affect brightness, porosity, blistering, roughness, hardness, solderability, and leveling.

Brightness. Bright copper coatings are generally obtained by the addition of brighteners to the electrolyte, although buffing of the electrodeposited coating provides a high luster. Plating from high-concentration cyanide baths with current interruption or periodic reversal of current also improves the luster of the copper coating.

Buffing or electropolishing the work before plating it in an electrolyte not containing a brightener results in the deposition of a smooth and sometimes semibright coating. If an electrolyte containing a brightener is used, the luster of the coating is enhanced. The high cost of labor is a primary concern when buffing is considered as the method of brightening the coatings. Plating from high-efficiency cyanide baths with current interruption or periodic reversal of current also improves the luster of the deposits. Improved casting techniques and mechanical finishing before plating can improve the quality of the copper deposit.

Adhesion. Careful selection of substrate surface and proper preparation of the surface before plating are important for good adhesion. In general, cast and other porous surfaces are less receptive to good-quality electrodeposited coatings than wrought surfaces.

The kind of material to be electroplated with copper is another important consideration. For magnesium-base or aluminum-base die castings, the zincate layer between the substrate and the copper deposit is a critical control factor. For a properly activated stainless steel surface, a controlling factor for ensured adhesion of copper is the speed with which the workpiece is immersed in the bath. Some brighteners, especially organic brighteners, may adversely affect adhesion of subsequent electrodeposited coatings. Adhesion of copper electrodeposits from acid baths can be ensured only if a strike from a cyanide copper bath precedes copper plating.

Porosity. The degree of porosity in a copper coating can be controlled by the kind of copper plating bath selected, the composition and control of the electrolyte, the basis material to be plated, and the condition of the surface to be plated. The degree of porosity on the surface of the metal to be plated also dictates the techniques needed to minimize porosity in the coating. A porous surface has high surface area and requires high current density for efficient plating.

Blistering of copper plate, particularly when the plated work is subjected to heat, occurs mostly on zinc-base die castings. Blistering can also occur on parts made of magnesium or aluminum in any form, as a result of poor quality of castings, poor surface preparation, or both. Blistering of copper plate on zinc-base die castings plated in a cyanide strike electrolyte and then subjected to heat can be reduced by lowering the pH of the cyanide strike bath from the range of 12.0 to 12.6 to about 10. Caution must be used because operation at a pH value this low may result in the release of poisonous hydrogen cyanide gas. It is imperative that the plating bath be thoroughly vented.

Blistering of copper-plated magnesium and aluminum, especially during subsequent soldering or heating in service, is caused by poor adhesion at the zincate-copper interface. Unfortunately, blistering often does not become evident until subsequent electrodeposits have been applied and the coating has been subjected to heat. Exposing all copper-plated magnesium and aluminum parts to controlled heat representative of that to be subsequently encountered is good practice. This causes blistering before deposition of subsequent metal coatings if there is poor adhesion at the interface.

Roughness in copper deposits is often caused by foreign particles present in the bath as the result of faulty cleaning, or by the migration to the cathode of metallic copper or cuprous oxide particles that form at the anode. Such roughness is especially likely to occur with the sodium cyanide high-concentration electrolytes and can be prevented by using anode bags.

Solderability of the coating is good when the copper surface is free of oxide, the coating is thick enough, and the adhesion of the copper plate is superior. Direct soldering of electrodeposited copper is not unusual for parts that are subsequently contained in hermetically sealed units.

Soldering is a routine operation for aluminum and magnesium electronic parts used in aerospace applications. A copper strike and copper plate frequently comprise the initial metal coating over the zincated surfaces of these parts, after which electrodeposits of other metals are applied before soldering. A top coat of tin, or of cadmium plate that has been chromate conversion coated, is a particularly effective means of producing a good combination of solderability and corrosion resistance for parts exposed to the atmosphere.

Hardness. Without the use of addition agents, cyanide electrolytes produce harder coatings than acid baths. With the use of addition agents, the hardness of copper deposits from any electrolyte can be increased. Hardness of the electrodeposit is generally associated with fine grain, but hardness can be increased by introducing preferred crystal orientation in the absence of grain refinement. Changes in the copper sulfate or sulfuric acid concentration of acid baths have little effect on the hardness of copper plate.

Leveling has a significant effect on the appearance of the copper coating, as well as on the appearance of the final product when other metals are subsequently plated over the copper. Often, the substrate metal does not have the degree of smoothness that is desired of the plated surface. Metal substrate surfaces can be mechanically or chemically worked to reduce surface roughness before electroplating; however, some copper electrolytes can produce substantial leveling in the deposited coating, thus reducing cost related to elaborate prepolishing or other means of smoothing the surface. The high-concentration potassium cyanide electrolytes produce excellent leveling when certain addition agents are added and interrupted current or periodic reversal is used during plating. Although somewhat less effective, high-concentration sodium cyanide baths, mixed sodium and potassium electrolytes, and Rochelle cyanide electrolytes also have good leveling characteristics with interrupted or periodically reversed current. Acid copper sulfate electrolytes also provide very good leveling characteristics.

Copper in Multiplate Systems

Electrodeposited copper is widely used as a basis for subsequent plated coatings in multiplate systems. The use of copper plate in copper-nickel-chromium systems is discussed in the article "Decorative Chromium Plating" in this Volume.

Cost

The cost of copper plating is influenced largely by the type of installation. In a modern, automated, multiple-phase shop, brighteners and wetting agents probably are the greatest cost factor. In a still-tank operation, the cost of labor is of major importance. An increase in current density reduces cost because of the reduction in time required to deposit a given thickness of coating.

For a routine plating operation, the cost of the copper deposited can be estimated with the aid of Fig. 5. For example, Fig. 5 shows that 120 g (4 oz) of copper is required for plating an area of 0.7 m^2 (7 ft^2) with a coating 20 μm (0.8 mil) thick. The cost of the copper coating is obtained by multiplying the weight of copper required by the cost of copper anodes. For areas larger than 2.4 m^2 (10 ft^2), multiply by the proper factor.

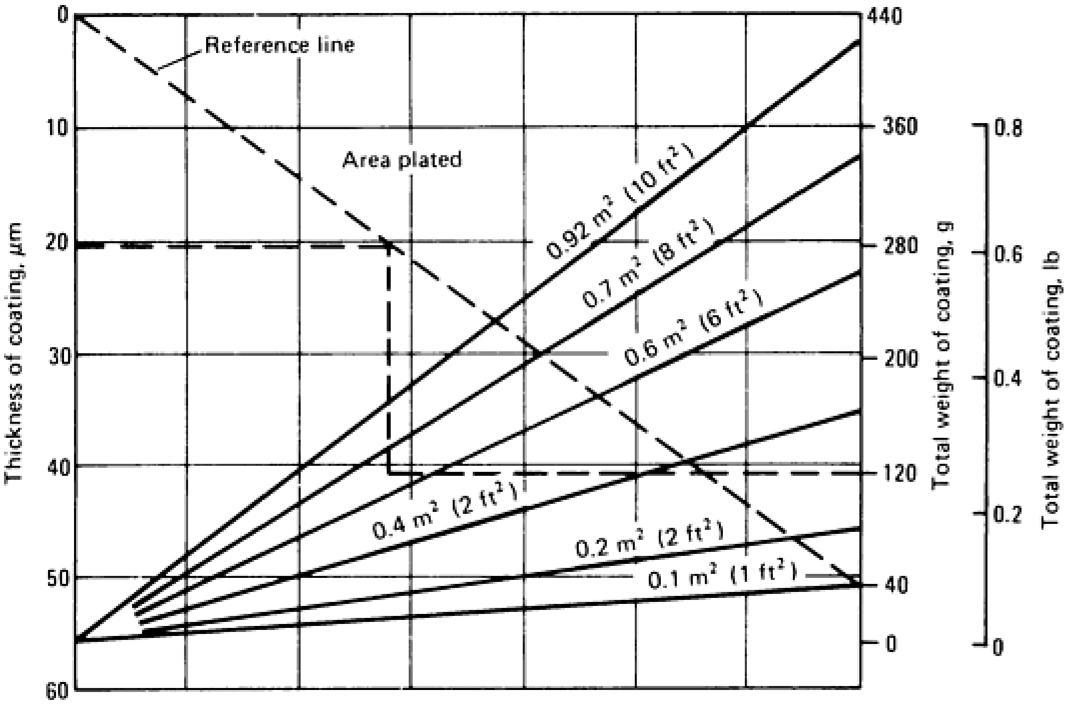


Fig. 5 Copper required for covering an area with a specific thickness

Industrial (Hard) Chromium Plating

Revised by Kenneth R. Newby, Atotech USA

Introduction

HARD CHROMIUM PLATING is produced by electrodeposition from a solution containing chromic acid (CrO_3) and a catalytic anion in proper proportion. The metal so produced is extremely hard and corrosion resistant. The process is used for applications where excellent wear and/or corrosion resistance is required. This includes products such as piston rings, shock absorbers, struts, brake pistons, engine valve stems, cylinder liners, and hydraulic rods. Other applications are for aircraft landing gears, textile and gravure rolls, plastic rolls, and dies and molds. The rebuilding of mismachined or worn parts comprises large segments of the industry. One specialized application is a thin chromium layer used as a lacquer adhesive layer in the manufacture of "tin" cans.

Hard chromium plating is also known as industrial, functional, or engineering chromium plating. It differs from decorative chromium plating in the following ways:

- Hard chromium deposits are intended primarily to increase the service life of functional parts by providing a surface with a low coefficient of friction that resists galling, abrasive and lubricated wear, and corrosion. Another major purpose is to restore dimensions of undersized parts.
- Hard chromium normally is deposited to thicknesses ranging from 2.5 to 500 μm (0.1 to 20 mils) and for certain applications to considerably greater thicknesses, whereas decorative coatings seldom exceed 1.3 μm (0.05 mil).
- With certain exceptions, hard chromium is applied directly to the base metal; decorative chromium is

applied over undercoats of nickel or of copper and nickel.

Principal Uses

The major uses of hard chromium plating are for wear-resistance applications, improvement of tool performance and tool life, and part salvage. Table 1 lists parts to which hard chromium plate is applied and representative data regarding plate thickness and plating times. Plating times can be reduced by using high-efficiency or mixed-catalyst solutions.

Table 1 Typical thicknesses and plating times for selected applications of hard chromium plating

Part	Base metal	Thickness of plate		Plating time[a]
		µm	mils	
Computer printer type	Carbon steel	25	1	60 min
Face seals	Steel or copper	75-180	3-7	10 h
Aircraft engine parts	Nickel-based alloys, high strength steel	75-180	3-7	10 h
Plastic molds	Tool steel	5-13	0.2-0.5	30 min
Textile guides	Steel	5-100	0.2-4	20-240 min
Piston rings	Steel or cast iron	150-255	6-10	8 h
Balls for ball valves	Brass or steel	7.5-13	0.3-0.5	20 min
Micrometers	Steel	7.5-13	0.3-0.5	20 min
Golf ball molds	Brass or steel	7.5-25	0.3-1	20-60 min
Lock cases	Brass	5-7.5	0.2-0.3	20 min
Cylinder	Cast iron	255	10	300 min
Bushing	1018 carburized, 56 HRC	25	1	45 min
Crankshafts	Steel	255-3800	10-150	. . .
Cutting tools	Tool steel	1.3	0.05	5 min
Forming and drawing dies	Steel	25	1	60 min

Part	Base metal	Thickness of plate		Plating time[(a)]
		µm	mils	
Gage	Steel	125	5	150 min
Gun barrels, 30 caliber[(b)]	Steel	25	1	40 min
Hydraulic cylinder	1045 steel	13	0.5	40 min
Pin	Steel	13	0.5	30 min
Pin	1045 steel, 60 HRC	125	5	40 min
Plug gage	1040 steel, 55 HRC	125	5	150 min
Relief-valve plunger	1113 steel, soft	100	4	60 min
Ring gage	Steel	205	8	240 min
Rolls	Steel	13-255	0.5-10	20-300 min

(a) Times shown are for conventional plating solutions; plating times for the proprietary fluoride-free solution are half of those shown.

(b) M-16 rifle, barrel and chamber

Wear Resistance. Extensive performance data indicate the effectiveness of chromium plate in reducing the wear of piston rings caused by scuffing and abrasion. The average life of a chromium-plated ring is approximately five times that of an unplated ring made of the same base metal. Piston rings for most engines have a chromium plate thickness of 100 to 200 µm (4 to 8 mils) on the bearing face, although thicknesses up to 250 µm (10 mils) are specified for some heavy-duty engines.

In the automotive industry, hard chromium is also applied to shock absorber rods and struts to increase their resistance to wear and corrosion. Valve stems are plated with a flash coating (about 2.5 µm, or 0.1 mil) to reduce wear. Hydraulic shafts for all kinds of equipment are plated with 20 to 30 µm (0.8 to 1.2 mil) of hard chromium to increase service life.

Tooling Applications. Various types of tools are plated with chromium to minimize wear, prevent seizing and galling, reduce friction, and/or prevent or minimize corrosion. Steel or beryllium copper dies for molding of plastics are usually plated with chromium, especially when vinyl or other corrosive plastic materials are to be molded. Plating thicknesses of 2.5 to 125 µm (0.1 to 5 mils) usually are recommended for preventing wear in parts sticking in molds and for reducing frequency of polishing when plastics that attack steel or beryllium copper are being molded. Chromium-plated dies should not be used when plastics containing fire-retardant chlorides are molded.

The service life of plug gages and other types of gages may be prolonged by hard chromium plating. Most gage manufacturers provide chromium-plated gages. Records in one plant indicate that plug gages made from hardened O1 tool

steel wore 0.0025 mm (0.0001 in.) after gaging 5000 cast iron parts. Hard chromium plating of these gages allowed the gaging of 40,000 parts per 0.0025 mm (0.0001 in.) of wear.

Worn gages can be salvaged by being built up with hard chromium plate. Also, chromium plate provides steel gages with good protection against rusting in normal exposure and handling. Chromium plating is not recommended, however, for gages that are subjected to impact at exposed edges during operation.

Deep drawing tools often are plated with chromium, in thicknesses up to 100 μm (4 mils), for improvement of tool performance and/or building up of worn areas. The life of draw rings and punches may be prolonged by plating. In addition, plating reduces frictional force on punches and facilitates removal of workpieces from punches in instances where sticking is encountered with plain steel surfaces. If deep drawing tools are chromium plated, the base metal should be harder than 50 HRC. Steel dies used for drawing bars and tubes are often plated with relatively heavy thicknesses (up to 250 μm, or 10 mils) of chromium to minimize die wear, reduce friction, and prevent seizing and galling.

The service life of cutting tools is often extended by chromium plate, in thicknesses ranging from less than 2.5 to 13 μm (0.1 to 0.5 mil). Taps and reamers are examples of tools on which chromium plate has proved advantageous. In one case, a flash plate on taps used to thread cold-worked 1010 steel improved tap life from 250 (for unplated taps) to 6000 parts per tap. The poor tool life of the unplated taps was caused by buildup of metal on the cutting edges. Hard chromium plating is not recommended for cold extrusion tools for severe applications where extreme heat and pressure are generated, because the plate is likely to crack and spall and may be incompatible with phosphate-soap lubricants.

Part Salvage. Hard chromium plating is sometimes used for restoring mismachined or worn surfaces. Since 1970, the use of this process for part salvage has been frequently replaced by thermal spraying and plasma coatings, which can be applied more quickly. The fact that a chromium deposit can significantly reduce fatigue strength must be considered in determining whether chromium plating can be safely used.

Hard chromium plating is used to restore to original dimensions the worn surfaces of large crankshafts for diesel and gas engines and for compressors. In these applications, in which coating thicknesses usually range from 125 to 1250 μm (5 to 50 mils), the excellent wearing qualities and low coefficient of friction of chromium are highly advantageous. The plate is prevented from depositing in fillet areas as a precaution against fatigue failure.

The extremely close dimensional tolerances specified for components of compressors for jet aircraft engines are not always correctly met in machining. Hard chromium plating is sometimes used to salvage mismachined parts. Most frequently mismachined are the diameters of rotor disks and spacers. The maximum thickness of plate on these components, which are made of 4130 and 4340 steels, generally does not exceed 380 μm (15 mils).

Other Applications. Hard chromium plate is applied to printing plates and stereotypes, especially to those intended for long runs, because compared to other materials or coatings used for this application, it wipes cleaner, provides sharper reproduction, and increases the length of press runs. It is used on press rams because of its excellent resistance to corrosion, seizing, galling, and other forms of wear.

Selection Factors

The decision to use hard chromium plating on a specific part should take into account the following characteristics:

- The inherent hardness and wear resistance of electrodeposited chromium
- The thickness of chromium required
- The shape, size, and construction of the part to be plated
- The type of metal from which the part is made
- Masking requirements (for parts that are to be selectively plated)
- Dimensional requirements (that is, whether or not mechanical finishing is required and can be accomplished in accordance with desired tolerances)

The hardness of chromium electrodeposits is a function of the type of chemistry selected and the plating conditions. In general, chromium plated in the bright range is optimally hard. Typically bright chromium deposits from conventional

plating solutions have hardness values of 850 to 950 HV; those from mixed-catalyst solutions have values of 900 to 1000 hV; and those from fluoride-free chemistries have values of 950 to 1100 HV or higher.

Size. Frequently, a very large part can be plated in sections or can be rotated so that only a portion of the part is immersed in the plating solution at any given time. The latter method has been used to plate large cylinders up to 4 m (12 ft) in diameter and up to 18 m (60 ft) long. When this technique is used, all of the surface to be plated that is exposed to the atmosphere must remain wet with plating solution.

Journal surfaces of the largest diesel crankshafts and bores of large naval guns and M-16 rifles are hard chromium plated on a production basis. Internal surfaces of very large cylinders have been plated by closing off the ends of each cylinder and retaining the plating solution with it.

Base Metal. Most hard chromium deposits are applied to parts made of ferrous alloys; however, numerous aerospace applications require the chromium plating of aluminum and nickel-base alloys. From the standpoint of processing, hard chromium plate may be applied to steels, regardless of their surface hardness or chemical composition, provided that the base metal is hard enough to support the chromium layer in service. Similarly, cast irons can be plated provided that the surface is capable of conducting the required current and is reasonably free of voids, pits, gross silicate inclusions, massive segregation, slivers, and feather edges.

Plating Solutions

Chromic acid is the source of metal in hard chromium plating solutions. However, a chromic acid solution does not deposit chromium unless a definite amount of catalyst is present. If there is either too much or too little catalyst, no chromium metal is deposited. Catalysts that have proved successful are acid anions, the first of which to be used was sulfate. Substitution of fluoride ions present in complex acid radicals for a portion of the sulfate improves the chromium-plating operation. In the late 1980s, a fluoride-free proprietary solution was developed. The secondary catalyst in this chemistry is a stable organic species. Reflecting this difference in catalyst, the principal types of solutions are designated as conventional sulfate (also called Sargent or Fink); mixed-catalyst, which refers to the sulfate and fluoride chemistry; and fluoride-free (proprietary) catalyst.

The fatigue limit of high-strength steel (steels with ultimate tensile strengths of 1240 MPa, or 180 ksi, and above) may be reduced by about 50% when chromium plated because of the inherent crack structure of hard chromium. However, special techniques using shot peening and postplate heat treatments may be used to retain most of the original fatigue strength.

Conventional Sulfate Solutions. Composition of conventional chromic acid solutions catalyzed by sulfate can vary widely, provided the ratio by weight of chromic acid to sulfate radical is within the range between 75 and 120 to 1. Throwing power, or distribution of plate, is optimum at ratios between 90 and 110 to 1; however, in the range between 75 and 90 to 1, brighter deposits are obtained, less burning occurs, and a higher current density can be used.

Solutions containing chromic acid in a concentration as low as 50 g/L (7 oz/gal) have been reported but are not practical for production because:

- Their plating range is too limited
- The solutions are more sensitive to contamination
- They have a higher electrical resistance
- They require a higher voltage for operation

Compositions and operating conditions for two chromic acid/sulfate solutions (low and high concentrations) for hard chromium plating are given in Table 2. The low-concentration solution is widely used for hard chromium plating because it minimizes dragout losses and associated environmental problems. The high-concentration solution has the advantage of being less sensitive to concentration changes; it is also easier to control and has better throwing power. Because the high-concentration solution is more conductive, it can be operated at lower voltages and heats up less in operation.

Table 2 Sulfate baths for hard chromium plating

Type of oath	Chromic acid[a]		Sulfate[a]		Current density		Bath temperature	
	g/L	oz/gal	g/L	oz/gal	A/dm^2	A/in.^{2}	°C	°F
Low concentration	250	33	2.5	0.33	31-62	2-4	52-63	125-145
High concentration	400	53	4.0	0.53	16-54	1-3.5	43-63	110-145

(a) Concentration usually can deviate ±10% without creating problems. It is recommended that adjustments be such that the concentrations listed above lie in the middle of the range permitted. For example, chromic acid can fluctuate by ±23 g/L (±3 oz/gal); therefore, the concentration range should be 225-270 g/L (30 to 36 oz/gal), rather than 205-250 g/L (27 to 33 oz/gal).

If available voltage is limited, it may be preferable to operate a solution with higher conductivity in the range of 300 to 405 g/L (40 to 54 oz/gal) of chromic acid, even though current efficiency is lower than with the less concentrated solutions. The lower current efficiency is offset by increased current density obtainable because of better solution conductivity. Usually, the best range of operation is from 195 to 300 g/L (26 to 40 oz/gal) of chromic acid. Even within this range, the solution containing 195 g/L (26 oz/gal) has the highest current efficiency, while the solution containing 300 g/L (40 oz/gal) has the best conductivity.

The mixed-catalyst solutions are similar to conventional sulfate solutions in conductivity, but they produce harder deposits and have higher intrinsic current efficiency than conventional solutions under identical conditions. They also have a higher current efficiency at higher concentration. Mixed-catalyst solutions can increase production rates 40 to 60% and more over those obtainable with conventional solutions, due to the greater current efficiencies of the mixed-catalyst solutions and their ability to operate at higher current densities without creating harmful effects on the deposit. One limitation of mixed-catalyst solutions is that they cause etching of unplated iron surfaces at areas of low current density, with a resulting increase in contamination that reduces the life of the solution. This etching can be prevented on significant surfaces by masking areas not to be plated. Mixed-catalyst solutions are seldom used on aluminum or copper substrates because of the attack by the fluoride chemicals.

Fluoride-free solution, a proprietary chemistry, is based on chromic acid, sulfate, and a stable organic catalyst. It provides deposit speeds and current density ranges slightly in excess of those obtained with mixed-catalyst solutions. Because the solution contains no fluorides or other halogens, it does not cause etching on exposed unplated surfaces or attack aluminum or copper substrates. These features alleviate the need for excessive protective masking operations. As with the mixed-catalyst chemistry, the fluoride-free solution provides much greater plating throughput while consuming about one-third less electricity than the conventional solution.

Deposit hardness and corrosion resistance improve as one moves from the conventional sulfate solution to the mixed-catalyst solution and on to the fluoride-free solution.

Solution Control

Chromium-plating solutions of all three types must be subjected to periodic chemical analyses for control of solution composition. With the exception of catalyst analysis, the species and methods are identical for all chemistries. Solution control can be simplified if a record is kept of the way a particular chromium solution changes in composition during its use. Change in chemical composition depends on the number of ampere-hours of current passed through the solution, the dragout of solution, and spray losses. Also, evaporation losses, if not compensated for, usually cause the concentration to change by about 2 to 5% during a day's operation. A complete solution analysis should be made at periodic intervals (weekly or monthly, depending on production rate) and the solution should be brought into proper balance.

Chromic acid content can be semi-quantitatively determined simply by placing a hydrometer in the plating solution, provided that other contaminants, such as iron or copper, are not present in significant quantities. Hydrometers calibrated in ounces of chromic acid per gallon at the operating temperature of the solution are available. Baumé hydrometers can be used in samples cooled to the calibration temperature marked on the hydrometer; the reading can be converted to

concentration by using Table 3. Impurities cause the Baumé reading to be higher than is warranted by the actual chromic acid content. Periodically, the chromic acid content should be quantitatively determined by chemical titration and a notation made of the differences between the contents as shown by chemical analysis and by hydrometer readings. Hydrometer readings should then be corrected by that amount. When a hydrometer reading shows 30 to 38 g/L (4 to 5 oz/gal) more chromic acid than is actually present, the solution should be discarded, because this is caused by a high metallic impurity level. Adjustments in chromic acid concentration are simplified by the use of Table 4.

Table 3 Determination of chromic acid in chromium baths with a Baumé hydrometer

Direct conversion of degrees Baumé to ounces of chromic acid per gallon, at 25 °C (77 °F)

°Bé	Chromic acid	
	g/L	oz/gal
10.5	113	15.0
11.0	119	15.8
11.5	124	16.5
12.0	130	17.3
12.5	137	18.2
13.0	144	19.1
13.5	149	19.8
14.0	153	20.4
14.5	159	21.2
15.0	165	22.0
15.5	172	22.9
16.0	178	23.7
16.5	184	24.5
17.0	191	25.4
17.5	198	26.3

18.0	204	27.2
18.5	211	28.1
19.0	218	29.0
19.5	224	29.8
20.0	230	30.9
20.5	237	31.5
21.0	244	32.4
21.5	250	33.3
22.0	257	34.2
22.5	264	35.1
23.0	271	36.0
23.5	279	37.1
24.0	287	38.2
24.5	294	39.1
25.0	301	40.0
25.5	308	4.09
26.0	315	41.9
26.5	323	42.9
27.0	331	44.0
27.5	338	45.0
28.0	346	46.0

28.5	354	47.1
29.0	362	48.2
29.5	370	49.2
30.0	378	50.2
30.5	387	51.5
31.0	399	53.0
31.5	406	54.0
32.0	415	55.2

Note: Impurities will cause the Baumé hydrometer reading to be higher than is warranted by the actual content of chromic acid.

Table 4 Conversion equivalents for chromic acid concentration in chromium baths

Values in table are based on the following formula, which may be used to compute values for which conditions are not given: Chromic acid required, kg(lb) = g/L(oz/gal) CrO_3 to be added × bath volume, in liters (gallons)/16

Chromic acid to be added		**Chromic acid required, kg (lb), at volume of bath, L (gal), of:**									
g/L	**oz/gal**	**380 (100)**	**760 (200)**	**1140 (300)**	**1510 (400)**	**1890 (500)**	**2270 (600)**	**2650 (700)**	**3030 (800)**	**3410 (900)**	**3790 (1000)**
4.0	0.5	1.4 (3.1)	2.9 (6.3)	4.3 (9.4)	5.7 (12.5)	7.1 (15.6)	8.5 (18.8)	9.9 (21.9)	11.3 (25.0)	12.7 (28.1)	14.2 (31.2)
7.5	1.0	2.8 (6.2)	5.7 (12.5)	8.5 (18.8)	11.3 (25.0)	14.2 (31.2)	17.0 (37.5)	19.9 (43.8)	22.7 (50.0)	25.5 (56.3)	28.3 (62.5)
11.0	1.5	4.3 (9.4)	8.5 (18.8)	12.8 (28.2)	17.0 (37.5)	21.3 (46.9)	25.5 (56.3)	29.8 (65.6)	34.0 (75.0)	38.3 (84.4)	42.5 (93.8)
15.0	2.0	5.7 (12.5)	11.3 (25.0)	17.0 (37.5)	22.7 (50.0)	28.3 (62.5)	34.0 (75.0)	39.7 (87.5)	45.3 (100.0)	51.3 (113.0)	56.7 (125.0)
19.0	2.5	7.1 (15.6)	14.2 (31.2)	21.3 (46.9)	28.3 (62.5)	35.4 (78.1)	42.5 (93.8)	49.4 (109.0)	56.7 (125.0)	61.0 (141.0)	70.8 (156.0)
22.0	3.0	8.5 (18.8)	17.0 (37.5)	25.5 (56.3)	34.0 (75.0)	42.6 (93.8)	51.3 (113.0)	59.4 (131.0)	68.0 (150.0)	76.7 (169.0)	85.3 (188.0)

26.0	3.5	9.9 (21.9)	19.8 (43.7)	29.8 (65.6)	39.7 (87.5)	49.4 (109.0)	59.4 (131.0)	69.4 (153.0)	79.4 (175.0)	89.4 (197.0)	99.3 (219.0)
30.0	4.0	11.3 (25.0)	22.7 (50.0)	34.0 (75.0)	45.3 (100.0)	56.7 (125.0)	68.0 (150.0)	79.4 (175.0)	90.7 (200.0)	102.0 (225.0)	113.0 (250.0)
34.0	4.5	12.7 (28.1)	25.5 (56.2)	38.3 (84.4)	51.3 (113.0)	64.0 (141.0)	76.7 (169.0)	89.4 (197.0)	102.0 (225.0)	115.0 (253.0)	127.0 (281.0)
37.0	5.0	14.2 (31.2)	28.3 (62.5)	42.5 (93.8)	56.7 (125.0)	70.8 (156.0)	85.3 (188.0)	99.3 (219.0)	113.0 (250.0)	128.0 (281.0)	142.0 (312.0)
41.0	5.5	15.6 (34.4)	31.2 (68.7)	46.7 (103.0)	62.6 (138.0)	78.0 (172.0)	93.4 (206.0)	109.0 (241.0)	125.0 (275.0)	140.0 (309.0)	156.0 (344.0)
45.0	6.0	17.0 (37.5)	34.0 (75.0)	51.3 (113.0)	68.0 (150.0)	85.3 (188.0)	102.0 (225.0)	119.0 (262.0)	136.0 (300.0)	153.0 (338.0)	170.0 (375.0)
49.0	6.5	18.4 (40.6)	36.8 (81.2)	55.3 (122.0)	73.9 (163.0)	92.1 (203.0)	111.0 (244.0)	129.0 (284.0)	147.0 (325.0)	162.0 (365.0)	184.0 (406.0)
52.0	7.0	19.8 (43.7)	39.7 (87.5)	59.4 (131.0)	79.4 (175.0)	99.3 (219.0)	119.0 (262.0)	139.0 (306.0)	159.0 (350.0)	179.0 (394.0)	198.0 (437.0)
56.0	7.5	21.3 (46.9)	42.5 (93.8)	64.0 (141.0)	85.3 (188.0)	106.0 (234.0)	128.0 (281.0)	149.0 (328.0)	170.0 (375.0)	191.0 (422.0)	213.0 (469.0)
60.0	8.0	22.7 (50.0)	45.4 (100.0)	68.0 (150.0)	90.7 (200.0)	113.0 (250.0)	136.0 (300.0)	159.0 (350.0)	181.0 (400.0)	204.0 (450.0)	227.0 (500.0)
64.0	8.5	24.1 (53.1)	48.1 (106.0)	72.1 (159.0)	96.6 (213.0)	121.0 (266.0)	145.0 (319.0)	169.0 (372.0)	193.0 (425.0)	216.0 (477.0)	241.0 (531.0)
67.0	9.0	25.5 (56.2)	51.3 (113.0)	76.7 (169.0)	102.0 (225.0)	127.0 (281.0)	153.0 (338.0)	179.0 (394.0)	204.0 (450.0)	230.0 (506.0)	255.0 (562.0)
71.0	9.5	26.9 (59.4)	54.0 (119.0)	80.7 (178.0)	108.0 (238.0)	135.0 (297.0)	161.0 (356.0)	189.0 (416.0)	215.0 (475.0)	243.0 (535.0)	269.0 (594.0)
75.0	10.0	28.3 (62.5)	56.7 (125.0)	85.3 (188.0)	113.0 (250.0)	142.0 (312.0)	170.0 (375.0)	199.0 (438.0)	227.0 (500.0)	255.0 (563.0)	284.0 (625.0)

Chromic acid content can also be determined by various analytical procedures. Some of these procedures use standard solutions that can be used for other determinations; this may be the deciding factor as to which procedure to use. The following procedure is simple and quite rapid:

Reagents

- *Acid mixture:* Mix 1 part sulfuric acid, 1 part phosphoric acid, and 1 part water.
- *Ferrous ammonium sulfate (FAS) 0.1 N:* Dissolve 40 g/L (5.3 oz/gal) FAS · $6H_2O$ and add 25 mL/L concentrated sulfuric acid. When in use, keep about 6500 mm^2 (10 $in.^2$) of aluminum metal in the container to maintain constant normality.
- Orthophenanthroline ferrous sulfate complex indicator
- *Potassium dichromate, 0.1000 N:* dissolve 4.900 g (0.173 oz) of $K_2Cr_2O_7$ (CP grade) and dilute to a liter.

Standardization of FAS

- 1. Pipette 25 mL of potassium dichromate standard into a 250 mL Erlenmeyer flask and dilute to 85 mL.
- 2. Add 15 mL of acid mixture and 3 drops of indicator.
- 3. Titrate with FAS to clear orange endpoint. Normality of FAS = 2.5 / (mL of FAS).

Procedure

- 1(a). Pipette 10 mL of chromium solution into a 250 mL volumetric flask and dilute to volume. Pipette a 10 mL aliquot into a 250 mL Erlenmeyer flask.
- 1(b). Pipette 0.4 mL of chromium solution sample into a 250 mL Erlenmeyer flask, using a 1 mL pipette graduated in hundredths of a milliliter.
- 2. Add 50 mL of water, 15 mL of acid mixture, and 3 drops of indicator.
- 3. Titrate with FAS to clear orange end point. Chromic acid in g/L = (mL of FAS) × (N of FAS) × (83.3). Chromic acid in oz/gal = (mL of FAS) × (N of FAS) (11.12).

Use either step 1(a) or 1(b), followed by steps 2 and 3. Step 1(b) is slightly less accurate than 1(a) but is much faster.

Sulfate in a chromium solution can be determined to a high degree of accuracy by a gravimetric method, or with reasonable accuracy using the much faster centrifuge method. Unless there is some reason for great precision, the centrifuge method is entirely satisfactory. Most graduated centrifuge tubes can be calibrated for sulfate; however, the technique should be checked regularly by analysis of a standard solution, or by the gravimetric technique.

With the centrifuge method, the amount of insoluble material in the sample must be determined before sulfate is precipitated. This can be done by running a blank sample or centrifuging the sample before precipitating the sulfate. Because sulfate determinations are made in duplicate, it is advisable to determine how closely the two tubes match in calibration. This can be done by pouring a small amount of mercury into first one tube and then the other. These tubes should be marked to be used together, and a notation should be made, if necessary, as to the amount of correction needed in the reading. Adjustments of sulfate concentration in chromium solutions can be simplified by using Table 5.

Table 5 Conversion equivalents for adjusting sulfate concentration in chromium baths

Values in table are based on the following formula, which may be used to compute values for which conditions are not given: Sulfuric acid (66 °Bé) fluid oz, = 0.522 × oz/gal H_2SO_4 to be added × bath volume, gal

Sulfuric acid to be added		Sulfuric acid (66 °Bé) required, mL (fluid oz), at volume of bath, L (gal), of:									
g/L	oz/gal	380 (100)	760 (200)	1140 (300)	1515 (400)	1890 (500)	2270 (600)	2650 (700)	3030 (800)	3410 (900)	3790 (1000)
0.08	0.01	15 (0.5)	30 (1.0)	47 (1.6)	62 (2.1)	77 (2.6)	92 (3.1)	109 (3.7)	124 (4.2)	139 (4.7)	154 (5.2)

0.15	0.02	30 (1.0)	62 (2.1)	92 (3.1)	124 (4.2)	154 (5.2)	186 (6.3)	216 (7.3)	249 (8.4)	278 (9.4)	308 (10.4)
0.22	0.03	47 (1.6)	92 (3.1)	139 (4.7)	186 (6.3)	231 (7.8)	284 (9.6)	323 (10.9)	370 (12.5)	417 (14.1)	465 (15.7)
0.30	0.04	62 (2.1)	124 (4.2)	186 (6.3)	249 (8.4)	308 (10.4)	370 (12.5)	432 (14.6)	494 (16.7)	556 (18.8)	619 (20.9)
0.37	0.05	77 (2.6)	154 (5.2)	231 (7.8)	308 (10.4)	385 (13.0)	462 (15.6)	539 (18.2)	619 (20.9)	696 (23.5)	773 (26.1)
0.45	0.06	92 (3.1)	186 (6.3)	284 (9.6)	370 (12.5)	462 (15.6)	556 (18.8)	648 (21.9)	740 (25.0)	835 (28.2)	926 (31.3)
0.53	0.07	110 (3.7)	216 (7.3)	323 (10.9)	432 (14.6)	539 (18.2)	648 (21.9)	758 (25.6)	864 (29.2)	974 (32.9)	1080 (36.5)
0.60	0.08	124 (4.2)	249 (8.4)	370 (12.5)	494 (16.7)	619 (20.9)	740 (25.0)	864 (29.2)	989 (33.4)	1113 (37.6)	1237 (41.8)
0.67	0.09	139 (4.7)	278 (9.4)	417 (14.1)	556 (18.8)	696 (23.5)	835 (28.2)	974 (32.9)	1143 (38.6)	1252 (42.3)	1391 (47.0)
0.75	0.10	154 (5.2)	308 (10.4)	465 (15.7)	619 (20.9)	773 (26.1)	926 (31.3)	1080 (36.5)	1237 (41.8)	1391 (47.0)	1545 (52.2)

Note: To neutralize excess sulfuric acid (thereby lowering the sulfate content) in a chromium bath, add approximately 1.5 g/L (0.2 oz/gal) of barium carbonate for each 0.8 g/L (0.1 oz/gal) of excess sulfuric acid. Additions of barium carbonate should be made slowly to the bath.

Contamination. In the operation of any chromium solution, the solution should be kept free of excessive amounts of contamination. Introduction of copper, iron, or trivalent chromium seriously decreases the conductivity of the solution and requires the use of a higher operating voltage to produce a given current density.

Trivalent chromium can be formed by the decomposition of organics, but more often it results from too low a ratio of anode-to-cathode area, a condition always encountered in plating interior surfaces cylinders. Trivalent chromium can be reoxidized to hexavalent chromium by electrolyzing the solution at 60 to 66 °C (140 to 150 °F), with an anode-to-cathode area ratio of about 30 to 1, and using a cathode current density of about 60 A/dm^2 (4 A/in.^{2}). About 50 A · h/L (200 A · h/gal) is required for reoxidizing 15 g/L (2 oz/gal) of trivalent chromium; ordinarily, this operation is performed during the weekend shutdown period.

Removal of copper, iron, and other contaminants is usually accomplished by disposing of part or all of the solution, or where permissible, by ion exchange or electrodialysis techniques. In addition to reducing the conductivity of the solution, impurities, particularly iron and trivalent chromium, also reduce current efficiency. (This is especially true for the mixed-catalyst type of chemistry because these contaminants reduce the activity of the fluoride catalyst.) Normally, the presence of 10 g/L (1.5 oz/gal) of iron in solution reduces cathode current efficiency by about 30%. Iron and trivalent chromium can produce rougher deposits with more treeing. Other contaminants affect the throwing power and coverage.

Mandrel Test. When difficulties are experienced with the hard chromium production solution, it may be useful to use the mandrel test, so named because it is usually performed by plating a low-carbon steel rod or mandrel (9.5 mm diameter

by 75 mm long, or $\frac{3}{8}$ in. diameter by 3 in. long) with a conforming circular anode to give uniform current distribution. A convenient procedure is to use 540 mL of the solution in a 600 mL beaker made of heat-resistant glass. The steel mandrel is buffed to a bright finish, and the top 25 mm (1 in.) that projects out of the solution and into a holder is stopped-off to indicate the exact size of the plating area.

The mandrel is immersed in the test solution, which is heated to 55 °C (130 °F) in a water solution, treated anodically at 15 A/dm^2 (1 $A/in.^2$) for 15 s, and then plated at 30 A/dm^2 (2 $A/in.^2$) for 1 h. The temperature of the water solution should be reduced to about 52 °C (125 °F) during plating to compensate for the heat generated by the current. The mandrel is then removed, rinsed, dried, and inspected.

Better temperature control through the plating process is obtained by using 1 L of solution in a 1.5 L beaker. The solution is heated with a 125 W quartz heater controlled by a thermoregulator and relay. The process operates at 55 °C (130 °F).

A hard chromium solution in proper adjustment gives a bright plate under these conditions. If the deposit is dull, the solution is contaminated or out of balance. Burning on the bottom edge of the mandrel also indicates that the solution is out of adjustment. A high content of trivalent chromium causes dullness and growth of metal whiskers from the bottom edge of the mandrel.

Current efficiency and plating speed can be checked with the same setup, but this is more conveniently done with a flat steel panel and flat anodes. A polished steel panel, 25 by 75 mm (1 by 3 in.), can be used, with the bottom 50 mm (2 in.) marked off as the plating area. Plating conditions would be 30 A/dm^2 (2 $A/in.^2$) for 15 min at 55 °C (130 °F), but other conditions can be tested as desired. The steel panel is accurately weighed before and after plating (without current reversal). Current efficiency, thickness of chromium, and plating speed are calculated as follows:

- Current efficiency, % = (weight, in grams, of chromium × 100) / (ampere-hours × 0.323)
- Thickness of deposit, mils = (weight, in grams, of chromium) / (4 × 0.116)
- Plating speed, mils/h = (thickness of deposit, in mils × 60) / plating time, min

Process Control

In addition to solution composition, the principal variables that must be controlled for satisfactory hard chromium plating are the anodes, the current density, and the solution temperature.

Anodes. In contrast to other plating solutions, which use soluble anodes to supply the solution with a large part of the metal ion being plated, chromium plating solutions are operated with insoluble lead alloy anodes. Usually about 7% Sn or Sb or a combination of the two are used to alloy the lead. As a consequence of using inert anodes, additions of chromic acid must be made to keep the plating solution supplied with chromium metal ions.

A coating of lead peroxide forms on the lead alloy anodes during electrolysis. This coating is usually dark charcoal brown, which indicates that the anodes are functioning correctly. The presence of an orange-to-yellow lead chromate coating indicates that the anodes are not passing current properly. Periodic cleaning of the anodes and their hooks is mandatory for efficient operation.

Insoluble antimonial lead (93Pb, bal Sb + Sn) and lead-tin alloy (93Pb-7Sn) are the most widely used anode materials in chromium plating solutions. These alloys minimize corrosion of the anode; the antimony in the first composition stiffens the anode against shape changes. Each anode must have sufficient cross-sectional area to pass the requisite current without overheating. If high current densities are to be used with mixed-catalyst or fluoride-free solutions, it may be necessary to use larger anode cross sections than would be the case in the low-current-density conventional solutions. In any case the bottom of each anode should be at least 150 mm (6 in.) above the bottom of the plating tank to avoid possible electrical shorts.

Conductivity of the chromium solution is based on chromic acid concentration. Concentrations higher than 250 g/L (33 oz/gal) require lower operating voltage; however, current efficiency decreases with increasing chromic acid concentration. Concentrations below about 180 g/L are usually impractical unless high-voltage rectifiers are available.

Current Density and Efficiency. Cathode current efficiency varies with current density and temperature of the plating solution. Efficiency increases significantly with increasing current density and slightly with decreasing temperature. These two variables have a definite effect on the appearance and hardness of the deposit. A high solution temperature results in a milky, dull, and softer deposit at lower current efficiencies, unless the current density is increased substantially. Raising current density causes the deposit to change successively at specific temperatures (Table 6). Because tank time is an important economic factor, the highest rates of deposition that are produced by the highest available currents may determine which plating solution temperature is most useful.

Table 6 Effect of bath temperature and current density on appearance and hardness of chromium deposits plated from a conventional sulfate solution

Bath contained 406 g/L CrO_3; ratio of CrO_3 to SO_4 ranged from 90-to-1 to 100-to-1

Current density		Appearance of deposit	Hardness[(a)], DPH
A/dm^2	A/in.^{2}		
Plating bath at 43 °C (110 °F)			
Below 8.53	Below 0.55	Dull matte	[(b)]
8.53	0.55	Semibright	695
17.1	1.10	Bright	900
25.6	1.65	Bright, pebbly	Over 940
34.1	2.20	Dull, nodular[(c)]	Over 940
Plating bath at 49 °C (120 °F)			
Below 10.9	Below 0.70	Dull matte	510-595
10.9	0.70	Semibright	695
21.7	1.40[(d)]	Bright	900
32.6	2.10	Bright, pebbly	Over 940
43.4	2.80	Dull, nodular[(c)]	Over 940
Plating bath at 54 °C (130 °F)			
Below 14.0	Below 0.90	Dull matte	510-595
14.0	0.90	Semibright	695

27.9	1.80[d]	Bright	900
41.9	2.70	Bright, pebbly	Over 940
55.8	3.60	Dull, nodular[c]	Over 940

(a) Hardness of mounted and unmounted specimens was determined with a tester employing a Vickers diamond, a load of 200 g, and a magnifaction of 200×. Mounted specimens were mounted flat (not cross section).

(b) Current density too low to plate a sufficient amount of chromium for hardness test.

(c) Specimens polished lightly to smooth out nodules.

(d) Optimum current density

Deposition Rates. Times required to plate hard chromium deposits of various thicknesses are shown as a function of current density in Table 7 (for low-concentration solutions) and Table 8 (for high-concentration solutions).

Table 7 Rates of deposition of hard chromium from low-concentration baths

Thickness of plate		**Plating time, h:min, at current density, A/dm^2 (A/in.^{2}), of:**		
µm	**mils**	**31 (2.0)**	**47 (3.0)**	**62 (4.0)**
Conventional sulfate bath[a]				
25	1	1:05	0:40	0:25
50	2	2:05	1:20	0:55
125	5	5:20	3:20	2:20
Mixed catalyst bath[b]				
25	1	0:50	0:30	0:20
50	2	1:40	1:00	0:40
125	5	4:05	2:25	1:45

Fluoride-free bath[c]				
25	1	0:40	0:27	0:17
50	2	1:25	0:53	0:37
125	5	3:35	2:15	1:30

(a) Bath containing 250 g/L (33 oz/gal) of chromic acid with 100-to-1 ratio of chromic acid to sulfate, operated at 54 °C (130 °F).

(b) Proprietary bath containing 250 g/L (33 oz/gal) of chromic acid, operated at 54 °C (130 °F).

(c) Proprietary bath containing 250 g/L (33 oz/gal) of chromic acid, operated at 54 °C (130 °F)

Table 8 Rates of deposition of hard chromium from high-concentration baths

Thickness of plate		**Plating time, h:min, at current density of:**				
µm	**mils**	**23 A/dm² (1.5 A/in.²)**	**31 A/dm² (2.0 A/in.²)**	**39 A/dm² (2.5 A/in.²)**	**47 A/dm² (3.0 A/in.²)**	**54 A/dm² (3.5 A/in.²)**
Conventional sulfate bath[a]						
25	1	2:20	1:35	1:15	0:55	0:45
50	2	4:35	3:10	2:30	1:55	1:30
125	5	11:30	8:00	6:15	4:40	3:50
255	10	23:00	16:00	12:30	9:25	7:35
380	15	34:30	24:00	18:45	14:05	11:25
510	20	46:00	32:00	25:00	18:50	15:10
Mixed catalyst bath[b]						
25	1	2:00	1:10	0:55	0:40	0:30
50	2	4:00	2:20	1:50	1:20	1:00

125	5	10:00	5:50	4:30	3:20	2:30
255	10	20:00	12:00	9:00	6:40	5:00
380	15	30:00	18:00	13:00	10:00	7:30
510	20	40:00	24:00	18:00	16:40	12:30
Fluoride-free solution[(c)]						
25	1	1:50	1:05	0:50	0:37	0:27
50	2	3:40	2:10	1:40	1:15	0:55
125	5	9:10	5:30	4:10	3:10	2:15
255	10	18:20	11:00	8:20	6:20	4:30
380	15	27:30	16:30	12:30	9:30	6:45
510	20	36:40	22:00	16:40	12:40	9:00

(a) Chromic acid content, 400 g/L (53 oz/gal); ratio of chromic acid to sulfate, 100:1; operating temperature, 55 °C (130 °F).

(b) Chromic acid content, 400 g/L (53 oz/gal); sulfate content, 1.5 g/L (0.20 oz/gal); contains sufficient fluoride catalyst to give 100-to-1 ratio results.

(c) Chromic acid content, 400 g/L (53 oz/gal); contains appropriate amount of proprietary catalyst; operating temperature, 55 °C (130 °F)

Solution temperature affects both the conductivity and the current required. If limited power is available, satisfactory hard chromium plating deposits can be obtained at lower temperatures (43 to 49 °C, or 110 to 120 °F), but if power supply is adequate, it is advantageous to work at higher temperatures (up to 60 °C, or 140 °F) because of the faster deposition rate and the improved durability of the deposit. At 43 to 49 °C (110 to 120 °F), current densities of 8 to 30 A/dm^2 ($\frac{1}{2}$ to 2 A/in.^{2}) are satisfactory; at 60 to 66 °C (140 to 150 °F), 45 to 60 A/dm^2 (3 to 4 A/in.^{2}) may be required, and as high as 80 to 90 A/dm^2 (5 to 6 A/in.^{2}) can sometimes be needed. At all temperatures, increased agitation will allow higher current densities.

Control of solution temperature to within a narrow range is necessary because of the marked influence of temperature on deposition rate and deposit quality. An increase of 2 °C (5 °F) in mean solution temperature, for example, can cause a reduction of 5% or more in mean chromium thickness, thus necessitating a sizable adjustment in either plating time or current density. The solution temperature should be maintained within 1 °C (2 °F). Solution temperature is usually controlled automatically. Manual control is impractical for a production operation.

For automatic control, it is important that the thermostat be placed in the plating solution in a location where it can readily sense any significant change in solution temperature. Obviously, the thermostat must not be in close proximity to a heating or cooling pipe or to an electric heating element. Location of the thermostat is greatly simplified when an external heat exchanger is used and the solution is pumped from the heat exchanger to the solution. Rapid movement of the solution or air agitation helps to promote temperature uniformity.

Problems and Corrective Procedures

Faulty operation of a chromium-plating solution can result in slow plating speed or deposits with undesirable characteristics. The problems encountered in hard chromium plating are similar for all three chemistries. Possible causes and suggested corrective procedures include:

Poor coverage

- Low chromic acid content
- Low ratio of chromic acid content to total catalyst content. Correct by adding chromic acid or by precipitating sulfate, if too high, with barium carbonate.
- Temperature too high
- Current density too low
- Passive or scaled anodes. Correct by cleaning and reactivating anodes, using high current density until uniform gassing is obtained, and checking for good anode contact.
- Rack contacts too heavily built up with metal, causing rack to rob plate
- Thieves too large or too close
- Open holes preventing uniform plate in adjacent areas. Correct by using nonconducting plugs in holes.
- Gas entrapment preventing plating solution from reaching some areas. Correct by positioning parts in solution so that all gases can escape or by agitating parts while they are plating.

Burnt deposits

- Ratio of chromic acid to total catalysts too high. Correct by adding necessary catalyst or by lowering chromic acid content.
- Current density too high
- Temperature too low
- Large parts were colder than solution temperature when plating began.
- Some parts, in a load of different parts, receive too much current. Correct by adjusting anodes and contacts to ensure that each part receives correct current density.
- Excessive amount of anode within a given area for the part being plated. Correct by eliminating all excess anodes in the tank, designing the shape of conforming anodes to minimize current density at high-density areas, and, if necessary, using nonconducting shields at these areas.

Slow plating speed

- Chromic acid content too high
- Ratio of chromic acid to total catalyst too high
- Temperature too high
- Current density too low
- Scaled anodes
- Insufficient or inadequate sizes of conductors in anode or cathode circuits
- Thief obtains too much current. Correct by redesigning thief or by removing nodules from thief.
- Single phasing of rectifier caused by partial burnout. Correct by repairing rectifier.
- High contact resistance on busbars, racks, or jigs. Correct by cleaning contacts to lower contact resistance. Do not always rely on voltage for control, because it does not indicate the conditions present on the part; instead, control by amperage.

- Large variety of parts in same tank prohibiting proper current density for each part
- Tank overcrowded with parts
- High content of metallic impurities. Correct by discarding a portion of solution; readjust after dilution.

Nodular deposits

- Insufficient etching before plating in relation to thickness of deposit. Correct by increasing etching time.
- Rough surface before plating
- Chromic acid content too high. Correct by removing portion of solution; dilute the remainder and adjust.
- Low temperature
- Low sulfate content
- Current density too high

Pitted deposits

- Marking dye not completely removed
- Material suspended in solution. Correct by filtering out suspended material.
- Surface-activating agents caused deep pits when plating thick deposits. Correct by discarding as much of the solution as necessary to eliminate pits and replace with fresh solution. Prevent by discontinuing use of mist suppressors. Plastic parts that decompose, such as floats, can form decomposition products that also create pits.
- Gas bubbles adhering to part. Correct by improving surface finish before plating and by agitating part occasionally during plating.
- Part is magnetized. Correct by demagnetizing.
- Magnetic particles in the solution. Correct by removing particles with magnet.
- Insufficient cleaning prior to plating
- Particles falling on work from anodes or thieves. Correct by improving design of anodes and thieves and by cleaning both regularly to remove loose particles.
- Carbon smut on surface. Correct by scrubbing before plating.
- Excessively etched surface during reverse-etch or stripping operation

Poor adhesion

- Insufficient or no etching before plating
- Contaminants not completely removed from surfaces during cleaning
- Excessive grinding rate at edges or sharp projections, where base metal fractures and it may appear that plated material did not adhere
- Single phasing of rectifier caused by partial burnout. Correct by repairing rectifier.
- Current interruption during plating
- Cold solution

Macrocracks

- Highly stressed base metal; cracks are visible during grinding or when heat is applied. Correct by relieving stresses in base metal.
- Grinding at too fast a rate (heat checks)

Equipment

The discussion of equipment that follows is confined largely to considerations that are specific to chromic acid plating processes. Mixed-catalyst and fluoride-free solutions have essentially the same equipment requirements as conventional

sulfate solutions, except that all parts of the electrical system may need to be heavier to accommodate the increased current used. Equipment requirements for plating three specific parts are given in Table 9.

Table 9 Process and equipment requirements for hard chromium plating using conventional solutions

Item	Area of part		Area of load		No. of pieces/ 8 h	Thickness of plate		Current density		Plating time, min	Temperature of bath		No. of work rods	Tank dimensions	
	mm^2	$in.^2$	mm^2	$in.^2$		μm	mil	A/dm^2	$A/in.^2$		°C	°F		mm	in.
Small cutting tools	4,800	7.5	967,000	1500	10,000	1.3	0.05	30	2	5	50	120	1	1500 × 760 × 910	60 × 30 × 36
Shafts	20,000	30	600,000	930	200	25	1	30	2	63	50	120	2	1800 × 910 × 910	72 × 36 × 36
Gun barrels[(a)]	15,000	23	543,000	828	180	25	1	45	3	40	54	130	2	2400 × 910 × 610	96 × 36 ×

(a) Plating of inside diameter 30-caliber gun barrels

Tanks and Linings. Figure 1 illustrates a hard chromium plating tank arrangement. Most tanks for chromium plating are made of steel and lined with an acid-resisting material. Because of their excellent resistance to corrosion by chromic acid, lead alloys containing antimony or tin may be used as tank linings.

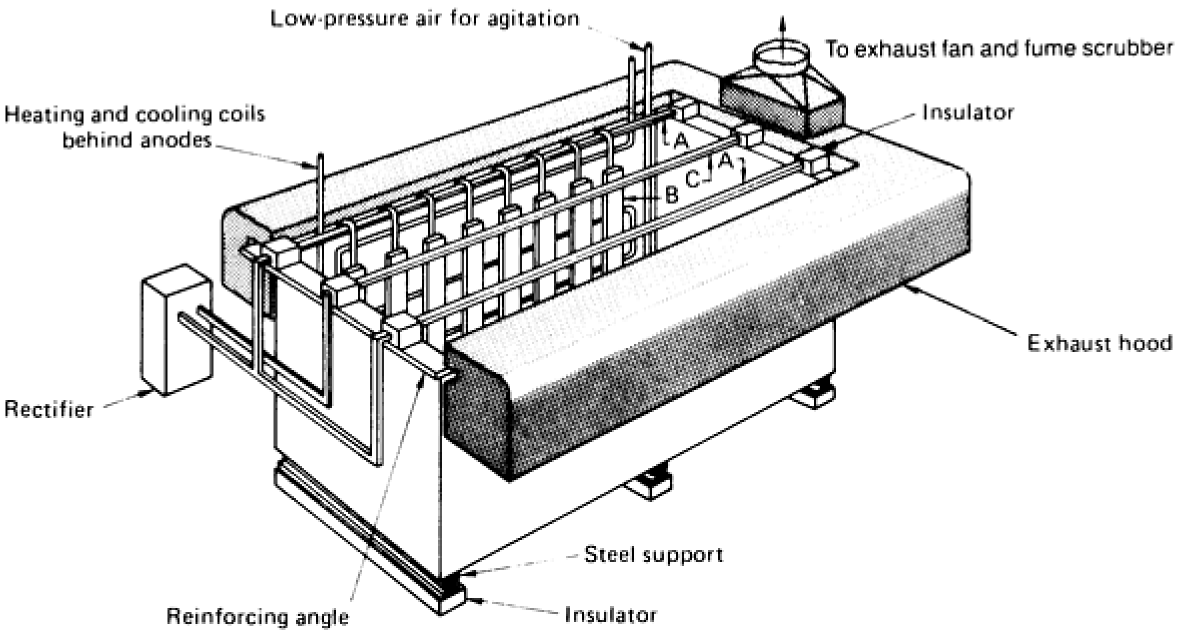


Fig. 1 Tank and accessory equipment used for hard chromium plating. A, anode rods; B, lead or lead-tin anodes; C, cathode rod

Acid-resistant brick has been used as a lining material. Because of its electrical insulating characteristics, acid-resistant brick lining has the advantage over metal linings of reducing possible current losses or stray currents. Some installations combine a lead lining or plastic sheet lining with an acid-resistant brick facing. With fluoride-containing solutions, a brick lining is suitable only for temporary use.

Almost invariably, plasticized polyvinyl chloride is used for all three types of chromium plating solutions, provided that the solution temperature does not exceed 66 °C (150 °F). Sheets of this plastic are cemented to tank walls and welded at joints and corners. Other plastic materials are equally resistant to chemical attack but are more likely to fail at the welds when exposed to an oxidizing acid. Fiberglass utilizing either polyester or epoxy is unsatisfactory for use in mixed-catalyst solutions, because exposed fiberglass will be attacked by the secondary fluoride catalyst.

Design specifications for low-carbon steel tanks for chromium plating are given in Table 10. Lining materials for low-carbon steel tanks are given in Table 11. Steel tanks should be supported at least 100 mm (4 in.) from the floor; steel I-beams are used to provide this support and are mandatory when side bracing is required. To provide insulation, reinforced strips of resin-bonded glass fiber can be placed between the floor and the I-beams. Glass brick can be used as insulation between electrodes and the plating tank.

Table 10 Design specifications for low-carbon steel tanks for hard chromium plating

Size of tank				Thickness of low-carbon steel		Width of rim		Tank reinforcing
Length		Depth						
m	ft	m	ft	mm	in.	mm	in.	
Up to 1	Up to 4	Under 0.9	Under 3	5	$\frac{3}{16}$	50	2	No
Up to 1	Up to 4	Over 0.9	Over 3	5	$\frac{3}{16}$	50	2	Yes
1-4	4-12	All	All	6	$\frac{1}{4}$	75	3	Yes

Table 11 Lining materials for low-carbon steel tanks for hard chromium plating

Tank length		Lining material					
		Lead alloy[(a)]		PVC[(b)]		Brick[(c)]	
m	ft	kg/m^2	lb/ft^2	mm	in.	mm	in.

Up to 2	Up to 6	40	8	5[d]	$\frac{3}{16}$ [d]	100	4
2-4	6-12	50	10	5[d]	$\frac{3}{16}$ [d]	100	4
Over 4	Over 12	60	12	5[d]	$\frac{3}{16}$ [d]	100	4

(a) Antimonial lead, or lead-tin alloy.

(b) Plasticized polyvinyl chloride.

(c) Acid-resistant brick. For further protection, brick may be backed up with 39 kg/m^2 (8 lb/ft^2) of antimonial lead or lead-tin alloy, or with plasticized polyvinyl chloride sheet.

(d) Lining should be 10 mm ($\frac{3}{8}$ in.) thick at top to 0.3 m (1 ft) below top of tank.

Heating and Cooling. Steam heating coils and cooling coils can be made of antimonial lead or silver-bearing lead. Titanium coils are preferred for conventional and fluoride-free plating solutions because of their relatively low cost and long life. Tantalum or niobium-clad coils should be used for mixed-catalyst solutions due to the fluoride attack on titanium. These coils are mounted on tank walls behind the anodes. Steel pipes carrying steam and cooling water to the tank must have a nonconducting section in each leg, so that the coils cannot become an electrical ground back through the power plant system.

Electric immersion heaters sheathed in fused quartz are suitable for heating chromic acid solutions. The quartz is fragile and must be handled with care. Similar immersion heaters are sheathed in either tantalum, titanium, or lead alloy. It is sometimes feasible to heat and cool a chromic acid solution by piping the liquid to a tube bundle, concentric, or tube heat exchanger located outside the plating tank. Preferably, heat exchanger tubes should be made of tantalum or titanium. This method has the disadvantage of requiring pumping of the solution.

Temperature-control planning should begin with selection of the volume of solution required in the plating solution. An ideal volume consists of 1 L or more of solution for each 13 W of plating power (1 gal or more of solution for each 50 W of plating power). About 60% of this plating power (30 W) produces heat and maintains the solution at temperature in an uninsulated tank of standard design. Power applications in excess of 13 W/L (50 W/gal) require cooling of the plating solution and cause relatively rapid changes in solution composition.

Agitation. A chromium-plating solution should be agitated periodically, particularly when the solution is being started, to prevent temperature stratification. Air agitation is effective, but oil from an air pump must not be permitted to leak into the air system. Preferably, the air should come from an oil-free low-pressure blower. A perforated pipe of rigid polyvinyl chloride may be used to distribute air in the solution.

Busbars. Anode and cathode busbars are usually made of round or rectangular copper bar stock. These rods should be adequately supported to prevent them from sagging under the weight of anodes and work. Generally, selection of bar size is determined by allowing 1 cm^2 of cross-sectional area for each 150 A (1 in^2 of cross-sectional area for each 1000 A), although mechanical strength for load support is also a factor in determining rod size. Anode and cathode rods are supported above the tank rim by insulators, which may be made of brick, porcelain, or plastic. Even metallic supports can be used if a strip of electrical insulating material is placed between the plating tank and the busbar.

Power Sources. Although dynamos or motor-generator sets were once the usual sources of power for low-voltage direct current for plating, rectifiers are now regularly used. In general, use of motor-generator sets is now restricted to larger and more permanent installations. Originally, plating rectifiers were made of copper oxide or magnesium-copper sulfide, but these have been largely replaced by silicon rectifiers. Silicon is favored for plating rectifiers because of its high resistance to thermal overload and small space requirement. Hard chromium platers often start plating on a piece by sweeping up applied voltage and current from very low values to the high values used for plating. Because silicon-controlled rectifiers have high ripple at low output, the output should be filtered. Tap-switch controls, however, produce relatively low ripple over the entire output range.

A 6 V power source can be used for chromium plating, but it is generally desirable or necessary to operate with 9 to 12 V available. Chromium plating requires full-wave rectification with a three-phase input and full control, giving a ripple less than 5% and no current interruptions. If a rectifier becomes partially burned out, it may single phase to some degree, and this can cause dull or laminated, peeling deposits.

Fume Exhaust. A chromium-plating process produces a chromic acid mist, which is toxic. The maximum allowable concentration for 8 h continuous exposure is 0.1 mg of chromic acid mist per cubic meter of air. This concentration value is in accordance with recommendations by the American Conference of Governmental Industrial Hygienists. Because of the extreme toxicity of this mist, it is mandatory to provide adequate facilities for removing it. The minimum ventilation rate should be 60 m^3/min per square meter (200 ft^3/min per square foot) of solution surface area. (It should be noted that these regulations are presently under revision and are subject to changes.)

Generally, fumes are exhausted from a chromium plating tank by means of lateral exhaust vents along both long sides of the tank. For narrow tanks, up to 600 mm (24 in.) wide, a lateral exhaust on one side of the tank should be adequate unless strong cross-drafts exist. Velocity of the air at the lateral exhaust hood slots should be 600 m/min (2000 ft/min) or more.

In the design of ductwork, condensate duct traps should be included to capture chromic acid solution. Drains from these traps should be directed to a special container and not to the sewer. In this way, chromic acid solutions can be returned to the tank or recovery system or be safely destroyed. A fume scrubber or a demister should also be included in the system to remove most of the chromic acid fumes before exhausted air is emitted to the atmosphere. Many communities have air pollution regulations requiring fume scrubbers. Fume exhaust ductwork may be made of carbon steel and coated with acid-resistant paint. Modern construction uses chlorinated polyvinyl chloride.

Rinse Facilities. Rinsing the work after chromium plating prevents it from becoming stained or discolored. Insufficient rinsing can result in contamination of cleaning solutions during subsequent cycling of racks. Multiple rinsing facilities are recommended. After being plated, parts should be rinsed in a nonrunning reclaim tank, which can be used to recover part of the chromium solution dragout. After they are rinsed in the reclaim tank, plated parts should be rinsed in counterflowing cold water and hot water tanks. Water should cascade from the hot water tank to the cold water tank. A multiple counterflowing arrangement requires much less water than two separate rinsing tanks.

If rinse water is being returned to a chromic acid waste disposal unit, the flow of water into the hot water tank should be controlled automatically by a conductivity-sensing element in the cold water tank. At a predetermined concentration of chromic acid in the cold water, the water inlet to the hot water tank should flow, causing an overflow of cold water to the waste disposal unit. This arrangement decreases the amount of water consumed and minimizes the required capacity of the waste disposal unit.

Cold water rinse tanks may be coated, sprayed, or otherwise lined with plasticized polyvinyl chloride. Hot water rinse tanks may be constructed of types 347, 304, or 316 stainless steel, or they may be made of carbon steel and lined with lead. Reinforced polyester glass fiber also may be used for either hot water or cold water rinse tanks.

Spray rinsing also effectively removes residual chromic acid. Because spraying does not always reach recessed areas, sprays should be positioned above a dip rinse. As parts are removed from the dip rinse, they may be sprayed with clean water, which, in turn, is returned to the dip tank.

Maintenance. Following is a maintenance schedule for a still tank installation for hard chromium plating:

- *Daily:* Check temperature. Check concentration of solution by density measurements. Clean busbars and electrical connections. Remove any parts that fall from racks.

- *Weekly:* Analyze for chromic acid and sulfate contents.
- *Monthly:* Remove all sludge and parts from tank, using a hoe and dragging the bottom. If tank is used for plating inside diameters, analyze for trivalent chromium.
- *Semiannually:* Check tanks for leaks and condition of lining. Clean and inspect rectifiers or motor-generating units. Check ammeter calibration.
- *As necessary:* Analyze for trivalent chromium, iron, nickel, copper, and zinc. Check condition of anodes.

This schedule is intended only as a guide; local conditions determine exact requirements. The rate of variation of solution constituents depends on the volume of solution, the method of operation for the solution, and the type and amount of work.

Racks and Fixtures

The following recommendations are offered regarding the design and use of plating racks:

- Racks should be designed to hold workpieces in a favorable position for plating uniformly on significant surfaces and to facilitate racking and unracking.
- Workpieces with protruding sections should be racked so that parts shield each other. If this is not possible, a current thief should be used to reduce current density at the protruding points.
- Electrical contact with the part should be made on an insignificant surface.
- The contact or rack tip should be rigid enough to hold workpieces securely and maintain positive contact. When the work is heavy enough to ensure positive contact, a hook often suffices.
- To minimize solution losses due to dragout, the work should be hung as nearly vertical as possible, with the lower edge of the work tilted from the horizontal to permit runoff at a corner rather than a whole edge. When recessed areas cannot be racked to allow proper runoff, provision should be made for drain holes or perhaps tilting of the rack when it is being withdrawn from the solution.

Although the design of racks and the methods of racking vary greatly, two basic types of racks are generally used. The first type consists of a single high-conductivity bar on which suitable supports have been mounted for holding the work to be plated; this rack is the cathode side of the plating circuit. The second type consists of two elements, the cathode and the anode; the work is held by the cathode and the cathode is attached to, but insulated from, the anode. Both types of racks are illustrated in Fig. 2. To prevent deposition of chromium or attack by the plating solution on parts of the rack that are immersed in the solution, these parts are covered with nonconducting material such as water-resistant tape, special insulating lacquer, or plastisol coatings.

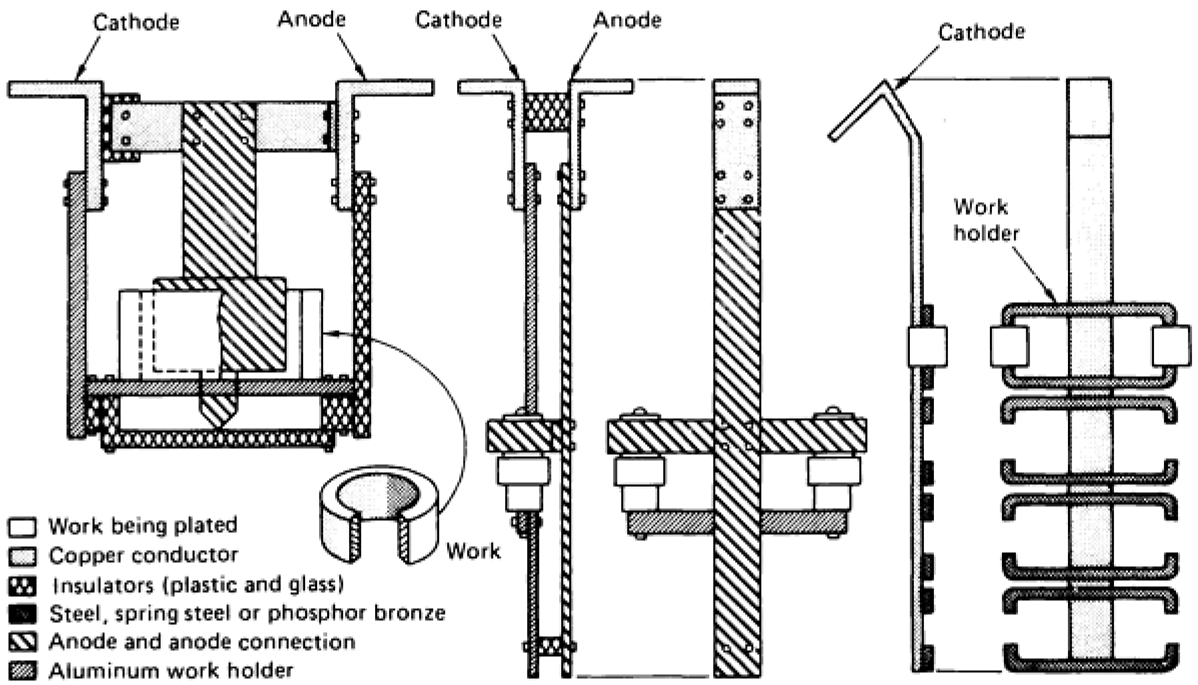


Fig. 2 Racks used in hard chromium plating

Surface Preparation

All soils and passive films must be removed from surfaces of ferrous and nonferrous metals before they are hard chromium plated. In addition to cleaning, certain surface-activating processes are often important in preparing the base metal for hard chromium plating. The processes include etching of steel, preplate machining, and nonferrous metals preparation.

Etching of steel before plating is needed to ensure adherence of the chromium deposit. Anodic etching is preferred for this purpose. Slight etching by acid immersion may be used for highly finished surfaces, but with possible sacrifice of maximum adherence.

Steel can be etched anodically in the chromium plating solution at its operating temperature for plating. A reversing switch is used so that the steel to be plated can serve as the anode for 10 s to 1 min (usually 30 s to 1 min) at a current density of about 15 to 45 A/dm^2 (1 to 3 A/in^2). Tank voltage should ordinarily be 4 to 6 V. Because mixed-catalyst solutions chemically attack the steel, causing etching of the surface, shorter electrochemical etching time frequently is required than is the case with conventional or fluoride-free chemistries. This process has the disadvantage of causing the solution to become contaminated with iron from the work and with copper from the conductors.

As an alternative, steel may be anodically etched in a separate chromic acid solution without sulfate additions and containing 120 to 450 g/L (16 to 60 oz/gal) of chromic acid. Solution temperature may range from room temperature to that of the chromic acid plating solution, or even higher, provided that current density and time of treatment are adjusted to suit the type of work being processed.

A sulfuric acid solution (specific gravity 1.53 to 1.71) may be used for anodic etching, provided that the solution temperature is held below 30 °C (86 °F), and preferably below 25 °C (77 °F). The time of treatment may vary from 30 to 60 s and the current density may vary from about 15 to 45 A/dm^2 (1 to 3 A/in^2) at tank voltages ordinarily between 4 and 6 V. A lead-lined tank with lead cathodes should be used. With the use of a sulfuric acid solution, however, two difficulties may be encountered. First, if the rinsing following etching is incomplete, the drag-in of sulfuric acid throws the chromium plating solution out of balance with respect to the ratio of chromic acid to sulfate. Second, in handling parts that are difficult to manipulate, there is danger that surfaces exposed to air more than a very short time will rust and that finely finished surfaces will be overetched.

For high-carbon steel, a sulfuric acid solution of 250 to 1000 g/L (33 to 133 oz/gal), used at a temperature of not more than 30 °C (86 °F) and preferably below 25 °C (77 °F), is effective for anodic etching. The addition of 125 g/L (16.6 oz/gal) of sodium sulfate, based on the anhydrous salt, is of benefit for many grades of steel. Anodic treatment in this solution usually does not exceed 1 min at a current density of about 15 A/dm^2 (1 A/in^2) (range of 15 to 45 A/dm^2, or 1 to 3 A/in^2). High acid content, high current density, and low temperature (within the ranges specified) minimize the attack on the base metal and produce a smoother surface. This sulfuric acid solution is stable and not appreciably affected by iron buildup.

Preplate Machining. Metal debris on the surface should be removed before etching (an activation procedure). The use of abrasive-coated papers is common, as is the use of successively finer grit stones in honing and grinding. To prepare a sound surface in superfinishing, 600-grit stones may be used. Electropolishing is sometimes used to remove highly stressed metal and metal debris from the surface of cold-worked steel. This process improves bond strength and corrosion resistance of electroplated coatings. It accomplishes this function without formation of smut, which may result from anodic etching. This treatment is not recommended for parts that are subjected to critical fatigue stresses and that are expensive to manufacture.

Preparation of Nonferrous Metals. Aluminum, in common with certain other metals, quickly develops a natural, passive oxide film after exposure to preplating cleaning cycles. This film must be removed before aluminum is plated. The most widely used method of preparing aluminum for plating involves a zincating treatment, which may be followed by a thin 5 μm (0.2 mil) copper electrodeposit. However, it is possible to plate chromium directly over the zincate.

Aluminum parts used in hydraulic systems require a nickel undercoat before being plated, to provide corrosion protection to all plated surfaces that are not completely and constantly immersed in hydraulic fluid or similarly protective fluids. A minimum thickness of 10 to 15 μm (0.4 to 0.6 mil) of nickel is usually specified. This undercoat may also be required for steel parts in similar applications.

Titanium and titanium alloys, as well as magnesium, also form a tight, stable oxide coating and are therefore difficult to plate. These metals can be pretreated with an electroless nickel plate or a coating deposited from a high-chloride nickel strike solution.

Variations in Plate Thickness

Variations in the thickness of hard chromium plate depend primarily on the potential field distribution. Potential field is controlled by the placement of anodes, shields, thieves, and other parts, as well as the relative position of the sides and surface of the tank. Variations in plate thickness also depend on surface preparation, control of solution conditions, and uniformity of the power source.

Methods of Measuring Plate Thickness. Several methods and types of instruments are available for determining the thickness of plate. These include electrolytic stripping, microscopic measurements of cross sections, torsion dynamometer measurements made with magnets of various strengths, measurement by eddy current instruments, and accurate measurement of the dimensions of the part before and after plating to determine thickness by difference.

Electrolytic stripping and microscopic measurements of cross sections are destructive methods that are most frequently used for purposes of verification, calibration, and sampling of production runs. When calibrating instruments with prototype plated parts, using microscopic measurements of cross sections as umpire checks, several calibration reference curves may be required, depending on the parts being plated.

Measurements by properly calibrated eddy current or torsion dynamometer instruments are affected by the surface finish of the deposit, width and thickness of the piece, surface contour, and composition of the base material. With a properly calibrated instrument, thickness measurements are usually within 10% of the actual thickness. Individual thickness measurements should not be used as the basis for acceptance or rejection; however, an average of several determinations from a well-calibrated instrument is an acceptable measure of the mean thickness from a controlled process.

The normal variation in plate thickness that can be expected when plating the outside diameter of cylinders, rods, or round parts racked as cylinders is ±0.2μm/μm (±0.2 mil/mil) of plate intended. This has been determined over a period of several years by average quality level thickness measurements on piston rings racked as cylinders.

This normal variation of 20% was confirmed in an actual production situation. In plating identical parts to a consistent thickness requirement, sample checks from 74 loads (110,000 parts) representing 27 days of operation were made to determine the plating tolerances that could be expected. The plating cycle was set to provide a plate thickness of 200 to 230 μm (8 to 9 mils) to meet a final requirement for a minimum plate thickness of 150 μm (6 mils) after light stock removal during the subsequent finishing operation. Results of this analysis are shown in Fig. 3.

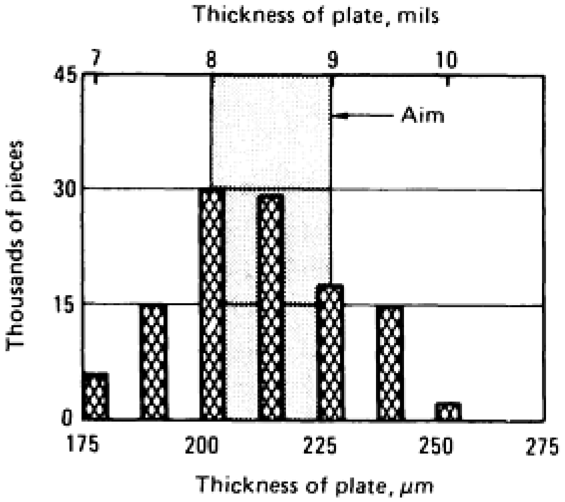


Fig. 3 Variations in hard chromium plate thickness for 74 loads, representing 110,000 parts of the same design plated over a period of 27 days of operation. Target thickness was 200 to 230 μm (8 to 9 mils) of hard chromium. Average thickness for the 74 loads was 215 μm (8.4 mils).

The throwing power of chromium-plating solutions is related to the ratio of chromic acid concentration to the catalyst concentration. Higher ratios give better throwing power at a given temperature and current density. This is evidenced by the fact that when a very low current density is present on certain areas of irregularly shaped parts, the cathode efficiency at that low current density is less for a solution high in sulfate than for a solution with lower sulfate content. Therefore, less metal is deposited on the areas of low current density from a solution of high catalyst content.

The current density at which no metal deposits is greater for high catalyst solutions than for lower catalyst solutions. Also, metal deposits from a solution of low catalyst concentration at a current density that would be too low for depositing from a solution with high catalyst concentration. Thus, the following factors must be considered to ensure successful plating of complex shapes: chemical balance, operating variables, type of anode, and design of fixtures or racks.

Chromium plating requires far more attention to the variables that affect current distribution than cadmium, zinc, copper, or nickel plating. It is theoretically impossible to obtain the same current density at an inside corner as on the flat adjacent to it. An outside corner without shielding or thieving always has the highest current density and hence the greatest plate thickness. Conforming anodes, shields, and thieves may be used to minimize thickness variation, but except on the simplest shapes, they do not eliminate it.

Some metal is deposited at low current densities in most other plating solutions, but in chromic acid solutions there is a minimum current density for a given solution at a given temperature below which no metal is deposited. If an area of an internal or irregular shape receives less than this minimum current density, no deposition of metal occurs in this area. This explains why it is so difficult to chromium plate recesses and internal shapes without special anodes. Special hardware, in the form of thieves or shields, is required for lowering the current density on areas such as edges to prevent excessive buildup of deposit.

In most electroplating solutions, the primary current distribution on an irregular object can be improved by increasing the tank anode-to-cathode distance. However, beyond a minimum distance, which depends on the shape of the part, no further improvement can be attained.

Because of the low throwing power of hard chromium plating solutions, an increase in the anode-to-cathode distance does not result in even plating of sharp reentrant surfaces such as those formed by internal angles. For plating parts containing shapes of this type, conforming anodes and/or current shields must be used.

Figure 4 illustrates the relation between thickness of deposit and distance of the anode from the part being plated. In this instance, an alternative to an increase in the anode distance is the use of an anode contoured to the curvature of the part.

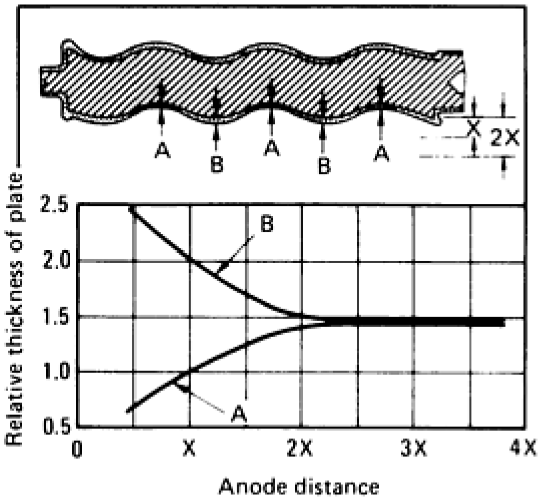


Fig. 4 Variation in thickness of chromium plate on feedworm as a function of the distance of the anode from the part. Values of *x* are about 25 mm (1 in.) or more.

Special Anodes. When the part contains sharp, narrow recesses, such as grooves, a reduction of the anode distance may help to increase the thickness of the deposit at the bottom of the grooves. However, some parts with sharp-cornered grooves, bosses, and undercuts cannot be uniformly covered even when contoured anodes are used. Examples of parts in this category and the areas of heavy deposits are illustrated in Fig. 5.

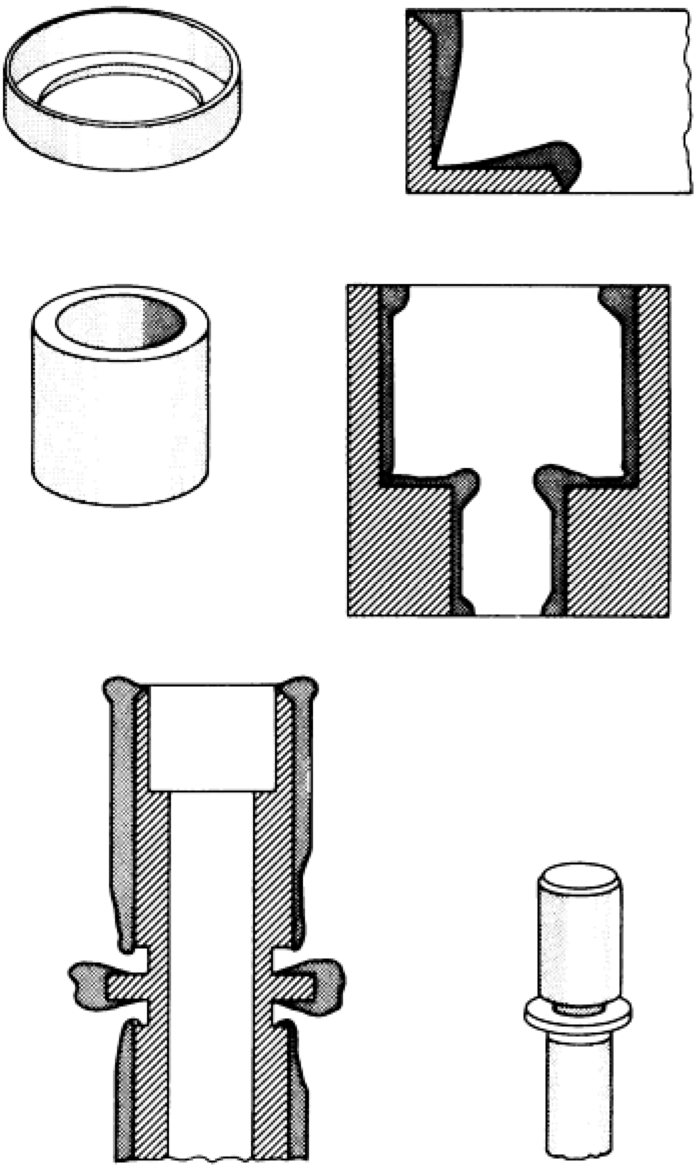


Fig. 5 Parts difficult to plate uniformly with hard chromium, even with the use of specially contoured anodes. Variations in plate thickness shown are approximately to scale.

Anodes used for plating recesses can be directly connected to the power supply, or they can be bipolar in nature. The bipolar anode has no direct electrical connection and takes advantage of the fact that current follows the path of least resistance. Bipolar anodes are an interesting curiosity that may have application in rare instances; however, direct connection of the anode to the positive direct current through a rheostat and ammeter, if required, is far more controllable.

The deposit on internal shapes can also be affected by the evolution of gas that occurs during plating. Gas can cause streaked deposits or produce a taper in a long bore. To minimize this effect, the parts should be positioned in a manner that permits the gas to move rapidly away from the part.

Because of fabrication problems encountered with lead alloys, complex-shaped anodes are made of steel, then coated with lead to produce the effect of solid lead anodes. These composite anodes are more economical and lighter in weight. However, the base metal can be destroyed if there are pores or throughholes in the lead alloy coatings. Brass or copper should never be used on the anode side, as they dissolve rapidly and seriously contaminate the solution. Low-carbon steel may be used alone for short runs, and lead-coated steel may be used for longer service.

Crack Patterns and Other Characteristics of Hard Chromium Plate

The quality of hard chromium plate is evaluated chiefly from the standpoint of thickness and thickness distribution, appearance, crack pattern, crack size, porosity, roughness, and adhesion of the plate to the base metal.

Surface Cracks. During the deposition of chromium deposits, microcracks form to relieve the internal stress. These cracks subsequently fill in with plated chromium. The chromium in these former cracks is more easily etched and has a different refractive index than the surrounding deposits. For this reason, with the use of a microscope one can determine where and how many microcracks were present at one time on the surface of the deposit. The pattern usually consists of crack-free areas and plateaus completely surrounded by crack boundaries. The plateaus from an average conventional sulfate solution are 2 to 3 times larger than those from a mixed-catalyst solution; that is, there are more cracks per inch in a deposit from the average mixed-catalyst solution. The fluoride-free chemistry gives yet an additional factor of 2 to 3 times more microcracks.

Interestingly, the more microcracks present, the shorter the penetration into the deposit of each one (i.e., with the conventional solution, a microcrack can extend all the way through a 1 mil thick deposit, while in the fluoride-free solution deposit they extend very short distances). Since these (former) cracks provide the pathway for corrosion, it is desirable to have as many discontinuities as possible as one progresses through the deposit to the substrate. It is for this reason that in corrosion applications, the solution that provides the greatest amount of microcracking possible is used.

Crack-Free Deposits. It is possible to plate chromium with virtually no microcracks. This is done by altering the current density and temperature, altering the catalyst concentrations, or using pulsed-current or periodic-reverse plating. Crack-free deposits are gray and have very poor wear properties. The corrosion resistance is also very poor due to residual stresses in the deposit, which eventually (in a few days or months) cause large cracks that extend through the entire deposit.

Some specialized applications for this type of deposit include broaches, cams, dies for metal forming, metalworking rolls, and stamping dies for embossing silverware. Complicated shapes create a large range of current densities and are difficult to plate with a crack-free surface. Corners, edges, or other high-current-density areas are most likely to crack during plating.

Porous Chromium. Although the cracks or porosity that characterize chromium deposits are not desirable for resistance to corrosion, a porous structure can be advantageous in wear applications in which lubrication is required, because it promotes wetting action and provides oil retention after initial lubrication. Engine cylinders are the outstanding application.

Most chromium-plated cylinder surfaces consist of some form of interrupted surface, generally porous chromium. An interrupted surface may be obtained by electrolytic or chemical etching of chromium after it is plated on a smoothly honed bore, as with porous chromium, or by preroughening the bore by shot blasting, knurling, or tooling and then reproducing this roughness in the final chromium plate or by machining in roughness after plating.

Two distinct types of porous chromium are produced. One has pinpoint porosity with many microscopic depressions in a honed chromium surface. This has been used in all types of engine cylinders except aircraft. The other type is also finish honed but is broken by randomly connected channels, leaving isolated bearing plateaus. For both types, the percentage of porosity is generally controlled between 20 and 50% of the total area. Average plateau diameter is further controlled between 0.25 to 0.75 mm (0.010 to 0.030 in.) with the channel type of porosity. Porosity as low as 5% approaches dense chromium and is susceptible to scoring because of sparse oil distribution. High porosity, such as 75%, may cause high initial ring wear and high oil consumption. In normal engine service, cylinders coated with chromium of optimum porosity give wear rates one-third to one-tenth better than those of uncoated cast iron or steel, hardened or unhardened.

Several methods--electrochemical, mechanical, and combinations of both--have been developed to provide controlled porosity in heavy chromium deposits. Mechanical methods entail either severe grit blasting of the surface to be plated or roughening of the surface with a fine knurling tool. The roughened surface is reproduced by the deposit. Using a patterned mask, the surface can also be roughened by chemical or electrochemical means before plating The most widely used techniques, however, involve chemical or electrochemical etching of the chromium deposit after plating. Note that the pattern or crack density and the size of the plateaus are largely determined by the composition (ratio) of the solution, and the plating temperature.

Etching is performed on plated thicknesses ranging from 120 to 180 μm (5 to 7 mils). Porosity is developed after plating by electrochemically etching anodically in chromic acid solution. The etched surface is finished by honing, polishing, or

lapping. Metal removal that exceeds the depth of porosity must be avoided. To avoid accelerated wear in service, finished surfaces must be thoroughly cleaned of abrasive and chromium particles.

Quality Control Tests. Usually, visual examination is sufficient for determining appearances and roughness of the surface of hard chromium plate. Magnetic particle inspection can be used to examine chromium plate up to 100 μm (4 mils) thick for cracks after grinding. The as-plated deposit prior to postfinishing should be as smooth as the base metal before plating and should be free of pits and nodules. The deposit should not exhibit excessive thickness variation. Particularly, deposits with dendritic growths (trees) should be rejected. Adequate plating control requires that such dendritic deposits occur on thieves rather than in functional areas.

For process development and quality verification, destructive testing may be used to determine the crack pattern and bond between the plate and base metal. The crack pattern can be developed by etchants such as a hot 50 vol% hydrochloric acid aqueous solution, or by short etching in a chromium plating solution.

The quality of the bond can be determined by punch testing, bend testing, examining the bond line metallographically, or judging of ground or hammered samples. Well-bonded chromium, because of its low ductility, does not fail by pulling away from the bond line; however, it fails by cracking and spalling if it is subjected to excessive stress or distortion in 45° diagonal tension.

Excessive porosity of thin (less than 25 μm, or 1 mil, thick) chromium plate on steel can be determined by applying an acidified copper sulfate solution to the plated areas. The pores permit the solution to copper coat steel by displacement, and the degree of copper coating thus indicates the degree of porosity. Porosity can also be determined by the ferroxyl test described in *Metal Finishing Guidebook,* 1982.

The mandrel test can also be used in quality control. If a portion of the chromium plate is made anodic for 3 min at 15 A/dm^2 (1 A/in^2) in a solution containing 250 g/L (33 oz/gal) chromic acid at 60 °C (140 °F), the crack pattern is developed. Counting the crack density under the microscope is an excellent procedure for noting the constancy of the composition (mainly ratio) and the temperature of the solution.

Hardness of Plate

Valid hardness measurements of chromium deposits are difficult to make, and values are dependent on test conditions, so hardness values should not ordinarily be used as quality control specifications and routine criteria. Rather, the as-plated brightness can serve as an indication of hardness.

The hardness of chromium plate cannot be accurately determined by the common hardness testers, such as Brinell and Rockwell, because hard chrome is generally too thin for these tests. The indentation produced in these tests distorts the base metal and is influenced by it, which usually results in low hardness readings.

The most reliable and most widely accepted hardness values are those obtained with the Vickers 136 diamond pyramid indenter or the Knoop indenter. With these, the hardness test must be made on a carefully prepared and polished surface, preferably on a cross section of the plate, to eliminate any possible influence of the base metal on the hardness values obtained.

Cracks in the chromium plate influence the hardness values, depending on the type of indenter used and the load applied. In general, lighter loads are more sensitive to hardness variations and result in higher hardness values. Cracks influence values obtained with heavy loads more than values obtained with light loads. Also, because of the smaller area covered by the Vickers 136 diamond pyramid indenter, hardness values determined with this indenter are influenced less by underlying cracks than values obtained with the Knoop indenter.

When conducting microhardness tests, it is important to make sharp and accurate impressions, particularly when using light loads. Also, when hardness values are reported, the load, type of indenter, and optical system used should be indicated. The importance of stating the load and type of indenter is shown by the following data obtained on chromium plate from one plating cycle (each range or average represents 25 tests):

Load, g	Hardness value	
	136° diamond pyramid	Knoop indenter
100	950-1110 (1040 avg)	940-1090 (1025 avg)

In an investigation of the scratch hardness of chromium deposits of all types, it was observed that bright or semibright deposits had the best combination of hardness and wear resistance, regardless of plating conditions. In this investigation, the wear resistance was measured by means of a specially constructed abrasion hardness machine. The machine contained a small grinding wheel that revolved at 18 rpm. The number of revolutions required to grind through a 25 μm (1 mil) deposit on steel was an indication of the abrasion hardness. Results are summarized in Table 12, which shows the relation between the appearance of deposits and their hardness and resistance to abrasive wear.

Table 12 Relation between appearance and hardness of hard chromium plate deposited from conventional solutions

Average appearance	Average scratch hardness[(a)], HB	Average relative abrasive hardness
Matte (cold bath)	640	25
Milky	830	100
Slightly milky	990	290
Bright	1000	300
Slighty frosty	1005	300
Frosty (smooth)	1020	235
Frosty (rough)	1060	125
Burnt	1165	110

(a) Converted to Brinell scale from values obtained with a Bierbaum microcharacter using a 9 g (0.3 oz) load

The effect of temperature on the hardness of electrodeposited chromium is often a significant factor in applications involving wear resistance. The electrodeposited metal begins to decrease in hardness when it is exposed to temperatures above about 205 °C (400 °F). Hardness decreases progressively with an increase in temperature (Fig. 6). As the hardness of chromium plate decreases, its resistance to wear may be affected adversely. Chromium plate should not be used for wear resistance in applications where service temperature exceeds 420 °C (790 °F).

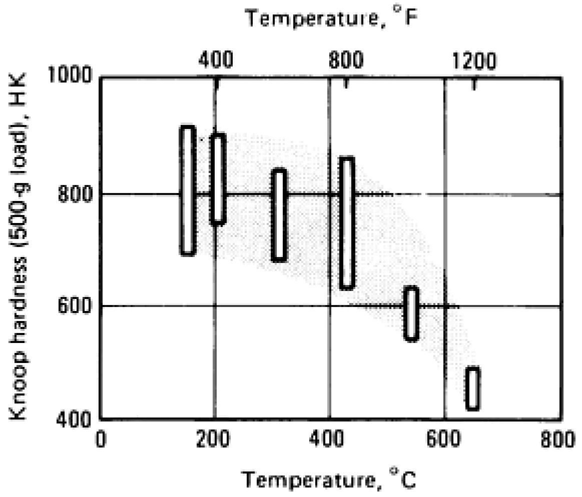


Fig. 6 Effect of annealing temperature on the hardness of chromium plate deposited during a single cycle in a mixed-catalyst solution. All data represent 25 measurements of each condition; every readable impression was accepted as valid. Heating cycles of 1 h were used.

Cost

The electroplating of hard chromium is very cost-effective, giving a high throughput with reliable, reproducible quality deposits that are unattainable by any alternative technology. The important cost factors are capital and labor expenses, followed by electricity, and, lastly, chemicals, which are relatively inexpensive. Almost always the fluoride-free solution is the least expensive chemistry to operate, followed by mixed-catalyst and then conventional sulfate solutions. Although the chemical costs increase going from conventional to mixed-catalyst to fluoride-free solutions, this increase is offset by savings in electrical costs, capacity improvements, and deposit quality improvements.

Factors that affect the relative cost of plating, regardless of the solution used, include the shape of the part, the design and arrangement of anodes, and special finishing techniques. Labor charges for hard chromium plating may be higher than for other plating processes, largely because many chromium plating operations are performed manually. Also, more labor is required to prepare some parts for plating or for finishing after plating.

The cost of plating increases with the complexity of the part design. Parts containing sharp notches, section changes, and unplated areas of cross-holes necessitate more handling during preparation and finishing than parts of simple shape. Also, anodes must more precisely conform to the shape of such parts for accurate control of plating thickness. Defects associated with chrome plate, such as dendritic growths and excessive buildups on external corners, can be minimized with tooling and special techniques. Depending on the nature of the part, these may increase costs. Special finishing techniques, primarily grinding and lapping, are required. Often a heat treatment of plated parts is necessary before they are ground or lapped.

For surfaces that are difficult to finish mechanically, even greater care must be taken in design and construction of anodes to approximate desired results closely. The cost of anode design and construction must be amortized over the number of parts plated. If sufficient production is required, refinement of masking and anodizing generally pays with decreased postplate finishing. Costs are affected also by the quality of the plate. Hard, high-quality plating finished to a bright luster is very expensive because of the rigid controls required in its production. As with other plating processes, costs vary because of local utility charges and ordinances pertaining to disposal of wastes. The availability of power and water, and the quality of the water available, can significantly affect cost. Safety requirements and waste disposal methods can be responsible for at least a 20% difference in plating costs among different plants.

Removal of Chromium Plate

Most manufacturers require salvage of misplated parts because of their high value. Further, in the aircraft industry, business machine industry, and plastic mold industry, significant numbers of parts are run for the life of the deposit and then overhauled by stripping worn deposits and replating.

Methods of Stripping. Chemical, electrochemical, or mechanical methods are used to remove hard chromium deposits. When the base material is steel, brass, copper, or nickel, hydrochloric acid at any concentration over 10 vol% and at room temperature or above removes chromium. In some operations, inhibitors are added to the acid solution to minimize attack on the steel substrate.

Chromium is removed electrochemically from steel or nickel by the use of any convenient heavy-duty alkaline cleaner at room temperature or above, at 5 to 6 V with anodic current. This method is unsatisfactory for nickel-base alloys, which should be stripped chemically in hydrochloric acid. Chromium may be stripped from aluminum by making the part the anode in a cold chromium (nonfluoride) plating solution or in conventional chromic acid or sulfuric acid anodizing solutions. Aluminum alloys with a high alloy content and alloys subjected to various heat treatments all react differently in stripping solutions, so precautions must be taken to prevent attack on the base metal. Anodic stripping operations result in formation of oxide films on the base metal. These films should be removed by one of the conventional deoxidizing processes prior to replating.

Stripping of chromium deposits from high-strength steel must be performed electrochemically in an alkaline solution. The parts are then stress relieved at 190 °C (375 °F) for a minimum of 3 h. The following solutions and operating conditions are recommended for removing chromium deposits from the materials indicated. Proprietary formulations having a longer operational life are also available.

Removal from steel or nickel-plated steel

- Sodium hydroxide, 45 to 320 g/L (6 to 30 oz/gal); anodic treatment at 3 to 8 A/dm^2) (0.2 to 0.5 A/in^2); solution temperature, 21 to 71 °C (70 to 160 °F)
- Anhydrous sodium carbonate, 45 to 60 g/L (6 to 8 oz/gal); anodic treatment at 2.5 to 5.5 A/dm^2 (0.15 to 0.35 A/in^2); solution temperature, 21 to 66 °C (70 to 150 °F). Use 2.3 A/dm^2 (0.15 A/in^2) with solution temperature of 66 °C (150 °F) to reduce possibility of pitting alloy steel.
- Sodium hydroxide, 52 g/L (7 oz/gal); sodium carbonate, 30 g/L (4 oz/gal); anodic treatment at 8 A/dm^2 (0.5 A/in.^{2})
- Concentrated hydrochloric acid at room temperature
- Hydrochloric acid, 50 vol%, at room temperature

Removal from aluminum and aluminum alloys

- Sulfuric acid, 67 vol%; glycerin, 5 vol%; anodic treatment at 1 to 3 A/dm^2 (0.1 to 0.2 A/in^2); solution temperature, 21 to 27 °C (70 to 80 °F)

Removal from magnesium and magnesium alloys

- Anhydrous sodium carbonate, 50 g/L (6.5 oz/gal); anodic treatment at 2 to 5 A/dm^2 (0.15 to 0.30 A/in^2); solution temperature, 21 to 27 °C (70 to 80 °F)

Grinding is used occasionally to remove heavy chromium deposits. Most defective chromium deposits are observed during subsequent grinding for finishing, so it is sometimes expedient to continue grinding to remove all of the plate and then replate. In the grinding of heavy deposits for the removal of several thousandths of an inch of chromium to attain required dimensions or surface finish, the most important requisites for successful results are:

- A soft grinding wheel
- A sufficient amount of coolant
- A light cut
- Correct peripheral speed
- Freedom from vibration
- Frequent wheel dressing

Because chromium is hard and brittle, a soft grinding wheel is essential. A hard wheel forms a glazed surface, which results in a temperature rise that causes the chromium to crack. A soft wheel breaks down rapidly enough to prevent formation of a glaze; however, too soft a wheel is not economical because of rapid wheel wear. Good performance can be obtained with an aluminum oxide resin-bonded wheel of about 60 grit and H-grade (hardness).

To prevent or minimize glazing, the contact area should be flooded with a coolant. Usually, the coolant is water with a small amount of soluble oil. Because of its hardness, excess chromium cannot be removed as rapidly as when grinding most other materials. The maximum thickness of metal removed should not exceed 5 μm (0.2 mil) per pass, and this amount should be reduced if there is any evidence of cracking. The optimum grinding speed is about 20.4 m/s (4000 sfm).

Effective grinding requires a rigid machine. Any appreciable vibration can cause cracking of chromium because of uneven contact pressure, and it also results in a wavy surface. Factors essential for a rigid machine include a well-fitting spindle bearing, a balanced wheel, a heavy bed, and a well-supported workpiece. Whenever there is the least indication of glazing or nonuniform wheel surface, the wheel should be dressed with a diamond point. Adherence to the preceding recommendations will result in a good surface with a finish of 0.35 to 0.5 μm (14 to 20 μin.). Subsequent lapping (240 grit) will produce a finish of 0.1 to 0.3 μm (5 to 10 μin.).

Special care should be taken when grinding chromium-plated parts made from high-strength steel (steel with an ultimate tensile strength of 1240 MPa, or 180 ksi, and above) that are to be used in stressed applications. Numerous failures have occurred due to formation of untempered martensite caused by the heat of the grinding operation. For information and guidelines on grinding chromium-plated high-strength steel parts, see military specification MIL-STD-866B.

Hydrogen Embrittlement

The susceptibility of chromium-plated parts to hydrogen embrittlement is affected by hardening of the steel, grinding, surface defects, pickling, cathodic cleaning, and the depth of plate relative to the thickness and hardness of the part being plated. (It should be noted that the chemistry of the chromium plating solution is not a factor.) Unless the hydrogen absorbed during pickling and cathodic cleaning is removed, subsequent plating further embrittles the part to such an extent that breakage can occur during plating. This effect becomes more prevalent with increasing hardness of steel and on parts of thin cross section.

The thickness of plate on thin steel sections is of importance from the standpoint of notch effect. This was illustrated in an actual production setting. Thin sections of steel, 2.5 by 0.5 mm (0.10 by 0.020 in.) and 25 to 38 mm (1 to $1\frac{1}{2}$ in.) long, were plated with chromium to a thickness of 8 to 13 μm (0.3 to 0.5 mil). The hardness of the steel was 57 to 59 HRC. These parts were aligned by being bent until permanently set. When the thickness of the chromium plate was increased to range from 15 to 23 μm (0.6 to 0.9 mil), the parts would break before taking a set. Baking them at 205 °C (400 °F) for 4 days did not relieve this condition. It was necessary to decrease the hardness of the steel to 53 to 55 HRC to prevent breakage of parts with heavier plate.

Stress Relieving before Plating. Surfaces to be chromium plated must be free from stresses induced during machining, grinding, or hardening. Stresses from the hardening operation may be further increased during grinding and result in microcracks. If the hardness of the steel is less than 40 HRC, it is unlikely that any damaging effect will occur as a result of residual stress. Steel with a hardness exceeding 40 HRC should be stress relieved before it is plated by heating at 150 to 230 °C (300 to 450 °F).

Baking after Plating. Steel parts with a hardness above 40 HRC should be baked at a temperature of at least 190 °C (375 °F) for 4 h after plating to ameliorate the effects of hydrogen embrittlement. This treatment should be started as soon as possible, preferably within 15 min after plating. The fatigue strength of parts subjected to alternating stresses is reduced by the baking treatment, so such parts should be shot peened before plating.

The use of shot peening and baking, as related to the hardness of steel to be chromium plated, is described in federal specification QQ-C-320B, amendment 1, as follows:

- Plated parts below 40 HRC and subject to static loads or designed for limited life under dynamic loads, or combination thereof, shall not require shot peening prior to plating or baking after plating.
- Plated parts below 40 HRC that are designed for unlimited life under dynamic loads shall be shot

peened in accordance with military specification MIL-S-13165 before plating. Unless otherwise specified, the shot peening shall be accomplished on all surfaces for which the coating is required and on all immediately adjacent surfaces when they contain notched fillets, or other abrupt changes of section size where stresses will be concentrated.

- Plated parts with a hardness of 40 HRC, or above, and subject to static loads or designed for limited life under dynamic loads, or combinations thereof, shall be baked after plating at 190 ± 14 °C (375 ± 25 °F) for not less than 3 h.
- Plated parts with a hardness of 40 HRC, or above, and designed for unlimited life under dynamic loads, shall be shot peened in accordance with military specification MIL-S-13165 before plating. Unless otherwise specified, the shot peening shall be accomplished on all surfaces for which the coating is required and on all immediately adjacent surfaces when they contain notched fillets, or other abrupt changes of section size where stresses will be concentrated. After plating, parts shall be baked at 190 °C (375 °F) for not less than 3 h.

Safety Precautions

All applicable OSHA, EPA, and local regulations pertaining to electroplating in general and specifically to chromium plating should be carefully reviewed and strictly followed. Material Safety Data Sheet forms should always be available, and precautions should be carefully noted, especially with respect to the incapability of mixing certain chemicals.

Personnel should wear rubber gloves, rubber aprons, and face shields when making additions to any plating or cleaning solution. Tank operators should wear proper protective clothing and eye protection at all times.

Health and safety concerns related to the use of chromium and possible alternative plating technologies are discussed in the article "Chromium Elimination" in this Volume.

Recovery and Disposal of Wastes

Chromic acid wastes may be either recovered or destroyed, and the choice of process should be based on a comparison of initial costs, labor costs for operation and maintenance, chemical costs, space requirements, and utility costs. The volume of wastes and the value of the chromic acid and rinse water saved can greatly influence the choice.

Local, state, and federal authorities are constantly increasing their attention to antipollution programs. Strict regulations are being enforced regarding the allowable limits for chromic acid wastes that leave the plating plant in any form. The prevailing limits for chromic acid contamination of waste water range from about 0.05 to 5 ppm. These limits vary for each locality, depending on the uses of the receiving body of water, supplementary water flows that affect dilution, and the ability of sewage plants to handle wastes. A new plater must check with federal, state, and local authorities to determine what limits are applicable at that time.

Preventive Measures. The problem of waste disposal can be greatly minimized if suitable measures are taken to minimize the amount of wastes produced. The following practices contribute to minimizing wastes:

- Extend drainage periods to permit more solution to return to the tank. In hand operations, this is made possible by providing a drainage bar over the tank to hold racks.
- Provide drip boards to return solution lost when going from tank to tank.
- If possible, rack parts in such a way as to eliminate cupping action.
- Use reclaim rinse tanks. The rinse solution can be used to maintain the level of liquid in the processing tank. Sometimes concentration methods may be profitable to facilitate use of rinse waters.
- Control drag-in of water to permit use of reclaim rinse tanks.
- Complete recovery should be used only in conjunction with technologies for the removal of metallic impurities.

Disposal of chromic acid wastes is most commonly based on reduction of hexavalent chromium to the trivalent form and, in either a batch or a continuous operation, precipitating the trivalent metal hydroxide by means of an alkali. The

actual chemicals used vary from locality to locality, depending on cost and availability. Chromic acid is first neutralized to a suitable pH and is then reduced with one of the sulfite compounds (sodium sulfite, sodium metabisulfite), sulfur dioxide, ferrous sulfate, iron, copper, or brass. After completion of reduction, trivalent chromium is precipitated as hydroxide with alkali. The amount of chemicals required to complete reduction can be governed by laboratory analysis, or, because the reaction is solely one of oxidation-reduction, it may be controlled automatically by use of electrodes.

The most commonly used reducing agent for large plants is sulfur dioxide gas. It can be obtained in liquid form in cylinders of various sizes, is comparatively inexpensive, and can be fed directly into the treatment tank. The rate of addition is easily controlled and gas is delivered from the cylinder under its own pressure. A lower initial acidity is required because the gas forms sulfurous acid when dissolved in water. The operating pH is 2 to 3, and the ratio of sulfur dioxide to chromic acid used commercially is slightly under 3 to 1. The sulfur dioxide method lends itself readily to an automatic system because the gas feed can be controlled by a flowmeter, and the reaction can be controlled by oxidation-reduction potentials.

Ferrous sulfate also is a widely used reducing chemical, especially in localities where large quantities are available from pickling plants. The quantity required can be easily determined by titration. The ratio of ferrous sulfate to chromic acid varies between 5 and 16 to 1. Reduction of chromium is followed by neutralization with lime or caustic. Above a pH of 7, the metals precipitate as hydroxides, together with calcium sulfate. The main disadvantage of the ferrous sulfate method is the large volumes of sludge that have to be handled.

The sulfite-containing compounds generally are slightly more expensive than sulfur dioxide or ferrous sulfate. In addition, several difficulties are involved in sulfite treatment, such as solubility, loss of hydrogen sulfide through hydrolysis, slightly lower pH, and, occasionally, the need for additional treatment to complete the process.

Regardless of the chemical treatment selected, all chromic acid disposal systems require collection, treatment, and settling tanks. The operating procedure consists of chemical additions, mixing, separation of precipitated metal, clarification, and sludge disposal. Variations in equipment design affect economy, time and labor requirements, and equipment costs.

In recent years several new companies have been formed that recycle chromium plating wastes into new products, thereby avoiding the long-term potential liabilities of landfill operations. No matter what method of waste disposal is selected, the plater is well advised to know what happens to the wastes and what the liability could be.

Stopoff Media for Selective Plating

During plating, part surfaces that are not to be plated may need to be protected from the solution by stopoff media, such as lacquers, foils, tapes, waxes, and machined reusable fixtures. Stopoff media must adhere well to the metal surface, not become soft at the temperature of the solution or brittle at room temperatures, be resistant to solutions used for cleaning, etching, and plating, and be easy to remove after plating.

Lacquers used to prevent surfaces from being plated can be easily applied by brushing, spraying, or dipping. After plating, the lacquer can be stripped off or dissolved in an appropriate solvent.

Lead sheet, foil, and wire not only provide a positive stopoff but also act as thieves to aid in current distribution. Lead can be pounded into holes, keyways, or slots and trimmed with a sharp knife.

Tapes of several kinds are used as stopoff media. They vary from adhesive tapes backed with lead foil to tapes made of vinyl and other plastics. Lead foil tapes combine a specially compounded lead foil with a highly pressure-sensitive adhesive to provide a quick and convenient stopoff for short runs. The lead backing is useful as a thief in areas of high current density, or it can be lacquered when used in areas of low current density for equalizing current distribution. It is soft enough to conform to various configurations. Vinyl and other plastic tapes are soft and pliable and have extruded edges for providing a lead-free seal on almost any contour.

Sheet Materials. For large production runs, it is convenient to make stop-off forms that can be reused many times. Plastic sheet, generally 0.1 to 0.15 mm (0.004 to 0.006 in.) thick, is excellent for masking simple plates, cylinders, or other configurations. Steel sheet is sometimes substituted for plastic if it is desirable to equalize current distribution. To prevent plating or corrosion of the base metal, the plastic or steel stopoff must adhere firmly to the area being masked. Snug-fitting cylinders can be made to fit inside or outside diameters. To mask areas that are flat or of irregular shape, lacquer may be used to glue the stop-off material to the part; the lacquer may be removed with a thinner after plating.

Waxes. Several waxes designed for use as stopoffs are obtainable commercially. The use of a dip tank, thermostatically controlled to maintain the temperature at 15 to 20 °C (30 to 40 °F) above the melting point of the wax, makes the use of these materials comparatively fast and simple. The portion of the part to be plated can be covered with masking tape to prevent wax from adhering, or, if desired, the whole part can be coated and the wax stripped with a knife from areas to be plated. The wax mixture should have a melting point low enough to allow removal of the bulk with boiling water. Because they evolve poisonous fumes when heated, waxes containing chlorinated naphthalene must be used with exhaust equipment. High-melting-point mineral and vegetable waxes are not dangerous to use.

Decorative Chromium Plating

Revised by: James H. Lindsay, General Motors; Donald L. Snyder, Atotech USA Inc.

Introduction

DECORATIVE CHROMIUM PLATING is different from hard chromium plating in terms of thickness and the type of undercoating used. The average thickness of decorative plating is actually very thin, usually not more than 1.25 μm (50 μin.). A decorative chromium deposit is used primarily for its pleasing blue-white color. Its highly reflective appearance is maintained in service because chromium can resist tarnish, chemicals, scratches, and wear. If the deposit is defect-free, then a level of corrosion resistance also is provided, because the deposit acts as a physical barrier to the environment. Decorative chromium is applied over undercoatings, such as nickel or copper and nickel, which give the chromium bright, semibright, or satin cosmetic appearances. Corrosion protection depends on the choice of undercoating, as well as the type of chromium being applied. Parts made from steel, copper and its alloys, zinc, stainless steel, and aluminum are typically plated with nickel-chromium or copper-nickel-chromium.

Most decorative chromium coatings have been applied using hexavalent chromium processes that are based on chromic anhydride. However, since 1975, trivalent chromium processes have become available commercially. They are increasing in importance because of their increased throwing and covering powers and because they offer environmental advantages. Both systems are considered in detail in this article.

Chromium Electrodeposits

Decorative chromium plating baths generally produce deposits that range from 0.13 to 1.25 μm (5 to 50 μin.) in thickness. These deposits generally reproduce the finish of the substrate, or, in a multilayer system, the undercoating that is applied prior to the chromium layer. Optimum luster of the final chromium deposit is obtained by plating the substrate coating to a uniformly bright condition. If the substrate is nonuniform, grainy, hazy, or dull, then it should be polished and buffed to a uniformly high luster before being plated with chromium. When a final chromium coating over a uniformly bright substrate is hazy in certain areas, these areas can be buffed on a wheel or the coating can be stripped and the substrate replated. Buffing of chromium is not allowed when corrosive service conditions will be encountered.

In addition to being lustrous, the final chromium deposit should cover all significant areas. When there is not adequate coverage, because of an improperly operated chromium bath, the chromium should be stripped, the substrate reactivated, if necessary, and the part replated.

Decorative chromium that has been applied over nickel, the typical undercoating, is readily stripped by immersion in a 1:1 solution of hydrochloric acid. An alternate method involves treating the part anodically in an alkaline cleaning solution. However, this method requires reactivation of the nickel surface prior to replating, which is typically accomplished by immersion in dilute sulfuric or hydrochloric acid. Cathodic, but never anodic, alkaline cleaning can also be used for activation.

Excessively high current densities, improper temperatures, and passivated substrates can produce hazy, nonuniform chromium deposits. Operating conditions for chromium plating should be in the specified ranges. Properly operated nickel baths and other similar precautions also are necessary to ensure uniformly lustrous chromium deposits.

The adhesion of chromium to an active or properly prepared substrate is usually not a problem. However, if chromium is plated on an undercoating that has been improperly applied and has questionable adhesion, then blistering or exfoliation can occur, either immediately after chromium plating or during storage or service. Organizations that generate standards,

such as ASTM, can provide procedures for checking adhesion if a related method has not been specified in the purchase agreement for the part being plated.

Microporosity and Microcracking. The key to the corrosion durability offered by decorative chromium deposits lies in controlling the type, size, and distribution of microdiscontinuities that form in the deposit. These can occur as either pores or cracks. In an outdoor corrosive environment, as well as in accelerated corrosion tests, corrosion has been observed to proceed by galvanic cell action between the nickel and the chromium, with the nickel acting anodically. Microcracks or micropores in the chromium expose the underlying nickel through a uniform, diffuse network of discontinuities. Because the rate of corrosion penetration through the nickel layer is a function of the anodic current density of the corrosion cell, the reduction of current density that is obtained by the increase in exposed nickel area prolongs the time required to penetrate a given thickness of nickel. The advantage of such a system lies in its ability to provide long-term corrosion protection without developing easily visible fine surface pits in the nickel, which eventually become corrosion sites. The use of microdiscontinuous chromium makes the surface pits much smaller, which means that the substrate will be protected from corrosion for a longer time. However, after excessive corrosion, these fine pits will become visible as a haze on the corroded surface.

Chromium deposits, up to a thickness of 0.13 μm (5 μin.), that are obtained from hexavalent processes are somewhat porous. Because porosity decreases with increasing thickness, at approximately 0.5 μm (20 μin.), the deposits become nearly pore-free when plated (Fig. 1). However, because of the hard, brittle nature of the highly stressed chromium deposits, they quickly become cracked during storage or service. These cracks do not improve the corrosion resistance, as do deposits with intentionally developed micropores or microcracks.

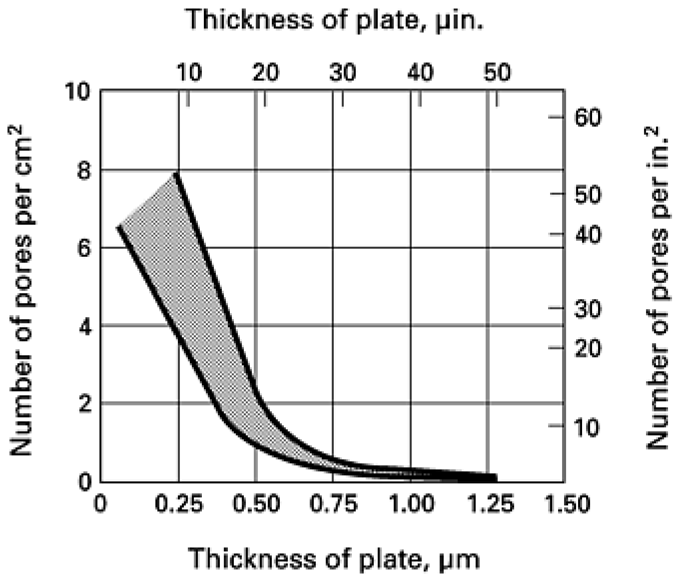


Fig. 1 Porosity in chromium plate as a function of plate thickness. Chromium deposited in low-temperature baths begins to crack at 75 μm (3000 μin.).

Except when special hexavalent chromium processes and conditions are used, hexavalent chromium deposits that are more than 0.5 μm (20 μin.) thick will have visible nondecorative microcracks. In contrast, chromium deposits from trivalent processes are microporous up to thicknesses of 0.5 to 0.6 μm (20 to 25 μin.), above which they become microcracked. Both features enhance the corrosion resistance of the part.

When hexavalent chromium is deposited from solutions operated below 50 °C (120 °F), the deposit will begin to craze when it exceeds 0.5 μm (20 μin.) in thickness, and a macrocrack pattern visible to the unaided eye will appear. This pattern generally has 5 to 10 cracks/cm (12.5 to 25 cracks/in.).

Either microcracked or microporous chromium deposits can be produced by altering the nature of the nickel undercoating. Microporous chromium can be obtained by plating over a thin layer of nickel deposited from a solution containing very fine, nonconductive particles. Chromium will not plate over these particles, which creates a microporous deposit with pore densities proportional to the amount of inert particles and additives in the nickel solution. An average pore density of

10,000 pores/cm^2 (60,000 pores/in^2) is the typical minimum specified for enhanced corrosion resistance. A disadvantage of this process is the addition of an extra nickel plating tank between the bright nickel and the chromium tanks. The pore count is also current-density dependent, and chromium deposits of 0.3 to 0.4 μm (12 to 16 μin.) in thickness have a tendency to bridge over the inert particles and reduce the pore count.

Trivalent chromium deposits provide pore counts of more than 16,000 pores/cm^2 (100,000 pores/in^2), without any special procedures. The pore count also is rather current-density independent.

Another very common method for obtaining microporous chromium deposits is to mildly blast the chromium deposit with an abrasive, such as sand or aluminum oxide. The brittle chromium fractures where it is hit by the particles, thus causing a microporous deposit to form. This method permits the pore count to be varied, based on the amount of particles used, and is independent of current density.

Microporous chromium is the most common microdiscontinuous chromium deposit used in North America to enhance the corrosion resistance of the decorative nickel-chromium type of electrodeposit. Microcracked chromium is somewhat more popular in the rest of the world.

Microcracking can be produced by using a thin layer, approximately 1.25 μm (50 μin.), of a highly stressed nickel deposit between the bright nickel and chromium deposits. Approximately 0.25 μm (10 μin.) of chromium is typically used with this procedure. A crack density of 275 to 790 cracks/cm (700 to 2000 cracks/in.) is typically produced. Thicker chromium deposits are required with other microcracking methods.

Microcracked chromium deposits can be obtained from systems using either a single or a dual specially formulated chromium solution. An example of the latter is duplex chromium. Although single-deposit systems are easier to operate, conditions that favor the formation of microcracks, such as high solution temperature, low chromic-acid concentration, and high fluoride content, usually have an adverse effect on the covering power of the chromium deposit. Duplex chromium systems have resolved this problem by using two successive chromium baths. The first obtains coverage and the second creates the microcrack pattern.

Satisfactory coatings are not too difficult to obtain on parts with relatively simple shapes, but complex parts can present a serious problem because it is difficult to obtain adequately thick chromium in areas of low current density. Auxiliary anodes can be used to increase the thickness in these areas.

Influence of Design on Quality and Cost

The cost of electroplating is often greatly influenced by the complexity of the workpiece. Simple shapes can be processed through all cleaning and plating sequences, with a minimum of approximately 33 μm (1300 μin.) of copper and nickel and 0.25 μm (10 μin.) of chromium, in approximately 50 min. Providing these minimum thicknesses on complex shapes requires longer plating periods, special fixturing, special anodes, and current shields. Plating costs are increased by each of these factors, although buffing and cleaning costs may be unchanged. Equipment and overhead costs per workpiece also increase in direct proportion to the plating time. In addition, the cost of materials is increased, because more metal is plated unnecessarily on projections and other areas of high current density. Figure 2 indicates the approximate increase of plating costs with plating time at a fixed current density.

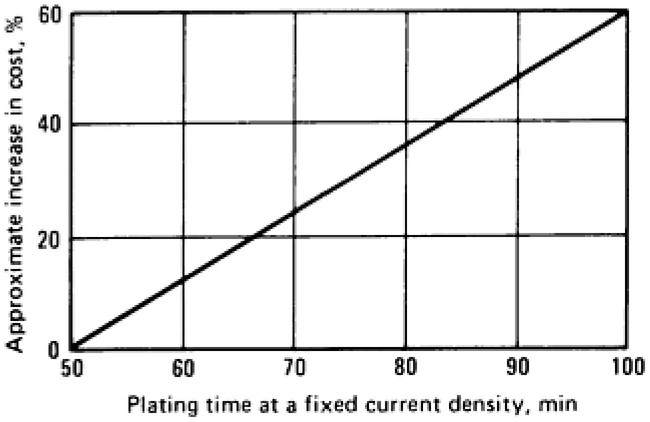
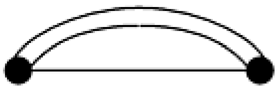
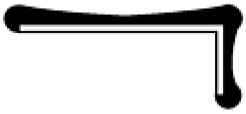
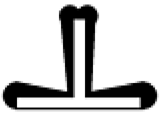
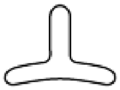
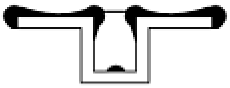
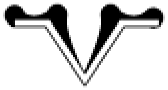
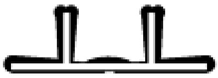
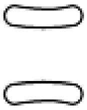
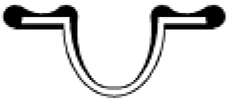
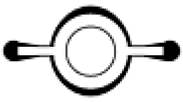


Fig. 2 Plating cost-time relationship

Extreme workpiece complexity can preclude the application of a truly corrosion-protective deposit by conventional plating procedures. The influence of some design features on platability and plating cost are described in Table 1.

Table 1 Influence of design on platability of zinc-base die castings

Design feature	Influence on platability	Better design
	**Convex surface.** Ideal shape. Easy to plate to uniform thickness, especially where edges are rounded.	
	Flat surface. Not as desirable as crowned surface. Use 0.015 mm/mm (0.015 in./in.) crown to hide undulations caused by uneven buffing.	
	**Sharply angled edge.** Undesirable. Reduced thickness of plate at center areas. Requires increased plating time for depositing minimum thickness of durable plate. All edges should be rounded. Edges that contact painted surfaces should have a 0.8 mm ($\frac{1}{32}$ in.) min radius.	
	**Flange.** Large flange with sharp inside angles should be avoided to minimize plating costs. Use generous radius on inside angles and taper abutment.	
	Slots. Narrow, closely spaced slots and holes cannot be plated properly with some metals (e.g., nickel and chromium) unless corners are rounded.	
	**Blind hole.** Must usually be exempted from minimum thickness requirements.	
	Sharply angled indentation. Increases plating time and cost for attaining a specified minimum thickness and reduces the durability of the plated part.	
	Flat-bottom groove. Inside and outside angles should be rounded generously to minimize plating costs.	
	**V-shaped groove.** Deep grooves cannot be plated satisfactorily; should be avoided. Shallow, rounded grooves are better.	
	**Fins.** Increase plating time and costs for attaining a specified minimum thickness and reduce the durability of the plated part.	

	Ribs. Narrow ribs with sharp angles usually reduce platability; wide ribs with rounded edges impose no problem. Taper each rib from its center to both sides and round off edges. Increase spacing, if possible.	
	**Deep scoop.** Increases time and cost for plating specified minimum thickness.	
	Spearlike jut. Buildup on jut robs corners of electroplate. Crown base and round all corners.	
	**Ring.** Platability depends on dimensions. Round corners; crown from center line, sloping toward both sides.	

Note: Distribution of electroplate on design shapes is intentionally exaggerated by solid black outline. Cross-hatched areas indicate part before plating.

Hexavalent Chromium Plating

The first hexavalent chromium plating bath used for decorative plating, sometimes referred to as the conventional bath, consisted of an aqueous solution of chromic anhydride (CrO_3) and a small amount of soluble sulfate ($SO_4^{=}$), referred to as the catalyst. The latter was added as sulfuric acid or as a soluble sulfate salt, such as sodium sulfate. When dissolved in water, the chromic anhydride forms chromic acid, which is believed to exist in the following equilibrium:

$$H_2Cr_2O_7 + H_2O \rightleftharpoons 2H_2CrO_4$$

The ratio of chromic acid to sulfate, generally given as the weight ratio of chromic anhydride to sulfate, governs the current efficiency for chromium metal deposition. The cathode current efficiency also is affected by solution variables, such as concentration of chromic acid, temperature, and content of metallic impurities. The latter variable is an important consideration for commercial operations, because an excessively high content of impurities such as copper, iron, zinc, and nickel seriously affects bath conductivity, cathode current efficiency, and both throwing and covering power, even if the ratio of chromic anhydride to sulfate is within optimum limits for the application.

Most decorative chromium is deposited within these operating limits:

- Chromic anhydride, 200 to 400 g/L (27 to 54 oz/gal)
- Chromic anhydride-to-sulfate ratio, 80:1 to 125:1
- Cathode current density, 810 to 1880 A/m^2 (75 to 175 A/ft^2)

These wide limits encompass a broad variety of decorative applications. As of 1994, the trend is toward using chromic-anhydride concentrations of 250 to 300 g/L (33 to 40 oz/gal) and avoiding more highly concentrated baths and their attendant environmental and recovery concerns. The ratio of chromic acid to sulfate ion is usually maintained at levels near 100:1.

With the development of duplex, microcracked, and crack-free applications, specialized bath compositions and operating conditions have come into use. However, many of these are either proprietary or are not subjects of general agreement. The compositions and operating conditions for a general, additive-free, decorative chromium plating bath and a bright, crack-free bath are given in Table 2.

Table 2 Compositions and operating conditions for two chromium plating baths

Constituent or condition	General decorative bath	Bright, crack-free bath
Chromic acid	250 g/L (33.0 oz/gal)	260-300 g/L (35-40 oz/gal)
Ratio of chromic acid to sulfate	100:1 to 125:1	150:1
Operating temperature	38-49 °C (100-120 °F)	52-54 °C (125-130 °F)
Cathode current density	810 - 1885 A/m^2 (75 - 175 A/ft^2)	2690 - 3230 A/m^2 (250 - 300 A/ft^2)

To meet specific requirements for plating speed, nickel activation, and crack pattern, the chromium anhydride and sulfate concentrations should be properly correlated with temperature and cathode current-density limits. In preparing a bath and establishing operating conditions, these relationships should be considered:

- An increase in the temperature of the bath, except for mixed-catalyst baths, will decrease the cathode efficiency, decrease the number of cracks per unit length, decrease coverage at low current density, increase the limiting current density at which burning occurs, and increase passivating action on nickel.
- An increase in the weight ratio of chromic anhydride to sulfate will decrease the crack density and increase the nickel passivity. The chromium will whitewash (have a milky appearance) when plated over passive nickel.
- An increase in sulfate, at a constant chromic-acid concentration, temperature, and cathode current density, will increase the cathode current efficiency to an upper limit; beyond this point, any further increase in sulfate concentration can cause a decrease in cathode current efficiency.

In dilute chromic-acid solutions containing as low as 150 g/L (20 oz/gal) of sulfate, any small carryover of soluble sulfates from earlier solutions can quickly upset the balance of the solution. However, dilute solutions do have a higher cathode efficiency and a slightly wider bright range, although they require higher tank voltages to maintain desired current density. Even when other plating conditions (such as temperature and current density) are held constant, the plating operation can be seriously disrupted by any change in the ratio of chromic acid to sulfate.

Because there are advantages and disadvantages to using either high or low chromic-acid contents, some compromise is necessary. The size and shape of the article to be plated and the available equipment and power often determine exactly which solution should be used. In decorative chromium plating, all variables must be kept in the proper relationship. Frequent bath analysis and prompt adjustments are essential to maintain balanced conditions.

Mixed-Catalyst Baths. Since the mid-1950s, a number of mixed-catalyst proprietary chromium plating baths have been developed. The advantages of these baths are increased cathode current efficiencies, increased activating action on nickel and stainless steel, improved coverage at low current density, broader bright plating ranges, and improved decorative chromium applications, including dual, microcracked, and bright or dull crack-free.

Mixed-catalyst compositions contain chromic acid, sulfate, and fluorine compounds (frequently, fluosilicate ions) as active ingredients. Proprietary baths, formulated to regulate the concentration of catalyst ions, contain strontium, calcium, or potassium salts, to control the solubility of fluosilicate ions. Details on mixed-catalyst compositions are provided in several U.S. patents and at least one British patent (see "Selected References" at the end of this article). Most control requirements applicable to standard baths also apply to proprietary baths.

With the exception of ratio control, the problems associated with low, medium, or high chromic-acid concentrations in mixed-catalyst baths are the same as those for conventional chromium baths. After optimum conditions are found, the same close control must be maintained to prevent mischromes (absence of plate) in areas of low current density and blue,

matte, or burnt deposits in areas of high current density. Because supplies for mixed-catalyst solutions are more expensive than chromic acid alone, using less-concentrated solutions can provide a cost advantage.

Baths for Microcracked Chromium. Typically, two chromium solutions are used successively to produce microcracked chromium plate. The first chromium solution can either be conventional or proprietary and is operated in a normal manner. A plating time of 8 min is preferred when recessed areas are involved, although plating times of 5 to 6 min are often used. Surging of the current can be used to increase coverage. Composition ranges and operating conditions for nonproprietary, first-plating solutions that are used to plate steel and zinc parts are given in Table 3.

Table 3 Bath compositions and conditions for plating microcracked chromium

Substrate material	Constituents				Chromic anhydride to sulfate ratio	Temperature		Current density	
	Chromic acid		Fluoride						
	g/L	oz/gal	g/L	oz/gal		°C	°F	A/m^2	A/ft^2
First plating bath									
Steel	338-375	45-50	. . .	. . .	100:1	46-52	115-125	1075-1615	100-150
Zinc	375-413	50-55	. . .	. . .	140:1	46-52	115-125	1290-1720	120-160
Second plating bath									
Steel	165-195	22-26	1.5-2.25	0.20-0.30	180:1	43-54	120-130	970-1345	90-125

The second chromium solution is similar to the first and can be either proprietary or nonproprietary. The chromic-acid concentration is lower and fluosilicate ions must be present in the bath to promote cracking. The plating time is approximately the same as in the first solution, 5 to 8 min, and current surging can be used, if desired. Composition ranges and operating conditions for the second chromium bath also are given in Table 3. The plating conditions are governed by the nature of the parts being plated. Solutions for parts having deep recesses should have a higher chromic acid and fluoride content and a lower sulfate content. However, thickness must be weighed against other influences on microcrack formation. For this reason, operating conditions can be established on a firm basis only by actual operation with the parts to be processed. On simple shapes, the second plating bath formulation can be used alone.

The use of a rinse or rinses between the two chromium solutions is not essential to the process, but it may help to avoid control problems, because of drag-out from the first chromium solution into the low-concentration second solution. When used, these rinses can be operated as reclaim tanks to minimize drag-out losses.

Solution Control. Regardless of which chromium bath is used, periodic analyses are required. Information on control procedures is provided in the article "Industrial (Hard) Chromium Plating" in this Volume.

Temperature. All chromium plating solutions require the control of temperature, current density, and solution composition. The exact temperature at which bright, milky, frosty, or burnt deposits occur depends on solution composition and current density. Chromium plating is usually performed within the range of 38 to 60 °C (100 to 140 °F), but the most common operating range is from 46 to 52 °C (115 to 125 °F). At room temperature, the bright plating range is impractically narrow. In a process set up to plate at 50 °C (120 °F) with all variables properly controlled, the temperature need vary only 1.5 or 2 °C (3 or 4 °F) to move the electrodeposit out of the clear, bright range. Consequently,

an accurate temperature controller and facilities for rapid cooling and heating of the bath are essential. Temperature variation outside the bright operating range can either cause an unacceptably high rejection rate or necessitate costly stripping and replating operations. The preheating of heavy parts is necessary to avoid plating solution cooling and temperature fluctuation.

Current Density. The standard sulfate bath is usually operated at 1075 to 1720 A/m^2 (100 to 160 A/ft^2). A current density of about 1075 A/m^2 (100 A/ft^2) is used for solutions maintained at 38 °C (100 °F). A higher current density, sometimes as high as 3230 A/m^2 (300 A/ft^2), is required for solutions operated at 55 °C (130 °F). The choice for a specific use depends on such variables as the complexity of the articles being plated and the equipment available. After the current density has been established, close control must be maintained.

Changes in the ratio of chromic acid to sulfate require compensating adjustments in current density. If the sulfate content is increased (lower ratio), then current density must be increased to maintain full coverage in areas of low current density. If the sulfate content is decreased (higher ratio), then current density must be decreased to prevent burning in areas of high current density.

An increase in temperature may require an increase in current density to ensure full coverage in areas of low current density. A decrease in temperature may require a decrease in current density to prevent gray (burnt) deposits in areas of high current density.

As chromic-acid content increases, higher current densities can be used. The average cathode efficiency of most conventional chromium solutions is about 13% over a wide range of concentration, making it possible to plate for shorter times when using the most concentrated solution. Rectifiers with low ripple, not exceeding 5%, must be used to maintain trouble-free, uniform deposition.

Anodes. In chromium plating, insoluble lead or lead-alloy anodes are almost always used. Chromium metal is supplied by the chromic acid in the electrolyte.

Pure lead anodes are often attacked excessively by idle baths, which causes the formation of a heavy sludge of lead chromate on the bottom of the tank, making pure lead anodes impractical for all but continuous operations. During plating, a coating of lead peroxide forms on the anode. The coating favors oxidation of trivalent chromium at the anode. However, when the bath is idle, the coating dissolves to some extent in the solution, making attack on the anode possible.

To reduce the attack of the chromic-acid bath on the anode, several lead alloys are used. For conventional sulfate baths, 6 to 8% antimonial (Sb) lead is preferred, whereas for solutions containing fluoride, lead alloys with 4 to 7% Sn are used.

For an anode to provide optimum throwing power and coverage, it must be positioned properly in relation to the workpiece and have a continuous, uniform film of lead peroxide on the entire surface. Anodes with crusty surfaces have low conductivity and should be cleaned periodically by wire brushing or alkaline cleaning to ensure proper current distribution. The function of the anode is not only to conduct the plating current, but to oxidize trivalent chromium, which forms at the cathode, back to hexavalent chromium. To accomplish this, the anode area should be adjusted to provide the optimum anode current density for the oxidation necessary to keep the trivalent chromium at the desired level, usually 0.25 to 1.0 g/L (0.033 to 0.13 oz/gal). In decorative chromium plating, an anode-to-cathode area ratio of 2:1 is common for proper reoxidation and balance. If trivalent chromium continues to increase above the desired level, then the anode area should be increased to the point where the trivalent chromium concentration remains stable. Overheating of the bath can occur if the anode area is so small that resistive heating becomes a factor.

Anodes with round cross sections are most commonly used. When maximum anode area is desired, corrugated, ribbed, ridged, and multi-edged anodes are used. The round anode is preferred, because its surface is active on its entire circumference, enabling it to carry higher amperage at lower voltage. The absence of inactive areas on this anode minimizes the formation of lead chromate film, reducing maintenance requirements. If the weight of the anode presents a problem, then hollow, round anodes can be used. Although such anodes provide a 25 to 40% reduction in weight, their current-carrying capacity is less than that of solid anodes.

Anodes are manufactured by extrusion. Contact with the bus bar can be provided by a copper hook homogeneously burned to the extruded anode. Pure nickel, nickel-plated copper, and lead-coated copper are also used for hooks. Several hook styles are used, but the knife-edge hook is preferred. The hook and the top of the anode are covered with plastisol for protection against corrosion by fumes and drag-out drip. Bags typically used to cover the anodes in nickel- and

copper-plating processes should not be used in chromium-plating processes. Roughness that is due to nonuniform anode corrosion is not a problem in chromium-plating operations. Therefore, the resulting particles do not have to be captured by the bags.

Control of Current Distribution. Chromium plating baths have poorer throwing and covering power than most other plating baths. To obtain thickness and coverage in areas of low current density, special auxiliary anodes are sometimes used.

Any workpiece of complex shape constitutes a problem of proper current distribution when nonconforming anodes are used. The current density and the thickness on a workpiece varies from highest on corners, edges, and areas closest to the anode to lowest on recesses and areas distant from the anode. Variations in current density result in differences of cathode efficiency, which accentuate the problems of uneven plate, burning, or complete absence of plate. These problems can be overcome, to some extent, by special racking and shielding techniques, such as:

- Wide spacing of concave parts on rack
- Increasing the distance between workpiece and anode
- Intentional shielding of a projection on one piece with a depression on an adjacent one
- Orienting areas of low current density toward the periphery of the fixture
- Moving the parts in the center of the rack closer to the anodes than those on the periphery of the rack

Improved coverage on areas of low current density can be achieved with striking, that is, plating at high current density for a short period of time. The striking time duration is kept to a minimum, usually 5 to 20 s, to avoid burning. Plating is continued at normal current density after the strike.

Current Shields. A nonconducting plate or panel (current shield) can be mounted on the plating rack to direct current away from areas of high current density or to direct additional current into areas of low current density. Figure 3 illustrates the use of a device to divert some of the current that would otherwise cause excessive current density and possible burning at the work areas closest to the anodes. The position and size of current shields are extremely important for their effective use and can be established best by trial and error. The use of shields, however, is always accompanied by some increase in drag-out.

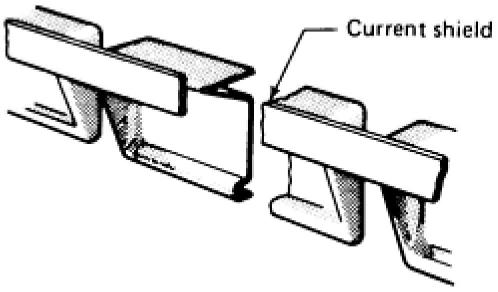


Fig. 3 Current shield

Thieves or robbers made of metal conductors can be positioned near edges and points to shunt away current from these areas. Rods with a diameter of 9.5 to 16 mm ($\frac{3}{8}$ to $\frac{5}{8}$ in.) are sometimes suspended vertically on both ends of a plating rack to prevent burning or rough plate on the edges of the cathodes. Maintenance of robbers is of utmost importance, because they can be the source of large drag-out losses if metal is allowed to build up excessively.

Auxiliary Anodes. Special racks and auxiliary anodes are used only when conventional techniques fail to produce satisfactory coatings. Parts with deep recesses, such as coffeepots and small appliance housings, require auxiliary anodes. Auxiliary anodes are also used for parts with concave surfaces that are difficult to plate uniformly (Fig. 4). Auxiliary anodes also offer potential cost reductions by directing the plate into areas of minimum plate thickness without the penalty of overplating areas of high current density. The use of such devices should be considered even for some parts

that do not present serious problems in meeting specifications for plate thickness. The shapes of many die castings make the use of auxiliary anodes particularly applicable. The current supply for auxiliary anodes can be the same as the major plating circuit with a separate current control, such as a rheostat. Greater flexibility is obtained if a separate current source is used for the auxiliary anodes.

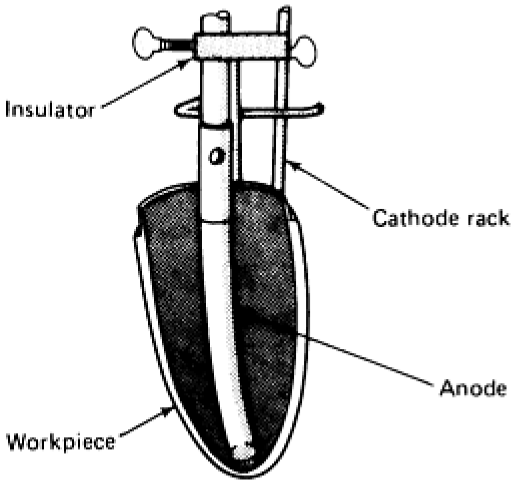


Fig. 4 Use of auxiliary anode for a part difficult to plate to uniform thickness because of concave surface

Auxiliary anodes are mounted on the plating rack, insulated from cathode current-carrying members, and provided with means of direct connection to the anodic side of the electrical circuit (Fig. 5). In still tanks, the connection can simply be a flexible cable equipped with battery clamps. In fully automatic machines, cables are permanently mounted on the carriers, and contact brushes riding on an anode rail are provided to pick up the current. Connections must be positive. An interruption or drastic reduction of current could cause the auxiliary anode to function as a robber or shield, resulting in local interruption of plate, with consequent darkening and loss of adhesion.

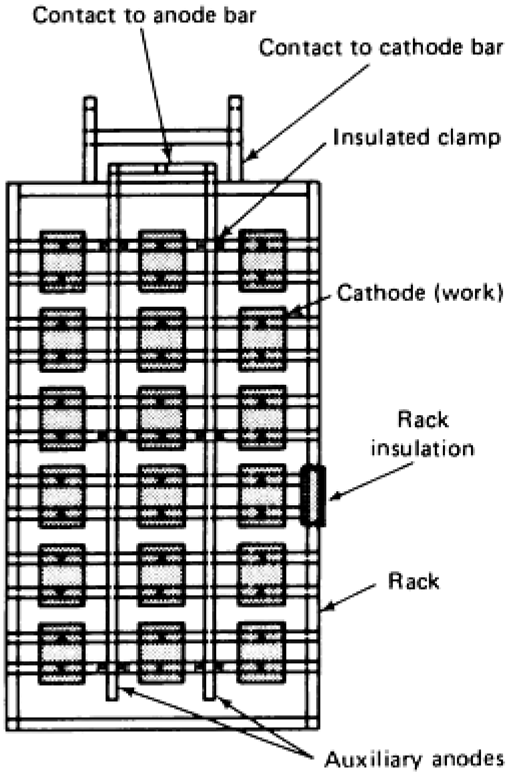


Fig. 5 Rack assembly for decorative chromium plating

The auxiliary anode need not follow the contour of the part closely. An anode-to-work spacing of 13 mm ($\frac{1}{2}$ in.) or slightly more is usually effective. The auxiliary anode mounting must be designed carefully to prevent the anode from interfering with efficient racking and unracking of parts. The anode can be designed for removal while parts are being loaded on the rack, but good contact must be preserved. The auxiliary anode should be held rigidly to prevent it from short circuiting against the cathode.

Some platers connect auxiliary anodes electrically only during chromium plating, a practice that is usually satisfactory for still tank operation, where an anode can be physically mounted immediately before chromium plating. In an automatic plating machine, however, the auxiliary anode should be connected in the acid-copper bath, the nickel bath (at least, in the last half of the tank), and the chromium bath to avoid low thicknesses and low current density effects that could detract from appearance and cause difficulty in chromium plating.

Unless they are made of insoluble material, auxiliary anodes are consumed in plating. Their design should therefore permit easy replacement. Plastisol-coated steel bushings with locking screw heads protected by stop-off lacquer are satisfactory. As anodes become thin, they must be carefully inspected for replacement to avoid shorting out. The diameter of rod used should be as large as is compatible with the size of the part and with construction requirements to minimize the need for frequent replacement. A diameter of 13 mm ($\frac{1}{2}$ in.) is suitable for a variety of parts, ranging from small brackets to instrument panels and moldings. On larger parts, diameters as large as 25 mm (1 in.) or specially cast sections can be useful.

Bags should not be used on auxiliary anodes, because of the resulting solution contamination from drag-in. Avoiding roughness from bare anodes requires serious consideration if the anodes are to be immersed in copper and nickel undercoating baths. Roughness is not a problem when the anode is to be immersed only in the chromium solution. Lead-alloy or steel anode material has been used satisfactorily for this purpose. Graphite rods also have been used to a limited extent. Auxiliary anodes are most frequently made of platinized titanium.

Bipolar anodes are a special variation of auxiliary anodes, in which current is not supplied by external connection. In use, collector plates are mounted at the cathodic end (the end closest to the tank anodes) of the bipolar anode to draw current from a larger section of the bath. Bipolar anodes can be used on conveyorized systems when a special bus bar is unavailable. Although adequate for some purposes, bipolar anodes are usually less effective than other auxiliary anodes and must be carefully maintained to avoid the problems of roughness from loosely adherent deposits of nickel and chromium on the collector plates. The metal deposited on the collector plates is often not reusable.

Stop-offs are not widely used in decorative chromium plating. However, when selective plating is required, a number of materials have the necessary qualifications, including ease of application and removal, resistance to hot cleaners and plating solutions, and excellent adherence and electrical insulation characteristics during use.

Special racks are sometimes used to prevent plating solution from entering tapped holes and areas where plate is not wanted. Figure 6 shows a plated lever with a 7.92 mm (0.312 in.) diameter hole that had to be free of plate. If conventional racking had been used, then the hole would have had to be reamed to remove the plate.

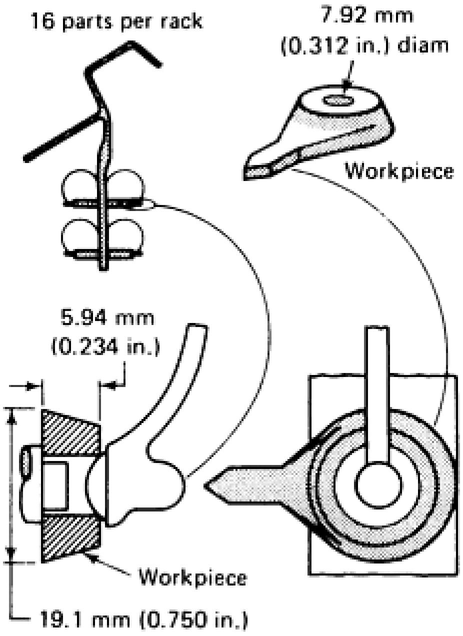


Fig. 6 Racking arrangement to prevent plating of chromium in the hole of a shift lever

Tanks. Chromium plating tanks can be constructed of steel and lined with flexible plastic-type materials, such as fiberglass or polyvinyl chloride (sheet form or sprayed) or lead alloy (6% Sb). Lead-alloy linings should be approximately 3.2 mm ($\frac{1}{8}$ in.) thick. Plastic liners should range in thickness from 2.4 to 4.8 mm ($\frac{3}{32}$ to $\frac{3}{16}$ in.). Plastic linings are preferred, particularly for proprietary baths with fluoride-containing anions, which may have a greater rate of attack on lead linings. Rubber mats or plastisol-coated metal ribs are often used to protect the sides or bottoms of lead-lined tanks from shorts that are due to either accidental contact or being punctured by dropped anodes or workpieces. Lead linings can cause serious bipolarity problems, because of their electrical conductivity.

Heating. Chromium plating tanks can be heated internally or externally. Internal heating, by steam coils or electric immersion heaters, is usually used for small tanks. External heating by heat exchangers is used for large tanks. Coils for internal heating can be made of lead, a lead alloy such as 4% Sn or 6% Sb, or tantalum. Titanium can be used for baths that do not contain fluoride ions. Immersion heaters should be quartz-covered. Heat exchangers can be made of tantalum, lead alloy (4% Sn or 6% Sb), high-silicon cast iron, or heat-resistant glass. Tantalum is preferred for heating coils or heat exchangers when proprietary solutions containing fluoride ions are used, because titanium is attacked by the fluoride. Consultation with vendors on specific material/process compatibility is suggested.

Plating Cycles. Typical system cycles for the application of six decorative chromium plating systems to identical workloads are given in Table 4. Each system is identified by the specific combination of metals successively deposited, the total thickness of plate, and the total plating time. The plating times and power requirements listed in Table 4 are theoretical values for perfect coverage. In practice, these values would be considerably higher to ensure adequate plate thickness in all areas. Table 5 provides the requirements for the design of several installed machines for the continuous plating of zinc die castings of average complexity. The higher-than-normal designed current density is related to potential future needs that exceed present requirements.

Table 4 Typical system cycles

System	Cycles	Total plate		Total time, min[a]
		μm	μin.	

Cu + Ni + Cr	A, B, D, F	50	1970	48
Cu + Cr	A, B, F	20	790	14
Ni + Cr	D, F	30	1180	36
Ni + Cr + Cr	D, G	32	1260	41.5
Ni + Ni + Cr	C, E, F	30	1180	36
Ni + Ni + Cr + Cr	C, E, G	32	1260	41.5

Operating parameters	
A: Copper strike	
Current density	325 A/m^2 (30 A/ft^2)
Plating time	2 min
Heat[(b)]	49-65 °C (120-150 °F)
Filtration	Yes
Agitation	Optional
B: Acid copper plate, high speed, bright (20 µm, or 790 µin.)	
Current density	430 A/m^2 (40 A/ft^2)
Plating time (100% efficiency)	10 min
Heat[(b)]	21-27 °C (70-80 °F)
Filtration and agitation	Yes
C: Nickel plate, semibright (23 µm, or 900 µin.)	
Current density	430 A/m^2 (40 A/ft^2)
Plating time(100% efficiency)	26 min

Heat[b]	55-65 °C (130-150 °F)
Filtration	Yes
Agitation	Usually
D: Nickel plate, bright (30 µm or 1180 µin.)	
Current density	430 A/m^2 (40 A/ft^2)
Plating time (100% efficiency)	34 min
Heat[b]	55-65 °C (130-150 °F)
Filtration	Yes
Agitation	Usually
E: Nickel plate, bright (8 µm, or 315 µin.)	
Current density	430 A/m^2 (40 A/ft^2)
Plating time (100% efficiency)	34 min
Heat[b]	55-65 °C (130-150 °F)
Filtration	Yes
Agitation	Usually
F: Chromium plate (0.3 µm, or µin.)	
Current density	1550 A/m^2 (144 A/ft^2)
Plating time	
Conventional (10% efficiency)	2 min
High speed (25% efficiency)	54 s
Heat[b][c]	46-65 °C (115-150 °F)

Filtration and agitation	No
Ventilation[d]	Yes
G: Chromium plate, microcracked (0.64 μm, or 25 μin.)	
Current density	1550 A/m^2 (144 A/ft^2)
Plating time (25% efficiency)	2.5 min
Heat[b][c]	45-65 °C (115-150 °F)
Filtration and agitation	No
Ventilation[d]	Yes

(a) Power requirements and plating times given are theoretical values for perfect coverage. In practice, these values would be approximately doubled to ensure adequate thickness of plate in all areas. Table 5 has data for practical conditions.

(b) For operating temperature indicated.

(c) Cooling as well as heating may be required.

(d) Chemical suppressant (mist or spray) may be used in addition to ventilation.

Table 5 Design basis of equipment for continuous chromium plating of zinc-base die castings

Metal deposited	**Designed current density**		**Minimum thickness of plate**		**Nominal thickness of plate**		**Plating time, min**
	A/m^2	**A/ft^2**	**μm**	**μin.[a]**	**μm**	**μin.**	
Copper cyanide strike	1075	100	. . .	. . .	0.25	10	3-4
Bright copper	320	30	15	590	20	790	25-30
Semibright nickel	810	75	15	590	20	790	30
Bright nickel	1075	100	5	197	7.5	295	17
First chromium	2150	200	0.3	12	0.5	20	6.5

Second chromium	1615	150	0.25	10	0.5	20	6.5

(a) On parts of moderate complexity

Maintenance. The importance of proper solution maintenance and electrical, mechanical, and other equipment used in plating processes cannot be overemphasized. Table 6 identifies the daily, weekly, monthly, and annual inspection and correction operations that should enable the setup of an adequate maintenance program for chromium plating.

Table 6 Chromium plating maintenance schedule

Frequency	Action
Daily	Fill plating tank with solution from save-rinse and boil-down tanks.
	Stir solution thoroughly, using low-pressure air agitation.
	Check solution for chromic acid, sulfate, and anti-spray additives; make corrective additions.
	Check temperature controls for satisfactory operation; adjust temperature to proper range.
	Inspect plating racks; repair as necessary.
	Check ground lights to see that plating circuits are clear; do not start plating until grounds are clear.
	Put dummy cathodes in tanks and electrolyze solutions at maximum voltage for 15 to 30 min at start of each day.
	Check hull cell.
Weekly	Boil down the save-rinse solution.
	Check auxiliary catalyst; make additions as necessary.
Monthly	Check solution for metallic impurity content (iron, zinc, copper, nickel).
	Clean and straighten anodes.
	Check solution for trivalent chromium content.
Annually	Check all ammeters and ampere-hour meters.
	Inspect and adjust all temperature controllers.

	Clean and repair outside of all tanks; clean and repair all ventilation hoods and ducts.
	Pump out solution, remove sludge. Clean and inspect tank and heating coil; repair as needed. Disconnect all bus bar connections; clean, draw-file and reconnect, including all anode and cathode joints. Inspect anodes; clean, straighten or replace as required.

Troubleshooting. Plating problems can still develop, even when proper maintenance is used. Some typical plating problems and solutions are given in Table 7. Examples of actual problems and solutions used with a variety of chromium-plated parts are given in Table 8.

Table 7 Chromium plating problems and corrections

Defect	Possible cause	Possible remedy
Poor covering power or low deposit thickness	Temperature too high	Adjust temperature to standard range.
	Current density too low	Increase current density.
	Low chromic acid	Adjust chromic acid to standard range.
	Fluoride catalyst too high	Reduce concentration (by dilution).
	Low chromic acid to sulfate ratio	Adjust ratio.
	Poor electrical contact	Correct electrical contact.
	Bath contamination	Remove impurities.
Burning in high current density areas	Temperature too low	Adjust temperature to standard range.
	Current density too high	Reduce current density.
	Chromic acid low	Raise chromic acid.
	High chromic acid/sulfate ratio	Adjust ratio.
	Fluoride catalyst too low	Adjust concentration of fluoride catalyst.
Deposit color nonuniform	Underlying surface not clean or active	Remove any interfering films and provide active surface.
	Bipolarity during entrance to chromium	Enter bath with precontact (live entry).

	Bath contamination by metallic impurities	Analyze bath, remove impurities.

Table 8 Case histories of plating problems

Condition	Cause and correction
Passivation	Nickel-plated business machine parts were stored submerged in cold water to await barrel chromium plating. Although these parts were acid activated before chromium plating, chromium coverage was poor to nil on parts that had been stored for only a few hours. To remedy the problem, parts were stored submerged in a 10% solution of potassium bitartrate (cream of tartar). After several days of storage, the parts could be electrolytically reactivated and barrel chromium plated satisfactorily.
Burning	Although bath composition and temperature were carefully controlled, burnt chromium deposits occurred on die castings plated at moderate amperage. This resulted from nonuniform distribution of current caused by the corrosion of mounting blocks attaching the bus bar to the anode bar. The situation was corrected by welding the bus bar to the anode rail, eliminating mounting blocks.
Poor electrical contact	L-shaped die-cast frames approximately 0.09 m^2 (1 ft^2) in area, although plated in identical racks in an automatic plating machine,exhibited nonuniformity of plate and, in some racks, burnt deposits. This was found to be caused by variations in current from rack to rack in the plating machine. To correct this, mechanical joints were eliminated from the electrical circuit. The mechanical joints were replaced by welding cables from the carrier contact brushes to the rack mounting bar.
Mischromes	Mischromes (absence of chromium on certain areas) occurred on die-cast window frames that occupied the lower portions of racks during plating in a full-return-type automatic plating machine. These defects were caused by the presence of short anodes at the exit end of the nickel plating tank. Replacement with anodes of the correct length solved the problem.
Inadequate rinsing	Inadequate rinsing after chromium plating, which failed to remove small amounts of bath impurities,resulted in nonuniform appearance of the plate on zinc die castings. The parts were given a hot rinse at 93 °C (200 °F) before customary room-temperature rinses to remove bath impurities.

Trivalent Chromium Plating

The use of the trivalent chromium ion, instead of the hexavalent ion, in solution to deposit chromium has been of interest for many years. The first commercially successful decorative trivalent chromium process began in England in 1975 and in the United States in 1976. Environmental, safety, and productivity advantages have been the driving forces for the commercialization of trivalent chromium processes.

Hexavalent chromium ions are also considered carcinogenic and can cause skin ulcerations. The trivalent chromium ion is estimated to be about 100 times less toxic than hexavalent chromium ions.

Trivalent chromium processes have reduced misting to the extent that scrubbers, such as those used with hexavalent chromium processes, are presently not required to meet federal and state air-quality discharge standards. Waste-treatment costs are reduced by a factor of 10, because less than one-tenth of the chromium contained in hexavalent processes is used in the trivalent process (8 to 23 g/L, or 1 to 3 oz/gal, versus 115 to 300 g/L, or 15 to 40 oz/gal). In addition, the solution drains faster, so that less solution is removed with the parts. Finally, the chromium in the rinse water is already in the trivalent state, which eliminates the expensive and sludge-volume-building reduction step required with hexavalent chromium ions.

Some of the trivalent chromium processes plate up to three times faster than hexavalent chromium processes. This increases productivity in some shops. Increased throwing and covering powers, lack of burning, and tolerance to current interruptions and ripple also reduce rejects and can increase the allowable number of parts on a rack.

One of the main difficulties with the development of trivalent chromium baths was the formation of hexavalent chromium at the insoluble anodes during plating. Hexavalent chromium ions are a contaminant in trivalent chromium processes. They initially cause a poor deposit appearance and eventually result in the cessation of plating.

Two well-known proprietary approaches were developed to address the problem of hexavalent chromium formation during plating. The oldest and most frequently used technique incorporates several lines of defense against hexavalent chromium ions. Under normal operating conditions, hexavalent chromium cannot form. If it does manage to get into the plating solution, then it is reduced to the trivalent state, which eliminates it as a contaminant. This technique is referred to as the single-cell process, in contrast to the second technique, which isolates the insoluble graphite anodes from the trivalent-chromium-containing plating solution to restrict the formation of hexavalent chromium.

This second technique, commonly referred to as the double-cell, or shielded anode, method, uses an ion-selective membrane to create a barrier around the anode. Conventional lead anodes are used in a 10% sulfuric-acid electrolyte. The membrane keeps the trivalent chromium from contacting the anode, thereby preventing the formation of hexavalent chromium.

Solution Compositions. Depending on the process used and its operating conditions, the trivalent chromium ion content typically ranges from 5 to 20 g/L (0.67 to 2.67 oz/gal). It is introduced as a water-soluble salt and forms a stable specie upon combining with the stabilizing agents/catalysts. These agents permit the trivalent chromium ion to be stable in solution until it is plated out at the cathode. However, the stability process is not strong enough to interfere with the normal precipitation sequence used with chromium during waste treatment.

In comparison to hexavalent chromium solutions, which have good conductivity, the conductivity of the relatively high-pH and low-metal-content trivalent plating solution is increased by the addition of conductivity salts/buffers. Lower amperes but higher volts are required for trivalent chromium processes, compared with hexavalent chromium process requirements. Surfactants are added to reduce the surface tension of the solution for mist suppression, as well as to act as additives in the plating operation.

Solution Operation. The typical operating conditions for trivalent chromium processes are summarized in Table 9. High current density spiking at the onset of plating increases the already excellent covering and throwing powers of trivalent chromium processes, when compared with those of hexavalent processes. In general, wherever nickel can be plated, trivalent chromium can be plated. Hexavalent chromium processes fall short, particularly around holes and slots and in low current density areas. Process control, while plating at high current densities, is not a serious concern for trivalent processes, because they have less tendency to produce burnt deposits, compared with hexavalent processes. However, some earlier trivalent processes did produce thick deposits, over 1.3 μm (50 μin.). This thickness is sufficient to produce macrocracking. The cathode efficiency decreases with increasing current density. Therefore, the plating speed does not increase proportionally with an increase in current density.

Table 9 Typical operating conditions for trivalent chromium processes

Parameter	Value
pH	2.3-4.0
Temperature	27-50 °C (80-122 °F)
Current density	
Cathode	430-1400 A/m^2 (40-130 A/ft^2)
Anode	540 A/m^2 (50 A/ft^2)

Agitation	Mild air
Rectifier voltage	6-15 V
Deposition rate	
Single-cell process	0.20-0.25 μm/min (8-10 μin./min)
Double-cell process	0.08-0.10μm/min (3-4 μin./min)

Once the operating range has been established for a particular plating installation, the pH and temperature must be controlled well, because they influence plating speed, covering power, and color. The buffering ability of the solution is strong enough that large pH fluctuations do not occur. As the pH increases, the plating rate decreases, but the covering power increases. In general, trivalent chromium deposits do not have the blue-white color of hexavalent chromium deposits. Generally, they have a deeper, slightly darker appearance. However, the newer trivalent processes can produce deposits very close in appearance to hexavalent chromium deposits. In most cases, the color difference is noticeable only when the part is placed next to a hexavalent chromium-plated part.

Temperature. Depending on the process selected, either cooling or heating might be required for temperature control to maintain a bath at desired operating parameters. When lower operating temperatures are desired, some degree of cooling might be required to offset the power used for deposition. Cooler operating temperatures increase the covering power of the process, but slightly darken the color.

Anodes and Agitation. Anode current density should be maintained below 540 A/m^2 (50 A/ft^2) to promote anode life and consistent bath operation. The insoluble graphite anode used in the single-cell process should last indefinitely, if it is not physically damaged. Lead anodes will form protective insoluble films as long as the anodic current density is properly maintained in the double-cell process, resulting in a limited production of lead salts. Mild and uniform air agitation is used around the parts to assist in obtaining metal distribution and appearance.

Contamination Control. The major contributor to a change in appearance of the trivalent chromium deposits is solution contamination. Trivalent chromium solutions are much more sensitive to bath contamination, but are much more easily purified than are hexavalent chromium solutions. Organic contaminants, a minor problem, are typically removed by filtration through carbon. Organic contamination appears in the chromium deposit as white smears that resemble a pattern typically associated with poor cleaning.

Inorganic contaminants, such as iron, nickel, copper, and zinc, cause the deposit to have dark streaks and/or to lose covering power. The newest and easiest method for removing inorganic impurities is to continuously purify the plating solution by passing it through a specially designed resin. Using this technique, the inorganic impurity levels can be maintained much below the level that will cause any operational or appearance problems.

Three other general methods can be used to remove these contaminants. The slowest approach is to plate them out whenever the bath is not being used for production. An alternative method is to set a small plating unit, connected by a recirculating pump, to the main plating tank. Dummy sheets are used in the small unit to continuously plate out impurities without interrupting production.

A third method that is available for some processes is to use chemical purifiers that can remove large quantities of inorganic contaminants during one or two hours of downtime. Although this method is very fast, it has two disadvantages. The chemical precipitates the impurities within the plating bath. The precipitation itself does not cause any plating problems, but the precipitates could adhere to the parts as they leave the tank, causing them to have an objectionable white film. If chemical purifiers are improperly used, then the solution chemistry can be affected, resulting in a darker deposit and poorcoverage.

Plating Problems and Corrections. Some of the plating problems experienced with trivalent chromium baths can be ascribed to common operational problems. Poor coverage is typically due to low pH, high temperature, low current density, or lead or zinc contamination. Dark clouds or smudges on the work can arise from metallic contamination or low complexant or surfactant concentrations. White patches on the work can be caused by high concentrations of surfactants or other organics, lead contamination, or high wetting agent concentration in the nickel bath used prior to chromium plating.

Trivalent and Hexavalent Deposit Comparisons. The choice of chromium plating solution, whether hexavalent or trivalent, depends on the individual application under consideration. The characteristics of these processes are compared in Table 10.

Table 10 Trivalent and hexavalent chromium comparison

Parameter	Trivalent chromium	Hexavalent chromium
Throwing power	Good	Poor
Covering power	Good	Poor
Current interruptions	Completely tolerant	Intolerant
Rectifier ripple	Completely tolerant	Intolerant
Deposit structure (microdiscontinuous):		
Single cell	Microporous and microcracked	Special processes required
Double cell	Microporous	. . .
Ease of burning	Very difficult	Easy
Ease of rinsing	Easy	Moderate
Color buffing requirement	Never	Occasional
Filtering requirement:		
Single cell	Only after purification	Never
Double cell	Daily with carbon	. . .
Conditioning/dummying:		
Single cell	Never	Start up to each day

Double cell	Start up and routinely	. . .
Passivity of nonplated surfaces	Needs post dip	"Chromate" surfaces
Color of deposit:		
Single cell:		
Ambient temperature	Pewter or stainless steel	Blue-white
Elevated temperature	Metallic white	. . .
Double cell:		
Elevated temperature	Metallic white	. . .
Waste treatment	Easy	Moderate
Relative safety	Similar to nickel	Similar to cyanide
Misting	Almost eliminated	Heavy
Odor	Almost eliminated	Strong and dangerous

Nickel Plating

Revised by George A. Di Bari, International Nickel Inc.

Introduction

THE NICKEL PLATING PROCESS is used extensively for decorative, engineering, and electroforming purposes because the appearance and other properties of electrodeposited nickel can be varied over wide ranges by controlling the composition and the operating parameters of the plating solution. Decorative applications account for about 80% of the nickel consumed in plating; 20% is consumed for engineering and electroforming purposes. Autocatalytic (electroless) nickel plating processes are commercially important but are outside the scope of this section. The annual worldwide consumption of nickel for electroplating is approximately 180 million pounds (81,700 metric tons) and accounts for 11 to 12% of world nickel consumption. Some basic information about nickel and common nickel salts for plating is given in the following table:

Nickel	Atomic weight 58.69. Valency 2. Specific gravity 8.90. Plating rate, at 100% cathode efficiency, 1.095 g/A · h (0.039 oz/A · h)

Nickel salts	
Nickel chloride	Formula is $NiCl_2 \cdot 6H_2O$. Contains 24.7% Ni.
Nickel sulfate	Formula is $NiSO_4 \cdot 6H_2O$. Contains 22.3% Ni.
Nickel sulfamate	Formula is $Ni(NH_2SO_3)_2$. Contains 23.2% Ni.
Nickel carbonate	Formula is $NiCO_3$. Contains about 46% Ni.

Decorative Plating. Modern decorative nickel plating solutions contain organic additives that modify the electrocrystallization process so that mirror-bright, highly-leveled nickel coatings are deposited directly from solution. Prior to the introduction of "organic" baths, decorative nickel coatings were produced by polishing nickel-plated parts mechanically, a practice that continued from 1870 to about 1945. Thin layers of chromium were electrodeposited over polished nickel coatings for the first time in 1927 to prevent the "yellowing" or tarnishing of nickel in outdoor atmospheres, and that practice continues with the "as-deposited" bright nickel coatings now available. An effort to develop improved decorative, electroplated nickel coatings began in the late 1940s and led to the development of multilayer nickel coatings (early 1950s) and microdiscontinuous chromium coatings (mid- to late 1960s). Modern multilayer nickel coatings in combination with microdiscontinuous chromium are capable of protecting and enhancing the appearance of most metals and alloys, plateable plastics, and other materials for extended periods of time.

Engineering Plating. The engineering applications of nickel plating include those where a fully bright appearance is not required. Engineering nickel deposits are usually sulfur-free and matte in appearance. These deposits may be specified to improve corrosion and wear resistance, to salvage or build up worn or undersized parts, to modify magnetic properties, to prepare surfaces for enameling or for organic coating, to function as diffusion barriers in electronic applications and for other purposes. Engineering applications exist in the chemical, nuclear, telecommunications, consumer electronics, and computer industries.

Electroforming. Nickel electroforming is electrodeposition applied to the manufacture of nickel products of various kinds, and it differs from electroplating in one major respect. In electroplating, the coating is metallurgically bonded to the substrate and is an integral part of the surface. In electroforming, nickel is deposited onto a mandrel or mold nonadherently so that the nickel can be separated from the mandrel when it is removed from the plating solution. Electroforming applications include the fabrication of molds and dies, mesh, and other products that are indispensable to operations in the textile, aerospace, communication, electronics, automotive, photocopying, and entertainment industries. Additional information is available in the article "Electroforming" in this Volume.

Basic Process Considerations

Before describing decorative, engineering, and electroforming plating processes, some basic facts are reviewed that make it possible to control the nickel plating process, predict the amount of nickel deposited, and estimate nickel coating thickness.

The Basic Process. Nickel plating is similar to other electroplating processes that employ soluble metal anodes. It requires the passage of direct current between two electrodes that are immersed in a conductive, aqueous solution of nickel salts. The flow of direct current causes one of the electrodes (the anode) to dissolve and the other electrode (the cathode) to become covered with nickel. The nickel in solution is present in the form of divalent positively charged ions (Ni^{++}). When current flows, the positive ions react with two electrons ($2e^-$) and are converted to metallic nickel (Ni^0) at the cathode surface. The reverse occurs at the anode, where metallic nickel is dissolved to form divalent positively charged ions, which enter the solution. The nickel ions discharged at the cathode are replenished by those formed at the anode.

Hydrogen Evolution and Cathode Efficiency. The discharge of nickel ions is not the only reaction that can occur at the cathode; a small percentage of the current is consumed in the discharge of hydrogen ions from water. This reduces the cathode efficiency for nickel deposition from 100% to 92 to 97%, depending on the nature of the electrolyte. The discharged hydrogen atoms form bubbles of hydrogen gas at the cathode surface.

Anode Efficiency. Under normal conditions the efficiency of dissolution at the anode is 100% and no hydroxyl ions are discharged from the water. If the pH of the solution is too high, however, hydroxyl ions may be discharged in preference to the dissolution of nickel, and oxygen will be evolved. Under those conditions, the nickel anode becomes passive and ceases to dissolve nickel. Activated nickel anode materials are available commercially that resist the onset of passivity and replenish the solution with nickel ions over a wide range of plating conditions.

Nickel Ion and pH Changes. Under normal operating conditions, the nickel ion concentration and the pH of the solution will slowly increase as plating proceeds. The rate of increase in nickel ion concentration depends on the difference between cathode and anode efficiencies. Because cathode efficiencies may vary from 92 to 97%, whereas anode efficiency is always 100%, the rate of increase in nickel ion concentration depends on the nature of the plating solution and not on the type of soluble nickel anode material that is used.

Faraday's Law for Nickel. The amount of nickel deposited at the cathode and the amount dissolved at the anode are directly proportional to the product of the current and time (Faraday's Law). The proportionality constant is equal to M divided by nF, where M is the molecular weight, n is the number of electrons involved in the electrochemical reaction, and F is Faraday's constant, equal to 96,500 coulombs (ampere-seconds). For nickel, the constant is 1.095 g/A · h. The constant for nickel deposition is calculated assuming that cathode efficiency is 100%; because a small part of the current goes to discharge hydrogen, the constant must be adjusted by multiplying by the cathode efficiency (for example, $1.095 \times 0.955 = 1.046$).

Faraday's Law for nickel may be expressed as $m = 1.095\ (a)\ (l)\ (t)$, where m is the amount of nickel deposited at the cathode (or dissolved at the anode), in grams; l is the current that flows through the plating tank, in amperes; t is the time that the current flows, in hours; and a is the current efficiency ratio for the reaction of interest. In almost all cases, the anode efficiency is 100% (a = 1). The cathode efficiency may vary from 92 to 97% and accordingly, a will vary from 0.92 to 0.97.

Average Nickel Thickness. The nickel electrodeposition data compiled in Table 1 have been calculated on the assumption that cathode efficiency is 95.5%, which approximates the case for most nickel plating solutions. From the table, one can estimate the time required to deposit a specified thickness of nickel at a specified current density. If the plating process is operated at 5 A/dm^2, for example, it takes about 20 min to deposit a nickel coating with an average thickness of 20 μm.

Table 1 Nickel electrodeposition data

Deposit thickness, μm	Weight per unit area, g/dm^2	Amp hours per unit, A · h/dm^2	Time (min) required to obtain deposit at current density (A/dm^2) of:									
			0.5	1	1.5	2	3	4	5	6	8	10
2	0.18	0.17	20	10	6.8	5.1	3.4	2.6	2.0	1.7	1.3	1
4	0.36	0.34	41	20	14	10	6.8	5.1	4.1	3.4	2.6	2
6	0.53	0.51	61	31	20	15	10	7.7	6.1	5.1	3.8	3.1
8	0.71	0.68	82	41	27	20	13	10	8.2	6.8	5.1	4.1
10	0.89	0.85	100	51	34	26	17	13	10	8.5	6.4	5.1

12	1.1	1.0	120	61	41	31	20	15	12	10	7.7	6.1
14	1.2	1.2	140	71	48	36	24	18	14	12	8.9	7.1
16	1.4	1.4	160	82	54	41	27	20	16	14	10	8.2
18	1.6	1.5	180	92	61	46	31	23	18	15	11	9.2
20	1.8	1.7	200	100	68	51	34	26	20	17	13	10
40	3.6	3.4	410	200	140	100	68	51	41	34	26	20

Note: Values are based on 95.5% cathode efficiency.

The data in Table 1 provide a means of estimating the average coating thickness. The actual thickness on an individual part depends on the uniformity of current density distribution. Under practical plating conditions, the thickness of the nickel on a batch of parts is measured in one or more trials, and adjustments are made, if necessary, as to how the parts are placed in the tank relative to the anode and how they are positioned on the plating racks. In some cases, shields and auxiliary anodes may be required to obtain acceptable thickness uniformity. Shields are made of nonconductive materials and may be placed on the anode, on the cathode, or between electrodes to block or control current flow. Auxiliary anodes may be either soluble or insoluble, and they are placed closer to the cathode than principal anodes so as to direct current to a recessed or relatively small area on the cathode. With care, current density distribution and coating thickness can be made reasonably uniform and predictable.

The Watts Solution and Deposit Properties

The nickel plating solution described by Watts in 1916 was a major milestone in the development of nickel plating technology. The solution eventually replaced all others in use up to that time. It remains the basis of most decorative nickel plating processes, and it is used for engineering applications and for electroforming. It is operated at elevated temperatures and is capable of being used with high current densities.

The composition of the modern Watts bath is included in Table 2. The constituents of the Watts bath have several functions.

- *Nickel sulfate* is available in commercially pure forms, is relatively inexpensive, and is the major source of the nickel ions in solution. A high nickel sulfate concentration is used when high current densities are required.
- *Nickel chloride* serves primarily to improve anode corrosion, but it also increases conductivity and uniformity of coating thickness distribution. Excessive amounts of chloride increase the corrosivity of the solution and the internal stress of the deposits. (*Internal stress* refers to forces created within the deposit as a result of the electrocrystallization process and/or the codeposition of impurities such as hydrogen, sulfur, and other elements. Internal stress is either tensile [contractile] or compressive [expansive] and may cause plating problems if excessively high.)
- *Boric acid* is used in nickel plating solutions for buffering purposes; its concentration may affect the appearance of the deposits. The deposit may first become frosty in high current density areas at 30 g/L (4 oz/gal) of boric acid, and then as the boric acid concentration approaches 15 to 23 g/L (2 to 3 oz/gal), the deposit may be burnt and cracked. No effect on appearance is observed at high boric acid concentrations up to saturation (45 g/L, or 6 oz/gal).
- *Wetting agents or surfactants,* formulated specifically for nickel plating solutions, are almost always added to control pitting. Their function is to lower the surface tension of the plating solution so that air

and hydrogen bubbles do not cling to the parts being plated.

Table 2 Nickel electroplating solutions

Electrolyte composition, [(a)] g/L	**Watts nickel**	**Nickel sulfamate**	**Typical semibright bath[(b)]**
Nickel sulfate, $NiSO_4 \cdot 6H_2O$	225 to 400	. . .	300
Nickel sulfamate, Ni $(SO_3NH_2)_2$	. . .	300 to 450	. . .
Nickel chloride, $NiCl_2 \cdot 6H_2O$	30 to 60	0 to 30	35
Boric acid, H_3BO_3	30 to 45	30 to 45	45
Operating conditions			
Temperature, °C	44 to 66	32 to 60	54
Agitation	Air or mechanical	Air or mechanical	Air or mechanical
Cathode current density, A/dm^2	3 to 11	0.5 to 30	3 to 10
Anodes	Nickel	Nickel	Nickel
pH	2 to 4.5	3.5 to 5.0	3.5 to 4.5
Mechanical properties[(c)]			
Tensile strength, MPa	345 to 485	415 to 610	. . .
Elongation, %	10 to 30	5 to 30	8 to 20
Vickers hardness, 100 gram load	130 to 200	170 to 230	300 to 400
Internal stress, MPa	125 to 210 (tensile)	0 to 55 (tensile)	35 to 200 (tensile)

(a) Antipitting agents formulated for nickel plating are often added to control pitting.

(b) Organic additives available from plating supply houses are required for semibright nickel plating.

(c) Typical properties of *bright* nickel deposits are as follows: elongation, 2 to 5%; Vickers hardness, 100 gram load, 600 to 800; internal stress,

12 to 25 MPa (compressive).

Good-quality nickel deposits can be produced within the ranges of solution pH, temperature, and current density given in Table 2. Although the maximum current density given in the table is 11 A/dm^2, higher rates of plating are possible with increased solution agitation and flow rates.

The physical and mechanical properties of nickel deposited from Watts solutions are affected by the operating conditions and chloride content of the solution as shown in Fig. 1, 2, 3, and 4. Figures 1, 2, and 3 show how pH, current density, and temperature affect properties such as internal stress, hardness, percent elongation, and tensile strength. Figure 4 shows how the chloride content affects those properties; the maximum ductility and softest deposits are produced when 25% of the nickel in solution is present as nickel chloride. Reference 2 is a comprehensive source of mechanical property data for electrodeposited nickel, nickel alloys, and nickel composite coatings.

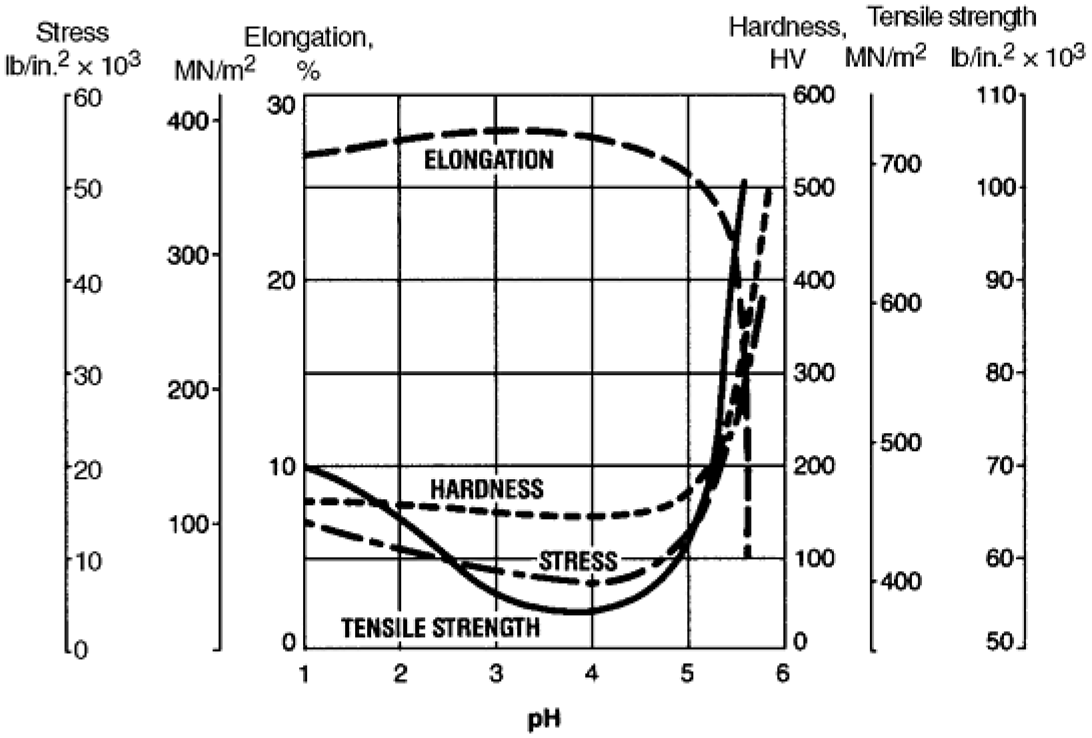


Fig. 1 Variation in internal stress, tensile strength, ductility, and hardness with pH. Watts bath operated at 54 °C and 5 A/dm^2. Internal stress is tensile (indicated by a positive number). Source: Ref 1

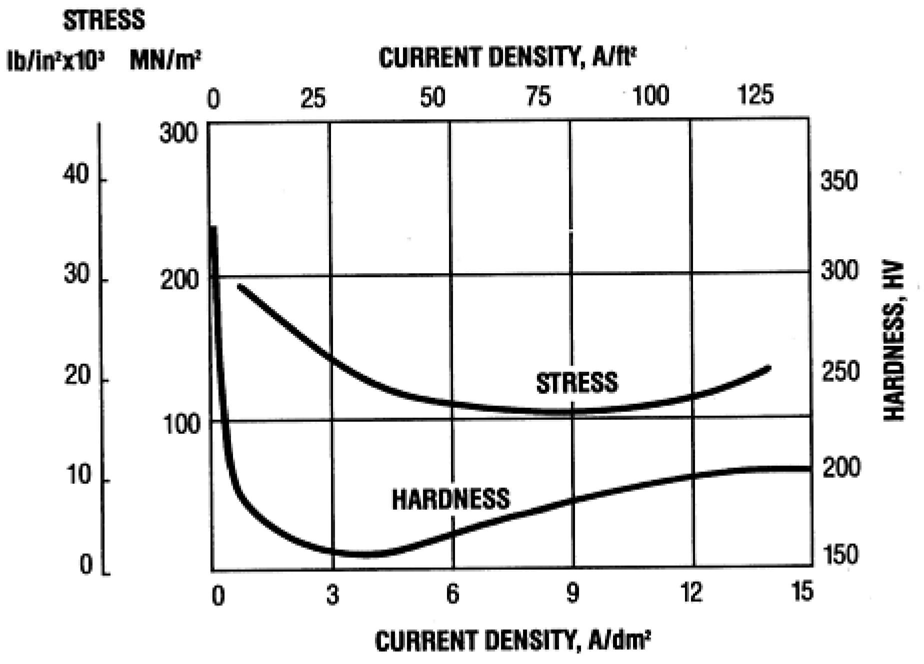


Fig. 2 Variation in internal stress and hardness with current density. Watts bath operated at 54 °C and pH 3.0. Internal stress is tensile (indicated by a positive number). Source: Ref 1

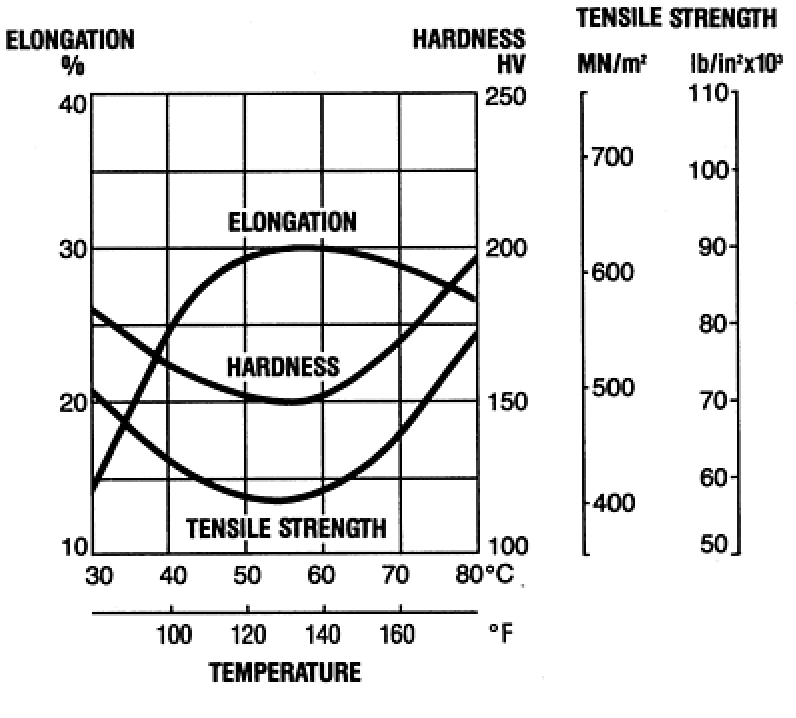


Fig. 3 Variation in elongation, tensile strength, and hardness with temperature. Watts bath operated at 54 °C and 5 A/dm^2. Source: Ref 1

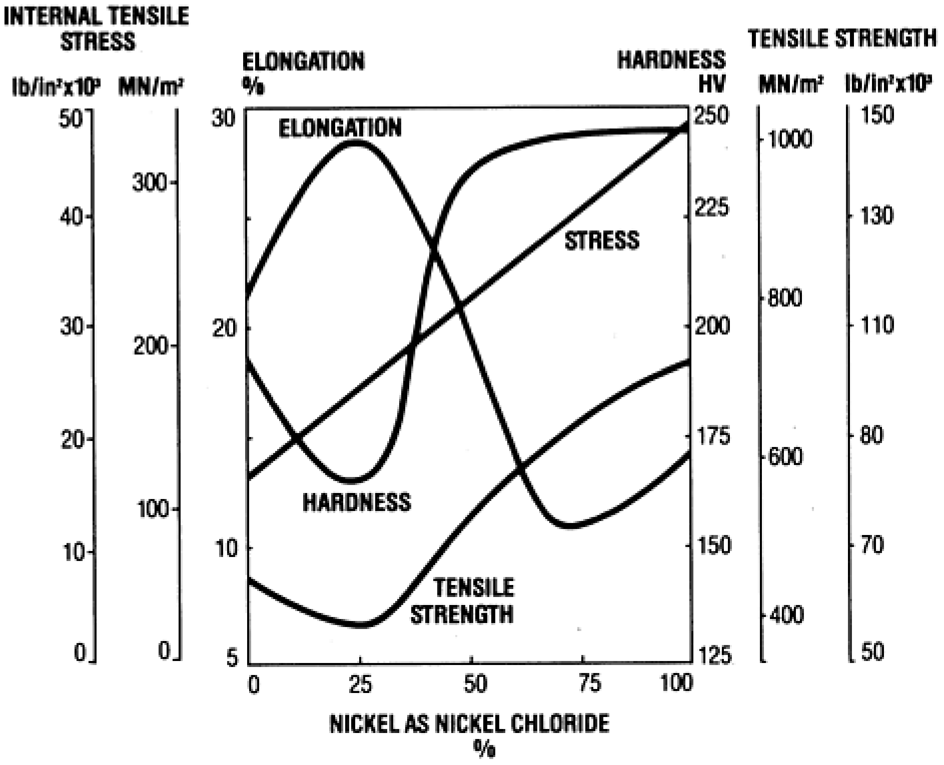


Fig. 4 Variation in internal stress, elongation, tensile strength, and hardness with chloride content in deposits from Watts solutions operated at 55 °C, pH 3.0, and 5 A/dm^2. Internal stress is tensile (indicated by a positive number). Source: Ref 1

The nickel plating processes used for decorative, engineering, and electroforming purposes are discussed in the following sections.

References cited in this section

1. *Plating,* Vol 39 (No. 365), 1952, p 1229
2. W.H. Safranek, *The Properties of Electrodeposited Alloys--A Handbook,* 2nd ed., American Electroplaters and Surface Finishers Society 1986

Decorative Nickel Plating Processes and Multilayer Coatings

The technology of decorative nickel plating has been improved continuously over the years. Prime examples include development of the organic bright nickel solutions, introduction of semibright nickel plating processes, development of multilayer nickel coatings, and the use of microdiscontinuous chromium in combination with multilayer nickel. The major result of these developments has been a remarkable improvement in the corrosion performance of decorative nickel plus chromium coatings without the need to increase deposit thickness.

Bright nickel plating solutions are modifications of the Watts formulation given in Table 2, but they contain organic and other additives that act to produce a fully bright finish suitable for immediate chromium plating without mechanical finishing. Portions of the addition agent molecules may be incorporated into the deposit, resulting in a hard, fine-grain coating that contains incorporated sulfur. The sulfur causes the deposit to be electrochemically more reactive than sulfur-free matte, polished, or semibright nickel deposits. Decomposition products of the additives accumulate in solution with time and are removed by purification with activated carbon. In modern solutions, continuous filtration through active carbon removes deleterious decomposition products without significant removal of the addition agents themselves.

Several substances--organic and inorganic--are used at appropriate concentrations to achieve brightness, leveling, and control of internal stress. (Leveling is the ability of the deposit to become smoother than the surface on which it is deposited as the thickness of the nickel is increased.) The substances used as additives in bright nickel plating solutions may be described by the following three terms: *carriers, auxiliary brighteners,* and *brighteners.* The terminology is not standardized, however, and alternative terms mentioned in the literature are shown in parentheses.

Carriers (brighteners of the first class, secondary brighteners, control agents, ductilizers) are usually aromatic organic compounds. They are the principal source of the sulfur codeposited with the nickel. Their main function is to refine grain structure and provide deposits with increased luster compared with matte or full deposits from baths without additives. Some of these additives can be used in Watts solution or high-chloride versions of the Watts solution (for example, solutions with 115 g/L nickel chloride). This class of brightener widens the bright range when used in combination with the auxiliary brighteners and brighteners discussed below. Some examples of carriers are saccharin (o-sulfobenzoic imide), paratoluene sulfonamide, benzene sulfonamide, benzene monosulfonate (sodium salt), ortho sulfobenzaldehyde (sodium salt), and naphthalene 1,3,6-trisulfonate (sodium salt). Carriers are used in concentrations of about 1 to 25 g/L (0.1 to 3 oz/gal), either singly or in combination. They are not consumed rapidly by electrolysis, and consumption is primarily by dragout and by losses during batch carbon treatment. (Batch treatment involves interrupting production and transferring the plating solution to a separate treatment tank where it is treated with activated carbon, filtered, and returned to the main tank.) The stress-reducing property of carriers is increased if they contain amido or imido nitrogen. For example, saccharin is a most effective stress reducer and often helps to decrease or eliminate hazes. It is generally used as sodium saccharin at a concentration of 0.5 to 4.0 g/L (0.07 to 0.5 oz/gal).

Auxiliary brighteners may be either organic or inorganic. Their functions are to augment the luster attainable with the carriers and brighteners and to increase the rate of brightening and leveling. Some examples are sodium allyl sulfonate; zinc, cobalt, cadmium (for rack and barrel plating); and 1,4-butyne 2-diol. The concentration of these additives may vary from about 0.1 to 4 g/L (0.01 to 0.5 oz/gal). The rate of consumption depends on the type of compound and may vary widely. These compounds may be of aromatic or aliphatic types and usually are heterocyclic or unsaturated. The inorganic metallic ions--zinc, cobalt, cadmium--are not often used anymore as auxiliary brighteners.

Brighteners (brighteners of the second class, primary brighteners, leveling agents), when used in combination with carriers and auxiliary brighteners, produce bright to brilliant deposits having good ductility and leveling characteristics over a wide range of current densities. Some of the compounds used as brighteners include reduced fuchsin, phenosafranin, thiourea, 1,4-butyne diol, n-allylquinolinium bromide) and 5-aminobenzimidazolethiol-2. Materials of this type generally are used in concentrations of 0.005 to 0.2 g/L (0.0006 to 0.02 oz/gal); an excess of brighteners may cause serious embrittlement. The rates of consumption of these materials may vary within wide limits.

Modern bright nickel plating solutions employ combinations of additives similar to those described and are formulated to produce bright deposits over a wide range of current densities. The deposits have excellent leveling or scratch-filling characteristics, produce deposits with fair ductility and low internal stress, produce bright deposits in areas of low current density, permit use of high average current densities and bath temperatures, are less sensitive to metallic contaminants than some of the solutions first commercialized, permit continuous purification of the plating solution by use of activated carbon on filters, produce breakdown products that can be removed by activated carbon, and are not overly sensitive to anode effects.

Multilayer Decorative Plating. The single-layer bright nickel coatings produced from solutions containing organic additives are less resistant to corrosion than polished nickel coatings. The lower corrosion resistance is due to the presence of small amounts of sulfur that originate from the organic additives present in solution. The amount of sulfur that is incorporated depends on exactly how the process is formulated and controlled. Single-layer bright nickel coatings are suitable for use in mildly corrosive service using a nickel thickness of 10 to 20 μm (0.39 to 0.79 mil). For severe and very severe conditions of exposure, especially where longtime resistance to corrosion is required, multilayer nickel coatings with microdiscontinuous chromium are used. The principal types are double- and triple- layer coatings.

Double-layer coatings involve the electrodeposition of two layers of nickel, one semibright and one bright, before the application of chromium. The first layer (semibright) is deposited from a Watts-type formulation containing one or more sulfur-free organic additives. Semibright nickel deposits contain less than 0.005 wt% S and are semilustrous, smooth, and fine-grain over a wide current density range. The deposits have a columnar structure and good ductility. The typical composition and operating conditions for a semibright nickel plating bath are given in Table 2. Deposit internal stress increases with increasing nickel chloride content; deposits also tend to be nonuniform in color and leveling at high chloride levels. The concentrations of the organic additives for semibright nickel solutions are usually fairly low, from 0.05 to 0.5 g/L (0.006 to 0.06 oz/gal). Examples of these additives are 1,4-butyne diol (or other aliphatic compounds with

olefinic or acetylenic unsaturation), formaldehyde, coumarin, and ethylene cyanohydrin. There are two families of semibright nickel plating processes that are usually referred to as *coumarin* and *noncoumarin* types. The latter were introduced more recently and offer advantages. Semibright nickel plating solutions usually contain anionic surfactants and antipitting agents, singly or in combination.

The bright nickel layer deposited on top of the semibright one may range in thickness from 5 to 8 μm (0.2 to 0.3 mil), or about 20 to 35% of the total nickel thickness. Ideally, it should be plated from a bath that is compatible with the semibright additive, or additives, because in most double-layer systems the semibright additive functions as either a brightener or an auxiliary brightener in the bright nickel bath.

Triple-layer coatings are similar to double-layer coatings except that a thin, high-sulfur-containing layer is deposited between the semibright and bright layers. The thin layer must contain greater than 0.15 wt% S. Some of the requirements for double- and triple-layer nickel coatings are summarized in Table 3. Why multilayer coatings improve corrosion performance is discussed in the section "Corrosion Performance" in this article.

Table 3 Requirements for double- or triple-layer nickel coatings

Type of nickel coating[(a)]	Specific elongation, %	Sulfur content, wt%	Thickness as a percentage of total nickel thickness	
			Double-layer	Triple-layer
Bottom (s--semibright)	Greater than 8	Less than 0.005	Greater than 60 (but at least 75 for steel)	Greater than 50 (but not more than 70)
Middle (b--high-sulfur bright)	. . .	Greater than 0.15	. . .	10 max
Top (b--bright)	. . .	Between 0.04 and	Greater than 10, but less than 40	Equal to or greater than 30

(a) s,semibright nickel layer applied prior to bright nickel; b, fully bright nickel layer that contains the amount of sulfur specified

Microdiscontinuous Chromium. Decorative, electrodeposited nickel coatings, whether single- or multilayer, are most often used in combination with electrodeposited chromium. The thin layer of chromium, initially applied over nickel to prevent tarnishing, now provides added resistance to corrosion because of the developments discussed in this and the next section.

Conventional or regular chromium deposits are low-porosity coatings, whereas microdiscontinuous chromium deposits have a high, controlled degree of microporosity or microcracking. Controlled microporosity or microcracking in the chromium is achieved by depositing a special nickel strike on top of the bright nickel layer just prior to chromium plating. When it is plated over with chromium, the thin layer of nickel, usually about 1 to 2 μm (0.04 to 0.08 mil), helps create microcracks or micropores in the chromium. Microporosity may also be achieved without the use of a special nickel layer by means of the Pixie process, a patented process that involves postplating treatment of the chromium to increase porosity on a microscopic scale. Traditionally, the chromium is deposited from conventional hexavalent processes, but within the last ten years, trivalent chromium plating processes have grown in popularity.

Microcracked chromium is produced by depositing the thin layer of nickel from a special bath formulated to produce nickel with a high internal tensile stress. When the chromium deposit is chromium plated, the thin nickel and the chromium then crack. Varying the conditions under which the nickel layer is deposited can provide variations in the crack density over a range of from 30 cracks/mm (750 cracks/in.) to 80 cracks/mm (2000 cracks/in.). The nickel bath usually consists of a basic nickel chloride electrolyte with additives that provide additional stress, such as the ammonium ion. Boric acid is not used, but other buffers such as the acetate ion may be added. Proprietary organic additives are also used to enhance the brightness and the ability of the deposit to crack, especially in the low-current-density areas. Temperature

and pH are controlled to vary the crack density; low temperature (23 °C, or 73 °F) and high pH (4.5) favor higher crack densities; high temperature (36 °C, or 97 °F) and low pH (3.5) favor lower crack densities. Cracking of the chromium deposit must occur subsequent to chromium plating. Aging or the use of a hot water dip may be necessary to promote the formation of all microcracks.

Microporous chromium is produced from Watts-type nickel baths using air agitation and containing very fine inert particles, usually inorganic, and the normal additives used for bright nickel plating. Chromium, plated over the resulting nickel-particle matrix, deposits around the particles, creating pores. The nickel baths are operated much like bright nickel solutions, with the exception that filtration cannot be performed. In some instances, auxiliary additives permit reduction of the particle concentration in the plating bath and still provide high pore densities. Pore densities can vary according to the concentration of particles, agitation rates, and additives. Generally, a minimum pore density of 100 pores/mm^2 (64,000 pores/in.^{2}) is specified. In either case, chromium thicknesses should not be allowed to exceed about 0.5 μm (0.02 mil) or the cracks and pores will start to heal.

Microcracked chromium deposits can also be produced directly from chromium baths by increasing thickness, or by depositing chromium over chromium. The latter, dual-layer chromium technique is no longer popular.

Corrosion Performance. The remarkable corrosion resistance of modern decorative nickel-plus-chromium coatings depends on the use of multilayer nickel in combination with microdiscontinuous chromium. The improved performance of multilayer nickel coatings is due to the fact that the combination of layers of nickel have different electrochemical reactivities. If one measures the corrosion potentials of various nickel deposits in the same electrolyte, one finds that the bright nickel deposits display more active dissolution potentials than do the semibright nickels. If bright and semibright nickel deposits (for example, in the form of foils separated from the substrate) are electrically connected in the electrolyte, electrons will flow from the bright nickel to the semibright nickel. The result is that the rate of corrosion of the bright nickel is increased, whereas the rate of corrosion of the semibright nickel is decreased. In a composite coating consisting of bright nickel over semibright nickel, this is manifested by enhanced lateral corrosion of the bright nickel layer and delayed penetration of the semibright nickel layer.

The extent to which bright nickel protects the underlying semibright nickel layer by sacrificial action is dependent on the difference between the corrosion potentials of the semibright and bright nickel. The difference should be at least 100 mV (as measured by the simultaneous thickness and electrochemical potential, or STEP test, described in the section "Quality Control of Nickel Plating" in this article), differences in potential are beneficial, especially in low-current-density areas of complicated parts. If the difference becomes too great, appearance suffers because of the accelerated corrosion of the bright nickel layer; that is, there is an optimum value that represents a compromise between preventing basis metal attack and controlling superficial corrosion. The result is that penetration of the coating and exposure of the underlying substrate occur slowly. Multilayer nickel coatings are thus more protective than single-layer bright nickel coatings of equal thickness.

The rate of pit penetration through the nickel layers varies inversely with the number of microdiscontinuities in the chromium layer. Pit penetration may occur rapidly with low-porosity, conventional chromium. When corrosion takes place at a pore in conventional chromium, the large cathodic area of chromium surrounding the pore accelerates the corrosion of the nickel, and pitting may occur rapidly. With microdiscontinuous chromium, a large number of microscopic pores or cracks are deliberately induced in the chromium deposit so that corrosion can start at many sites. The available corrosion current has to be spread over a myriad number of tiny corrosion cells, so that the rate of corrosion of the nickel is greatly reduced. For example, the approximate depth of pitting of nickel after 16 h of CASS testing (ASTM B 368, "Copper-Accelerated Acetic Acid Salt Spray [Fog] Testing") was 10 to 20 μm with conventional chromium and 1 to 6 μm with microdiscontinuous chromium.

Corrosion studies conducted by plating suppliers, nickel producers, and groups such as ASTM Committee B-8 have confirmed that multilayer nickel coatings are significantly more protective than single-layer bright nickel coatings, that microdiscontinuous chromium coatings provide more protection than conventional chromium coatings, and that the corrosion protection of decorative, electroplated nickel-plus-chromium coatings is directly proportional to nickel thickness and to the ratio of semibright and bright nickel in multilayer coatings. Table 4 is based on the results of a study conducted at the LaQue Center for Corrosion Technology, Wrightsville Beach, NC, and it summarizes the types of coatings that protected standard panels from corrosion for more than 15 years outdoors in a severe marine atmosphere.

Table 4 Coating systems on steel giving best performance after 15 years of outdoor marine exposure and 96 h of CASS testing

Type and thickness of coating, µm			ASTM performance ratings[(a)]	
Copper	Nickel[(b)]	Chromium[(c)]	Outdoor marine, 15 years	CASS, 96 h
. . .	38d	1.5 mc	10/8	10/8
12	26d	1.5 mc	10/9	10/8
. . .	38d	0.25 mp	10/7	10/7
12	26d	0.25 mp	10/9	10/7

Note: CASS testing ("Copper-Accelerated Acetic Salt Spray [Fog] Testing") is conducted according to ASTM B 368.

(a) A two-number system has been adopted by ASTM for rating panels after corrosion testing. The first, the protection number, is based on the percentage of the base metal that is defective due to corrosion. A rating of 10 on steel indicates that the panel did not rust. The second, the appearance number, is similarly based on percentage of defective area, but it rates the extent to which corrosion of the base metal as well as superficial corrosion, detract from the overall appearance. Appearance ratings of 7, 8, or 9 indicate that 0.25 to 0.5%, 0.1 to .25%, or 0 to 0.1% of the area, respectively, is defective due to superficial staining and corrosion.

(b) d, double layer. The double-layer nickel coatings in the program differed in reactivity. For details see G.A. DiBari and F.X. Carlin, Decorative Nickel/Chromium Electrodeposits on Steel--15 Years Corrosion Performance Data, *Plating and Surface Finishing,* May 1985, p 128.

(c) mc, microcracked; mp, microporous. The type of microcracked chromium used in this study is based on the addition of selenium compounds to a conventional chromium bath to obtain microcracking. Consistent crack patterns were obtained at the chromium thicknesses given in the table.

Standards and Recommended Thicknesses. ASTM B 456 provides information on specific requirements for decorative nickel-plus-chromium coatings to achieve acceptable performance under five different conditions of service. The standard defines several classes of coatings that differ in thickness and type, and it classifies the various coating systems according to their resistance to corrosion. The standard specifies the requirements for double- and triple-layer nickel coatings (Table 3), and it gives the classification numbers of coatings appropriate for each service condition number. For example, Table 5 specifies decorative nickel-plus-chromium coatings on steel.

Table 5 Decorative nickel-plus-chromium coatings on steel

Service condition number (typical applications)	Coating designation[(a)]	Minimum nickel thickness, µm
SC 5--Extended very severe (exterior automotive where long-time corrosion protection is a requirement)	Fe/Ni35d Cr mc	35
	Fe/Ni35d Cr mp	35
SC 4--Very severe (exterior automotive, boat fittings)	Fe/Ni40d Cr r	40

	Fe/Ni30d Cr mp	30
	Fe/Ni30d Cr mc	30
SC 3--Severe (patio and lawn furniture, bicycles, hospital furniture and cabinets)	Fe/Ni30d Cr r	30
	Fe/Ni25d Cr mp	25
	Fe/Ni25d Cr mc	25
	Fe/Ni40p; Cr r	40
	Fe/Ni30p Cr mp	30
	Fe/Ni30p Cr mc	30
SC 2--Moderate service (stove tops, oven liners, office furniture, golf club shafts, plumbing fixtures and bathroom accessories)	Fe/Ni20b Cr r	20
	Fe/Ni15b Cr mp	15
	Fe/Ni15b Cr mc	15
SC 1--Mild (toaster bodies, interior automotive accessories, trim for major appliances, fans, light fixtures)	Fe/Ni10b Cr r	10

(a) b, electrodeposited single-layer bright nickel; d, double-layer or multilayer nickel coating; r, regular or conventional chromium; mc, microcracked chromium; mp, microporous chromium. The numerals in the designations denote the thickness of the nickel coating in microns. The thickness of the chromium is assumed to be 0.3 μm unless otherwise specified. When permitted by the purchaser, copper may be used as an undercoat for nickel, but it cannot be substituted for any of the part of the nickel specified. Results of several test programs have raised doubt about whether coating systems involving regular chromium are satisfactory for SC 4 and SC 3.

The service condition number characterizes the severity of the corrosion environment, 5 being the most severe and 1 being the least severe. The classification number is a way to specify the details of the coating in an abbreviated fashion. For example, the classification number Fe/Ni30d Cr mp indicates that the coating is applied to steel (Fe) and consists of 30 μm of double-layer nickel (d) with a top layer of microporous (mp) chromium that is 0.3 μm thick. (The thickness value of the chromium is not included in the classification number unless its thickness is different from 0.3 μm.) The type of nickel is designated by the following symbols: "b" for electrodeposited single-layer bright nickel, "d" for double- or multilayer nickel coatings, "p" for dull, satin, or semibright nickel deposits, and "s" for polished dull or semibright electrodeposited nickel. The type of chromium is given by the following symbols: "r" for regular or conventional chromium, "mp" for microporous chromium, and "mc" for microcracked chromium.

Decorative nickel-iron alloy plating processes were introduced to conserve nickel and to lower anode material costs by substituting a portion of the nickel with iron. Decorative nickel-iron alloy deposits have full brightness, high leveling, excellent ductility, and good receptivity for chromium. Nickel-iron can be plated on steel, brass, aluminum, zinc die castings, or plastic substrates in either barrel or rack equipment. The operation and the proprietary additives used in commercially available processes are similar to those in conventional bright nickel plating. In addition, the bath requires special additives to stabilize the ferrous and ferric ions so that hydroxide compounds do not form and precipitate. The stabilizers are either complexers or reducing agents, depending on the nature of the proprietary process. The processes should be controlled within the limits recommended by plating supply houses. Deposits on steel or copper that is subsequently chromium plated have had good acceptance for interior applications as a substitute for bright nickel. Decorative nickel-iron alloy deposits are not often used for outdoor applications where corrosion conditions are severe, because the deposits tend to form a fine, superficial brown stain relatively quickly. The rate at which this occurs depends on the iron content of the deposits, and those with less than 15% Fe have been used in outdoor applications.

Engineering and Electroforming Processes

Electrodeposited nickel coatings are applied in engineering applications to modify or improve surface properties, such as corrosion resistance, hardness, wear, and magnetic properties. Although the appearance of the coating is important and the plated surface should be defect-free, the lustrous, mirror-like deposits described in previous sections are not usually required. Nickel electroforming is the specialized use of the nickel plating process to produce or reproduce articles by electroplating onto a mandrel that is subsequently separated from the deposit.

Watts and Nickel Sulfamate Processes. The two most popular solutions for depositing engineering nickel coatings and for electroforming, Watts nickel and nickel sulfamate, have been included in Table 2. The table summarizes the chemical composition, operating conditions, and typical mechanical property data for deposits from these solutions. The Watts solution is relatively inexpensive and easy to control; it has already been discussed.

Nickel sulfamate solutions are widely used for electroforming because of the low internal stress of the deposits, high rates of deposition, and superior throwing power. Throwing power is the relationship between current distribution and uniformity of coating thickness, as influenced by geometric factors (the shape and relative positioning of anode and cathode), and by the electrochemical characteristics of the solution (conductivity, cathode polarization, and cathode efficiency). Throwing power is a measure of the extent to which a solution will produce deposits that are more uniform than those that would be produced in the absence of cathode polarization and cathode efficiency effects. Because of the very high solubility of nickel sulfamate, a higher nickel metal concentration is possible than in other nickel electrolytes, permitting lower operating temperatures and higher plating rates.

A small amount of nickel chloride is usually added to nickel sulfamate solutions to minimize anode passivity, especially at high current densities. If nickel chloride is not added, sulfur-containing nickel anode materials with about 0.02% S are essential to avoid anodic oxidation of the sulfamate ion, which can result in the uncontrolled and unpredictable production of sulfur-containing compounds that act as stress reducers and that cannot easily be removed from solution. Bromide ions, instead of chloride, are sometimes added to nickel sulfamate solutions to promote anode dissolution.

Nickel sulfamate is so soluble that it cannot be readily recrystallized from solution. It is commercially available as a concentrated solution, usually prepared by reacting high-purity nickel powder with sulfamic acid under controlled conditions. Nickel sulfamate plating solutions are more expensive than those based on commercial grades of nickel sulfate and nickel chloride. The extra cost of using solutions that are as pure as possible is more than offset by savings in the preliminary purification procedures necessary otherwise.

Prolonged use of sulfamate solutions at temperatures above 60 °C (140 °F) or at a pH of less than 3.0 can hydrolyze the nickel sulfamate to the less soluble form of nickel ammonium sulfate. The ammonium and sulfate ions produced from the hydrolysis increase the internal tensile stress and hardness of the deposits.

Nickel electrodeposited from a well-purified sulfamate bath containing no stress-reducing agent and operated at 46 °C (115 °F), a pH of 4.0, and a current density of 2.0 A/dm^2 (20 A/ft^2) has a residual tensile stress varying from 15 to 40 MPa (2 to 6 ksi). The stress in a deposit produced from a similarly operated Watts bath would be about 170 MPa (25 ksi).

Sulfamate nickel plating baths are especially useful for applications requiring low residual stress in the electrodeposited nickel, such as in electroforming, and for coating objects that are susceptible to fatigue cracking. Steel crankshafts that are nickel plated for resistance to corrosion and wear should be coated with a low-stress nickel deposit, such as sulfamate

nickel, to minimize loss of fatigue strength. The fatigue limit of nickel-plated steel is reduced almost proportionally to the amount of residual tensile stress in the nickel plate, and the use of compressively stressed deposits provides additional benefits.

Other nickel plating solutions for engineering applications are listed in Table 6, along with available mechanical properties of the deposits. Many of these solutions were developed to meet specific engineering requirements; all are used to a lesser extent than Watts and nickel sulfamate solutions.

Table 6 Other nickel plating solutions and some properties of the deposits

Type	Composition[(a)],g/L	pH	Temperature, °C	Cathode current density, A/dm^2	Vickers hardness, 100 g load	Tensile strength, MPa	Elongation, %	Internal stress, MPa
Fluoborate	Nickel fluoborate, 225-300 Nickel chloride, 0-15 Boric acid, 15-30	2.5-4	38-70	3-30	125-300	380-600	5-30	90-200
Hard nickel	Nickel sulfate, 180 Ammonium chloride, 25 Boric acid, 30	5.6-5.9	43-60	2-10	350-500	990-1100	5-8	300
All-chloride	Nickel chloride, 225-300 Boric acid, 30-35	1-4	50-70	2.5-10	230-260	620-930	4-20	275-340
All-sulfate	Nickel sulfate, 225-410 Boric acid, 30-45	1.5-4	38-70	1-10	180-275	410-480	20	120
Sulfate chloride	Nickel sulfate, 150-225 Nickel chloride, 150-225 Boric acid, 30-45	1.5-2.5	43-52	2.5-15	150-280	480-720	5-25	210-280
High sulfate	Nickel sulfate, 75-110 Sodium sulfate, 75-110 Ammonium chloride, 15-35 Boric acid, 15	5.3-5.8	20-32	0.5-2.5	. . .	. . .	. . .	. . .
Black nickel (sulfate bath)	Nickel sulfate, 75 Zinc sulfate, 30 Ammonium sulfate, 35 Sodium thiocyanate, 15	5.6	24-32	0.15	. . .	. . .	. . .	. . .
Black nickel	Nickel chloride, 75 Zinc chloride, 30	5.0	24-32	0.15-0.6	. . .	. . .	. . .	. . .

(chloride bath)	Ammonium chloride, 30 Sodium thiocyanate, 15							
Nickel phosphorus	Nickel sulfate, 170 or 330 Nickel chloride, 35-55 Boric acid, 0 or 4 Phosphoric acid, 50 or 0 Phosphorous acid, 2-40	0.5-3.0	60-95	2-5	. . .	. . .	. . .	. . .

(a) The formulas of the compounds in the table are as follows: nickel fluoborate, $Ni(BF_4)_2$; nickel sulfate, $NiSO_4{\cdot}6H_2O$; nickel chloride, $NiCl_2{\cdot}6H_2O$; boric acid, H_3BO_3; ammonium chloride, NH_4Cl; ammonium sulfate, $(NH_4)_2SO_4$; sodium sulfate, Na_2SO_4; phosphoric acid, H_3PO_4; phosphorous acid, H_3PO_3; zinc sulfate, $ZnSO_4{\cdot}7H_2O$; zinc chloride, $ZnCl_2$; sodium thiocyanate, NaSCN.

Fluoborate. The fluoborate solution listed in Table 6 can be used over a wide range of nickel concentrations, temperatures, and current densities. The fluoborate anion is aggressive, and some materials that contact the solution are chemically attacked. Silica filter aids cannot be used on a continuous basis, although cellulose filters are satisfactory. Lead, titanium, and high-silicon cast iron are readily attacked. Stainless steels containing 20% Cr, 25 to 30% Ni, and 2 to 3% Mo are resistant. Anode materials can be encased in Vinyon, polypropylene, or Orlon anode bags to prevent insoluble particles and anode residues from entering the plating solution; nylon bags are unsuitable. Only sleeve-type glass electrodes for pH measurement should be used because of the formation of relatively insoluble potassium fluoborate with permanent junction types. The mechanical and physical properties of deposits produced by the fluoborate bath are similar to those from Watts solutions. The nickel fluoborate solution has been used primarily for high-speed deposition of thick nickel.

Hard Nickel. Developed especially for engineering applications, this solution is applied where controlled hardness, improved abrasion resistance, greater tensile strength, and good ductility are required (without the use of sulfur-containing organic addition agents). Close control of pH, temperature, and current density is necessary for this bath to maintain the desired hardness values. The tensile strength increases and the ductility decreases with an increase in pH and a decrease in temperature. The internal stress is slightly higher than in deposits from Watts solutions. The disadvantages of the hard nickel bath are its tendency to form nodules on edges and the low annealing temperature (230 °C, or 450 °F) of its deposits. Hard nickel deposits are used primarily for buildup or salvage purposes. For optimum results, the ammonium ion concentration should be maintained at 8 g/L (1.1 oz/gal). In those applications where the part being plated is not going to be exposed to elevated temperatures in service, it is simpler to add organic compounds such as saccharin, p-toluene sulfonamide, p-benzene sulfonamide, or other carriers to Watts or sulfamate solutions to achieve hardness without increased internal stress. Because the additives introduce 0.03% S (or more), this approach cannot be used for parts that will be exposed to high temperatures where sulfur severely embrittles the nickel deposit.

All-Chloride. The principal advantage of the all-chloride bath (Table 6) is its ability to operate effectively at high cathode current densities. Other advantages include its high conductivity, its slightly better throwing power, and a reduced tendency to form nodular growths on edges. Deposits from this electrolyte are smoother, finer-grain, harder, and stronger than those from Watts solutions, and more highly stressed. Because of the partial solubility of lead chloride, lead cannot be used in contact with the all-chloride solution. Mists from this solution are corrosive to the superstructure, vents, and other plant equipment, if not well protected. The solution has been used to some extent for salvaging undersize or worn shafts and gears.

All-sulfate has been applied for electrodepositing nickel where the principal or auxiliary anodes are insoluble. For example, insoluble auxiliary or conforming anodes may be required to plate the insides of steel pipes and fittings. To prevent pitting, hydrogen peroxide may be added to all-sulfate solutions, provided they contain no wetting agents or organic stress reducers. Oxygen is evolved at insoluble anodes in the all-sulfate solution, and as a result, the nickel concentration and pH decrease during plating. The pH is controlled and the nickel ion concentration is maintained by adding nickel carbonate. Another procedure that has been used in low-pH solutions replenishes the nickel electrolytically

by employing a replenishment tank with nickel anodes; the current in the replenishment tank is periodically reversed to keep the nickel anodes actively dissolving in the absence of chlorides. The insoluble anodes in all-sulfate solutions may be lead, carbon, graphite, or platinum. If a small anode area is required, solid platinum (in the form of wire) may be used; for large anode areas, platinum-plated or platinum-clad titanium is recommended. In some forms, carbon and graphite are too fragile; lead has the disadvantage of forming loose oxide layers, especially if it is immersed in other solutions in the course of a plating cycle. In chloride-free solution, pure nickel is almost insoluble and may function as an internal anode if properly bagged.

Sulfate/Chloride. The sulfate/chloride solution given in Table 6 has roughly equivalent amounts of nickel sulfate and nickel chloride and was developed to overcome some of the disadvantages of the all-chloride solution. It has high conductivity and can be operated at high current densities. Although the internal stress of the deposits is higher than in deposits from Watts solutions, the stress is lower than in the all-chloride solution. The other properties are about midway between those for deposits from Watts and all-chloride solutions. Lead may not be used for equipment in contact with this solution because of the high chloride content.

High Sulfate. The high-sulfate bath was developed for plating nickel directly on zinc-base die castings. It may also be used to plate nickel on aluminum that has been given a zincate or comparable surface preparation treatment. The high sulfate and low nickel contents, together with the high pH, provide good throwing power with little attack of the zinc. The deposits are less ductile and more highly stressed than nickel deposited from a Watts bath. For this reason, high sulfate nickel is sometimes used as a thin undercoating for more ductile nickel. In general, the deposition of copper from a cyanide solution directly on zinc-base die castings prior to the deposition of nickel is simpler and more reliable.

Black Nickel. There are at least two formulations for producing black nickel deposits; these incorporate zinc and thiocyanate (CNS^-) ions. Table 6 gives the composition and operating conditions for a sulfate and a chloride black nickel plating bath. The process was developed for decorative reasons--color matching and blending. The black nickel deposit has little wear or corrosion resistance and is usually deposited over a layer of nickel deposited from a bright or dull nickel plating solution. It is in commercial use, but it is limited in its applications.

Nickel phosphorus solutions result in the electrodeposition of nickel phosphorus alloys that are analogous to electroless deposits using sodium hypophosphite as the reducing agent. The hardness of the electrolytic deposits can be increased by heat treatment in the same way that the hardness of electroless nickel deposits can be increased, with maximum hardness occurring at 400 °C (750 °F). The phosphorus content of the deposits is best controlled by frequent additions of phosphite or phosphorous acid. The electrodeposition of nickel phosphorus alloys is receiving increased attention because deposits with greater than 10% P are amorphous and therefore have enhanced resistance to corrosion.

Nickel Alloy Plating and Composites. Although discussion of alloy plating is beyond the scope of this article, it should be noted that nickel alloy plating processes of commercial importance include nickel-iron (without brighteners), nickel-cobalt, nickel-palladium, and tin-nickel. An alloy plating process that is growing in importance is zinc-nickel, containing 8 to 12% Ni. In addition, the incorporation of inert particles within a nickel matrix is possible, and coatings that incorporate silicon carbide, diamonds, mica, polytetrafluoroethylene, and other materials are being applied for engineering purposes. Detailed information is available in the articles "Nickel Alloy Plating" and "Zinc Alloy Plating" in this Volume.

Quality Control of Nickel Plating

Achieving high quality involves controlling the bath composition, the purity of the plating solution, and the thickness and uniformity of the deposits. Eliminating rejects, troubleshooting, and the testing of deposits are important aspects of process and product control.

Control of Solution Composition. Control of the composition of the plating bath is one of the most important factors contributing to the quality of nickel deposits. At the outset, the bath must be prepared to the specified composition, adjusted to the proper pH, and purified before use. Thereafter, the composition and pH of the solution must be controlled within specified limits, and contamination by metallic and organic substances must be prevented.

Purification Techniques and Starting Up a New Bath. Before any freshly prepared nickel plating bath is used, contaminants such as iron, copper, zinc, and organics present in trace quantities in commercial salts must be removed to obtain the best results. Several treatments are available for purifying a freshly prepared nickel plating solution.

High-pH treatment consists of adding nickel carbonate to the hot solution until a pH of 5.0 to 5.5 is obtained. This precipitates the hydroxides of metals such as iron, aluminum, and silicon, which in turn frequently absorb other impurities. Addition of hydrogen peroxide oxidizes iron to the ferric state, making it more easily precipitated at high pH, and frequently destroys organic impurities.

Treatment with activated carbon removes organic impurities.

Electrolytic purification removes most of the harmful metallic and organic impurities. A complete purification procedure for a Watts solution would comprise the following steps:

1. Use a separate treatment tank (not the plating tank) to dissolve the nickel sulfate and nickel chloride in hot water at 38 to 49 °C (100 to 120 °F) to about 80% of desired volume.
2. Add 1 to 2 m/L (0.8 to 1.6 pints/100 gal) of 30% hydrogen peroxide (agitate briefly and allow to settle for 1 h).
3. Add 1.2 to 2.4 g/L (1 to 2 lb/100 gal) activated carbon and agitate thoroughly.
4. Heat to 66 °C (150 °F), then add 1.2 to 2.4 g/L (1 to 2 lb/100 gal) of nickel carbonate to the solution, with agitation to adjust the pH to 5.2 to 5.5. More nickel carbonate may be required and the mixture should be stirred to assist the dissolution of the carbonate. Allow to settle 8 to 16 h.
5. Filtering into the plating tank.
6. Add and dissolve boric acid; add water to bring bath up to its desired volume.
7. Electrolytically purify by using a large area of nickel plated corrugated steel sheets as cathodes. The average cathode current density should be 0.5 A/dm^2 (5 A/ft^2), and treatment should continue until 0.5 to 1.3 A · h/L (2 to 5 A · h/gal) have passed through the solution. The solution should be agitated and the temperature held at 49 to 60 °C (120 to 140 °F). It is useful to prepare deposits at normal current densities at some point to check appearance, stress, and sulfur content. If not acceptable, continue dummying until the properties are acceptable.
8. Remove the dummy cathodes and adjust the pH of the solution to the desired value.

Controlling the Main Constituents. The following basic constituents of nickel plating baths must be regularly controlled: the nickel metal content; the chloride concentration; the boric acid; and any organic addition agents. Nickel metal concentration is maintained between 60 and 80 g/L (8.0 and 10.5 oz/gal) in most commercial applications. It is desirable to have a minimum of 23 g/L (3 oz/gal) of nickel chloride in the solution to promote anode corrosion. (The chloride content is not critical for anode corrosion when sulfur-activated anode materials are used.) Boric acid is the most commonly used buffering agent for nickel plating baths. Boric acid is effective in stabilizing the pH in the cathode film within the ranges normally required for best plating performance. It is available in a purified form and is inexpensive. Organic addition agents must be controlled within the limits specified by the suppliers of proprietary processes, and they must be replenished due to losses from dragout, electrolytic consumption, and the effects of carbon filtration (or batch treatment).

Procedures exist for chemical analysis of nickel, chloride, boric acid, and organic addition agents in nickel plating solutions, and modern instrumental techniques are available to monitor the main ingredients on a regular basis with improved precision. High-performance liquid chromatography is one of the improved techniques for controlling organics that is growing in popularity.

Controlling pH, Temperature, Current Density, and Water Quality. The pH of the nickel plating solution will rise during normal operation of the bath, necessitating regular additions of acid to maintain the pH within the prescribed limits. A decrease in pH accompanied by a decrease in nickel ion concentration indicates that the process is not functioning properly.

The operating temperature may have a significant effect on the properties of the deposits, and it should be maintained within specified limits (±2 °C) of the recommended value. In general, most commercial nickel plating baths are operated between 38 to 60 °C (100 to 140 °F).

The nickel plating process should be operated at specified current densities by estimating the surface area of the parts and calculating the total current required. The practice of operating the process at a fixed voltage is not recommended.

Controlling cathode current density is essential for accurately predicting average nickel thickness, for achieving uniform coating thickness on complicated shapes, and for producing deposits with consistent and predictable properties.

Since current density determines the rate of deposition, it must be as uniform as possible to achieve uniformly thick nickel deposits. The nickel plating solution has an electrical resistance, and almost all components to be plated have prominent surfaces that are nearer the anode than recessed areas. The current density is greater at the prominences because the anode-to-cathode distance is shorter and therefore has less electrical resistance. The apportioning of the current in this way is called *current distribution.* This means that the recessed areas receive a thinner nickel deposit than the prominent ones. Current distribution is controlled by proper rack design and proper placement of components on those racks, by the use of nonconducting shields and baffles, and by the use of auxiliary anodes, when necessary. With care, relatively good thickness distribution can be achieved.

The quality of the water used in making up the bath and in replacing water lost by evaporation is important. Demineralized water should be used, especially if the local tap water has a high calcium content (greater than 200 ppm). Filtering the water before it is added to the plating tank is a useful precaution to eliminate particles that can cause rough deposits.

Controlling Impurities. Inorganic, organic, and gaseous impurities may be introduced into nickel plating solutions during normal operations. Continuing efforts to eliminate the sources of these impurities from the plating shop can improve the quality of the deposits, as well as productivity and profitability. The presence of small quantities of inorganic or organic contamination may result in plating defects.

Inorganic contaminants arise from numerous sources, including nickel salts of technical grade, hard water, carryover from acid dip tanks, airborne dust, bipolar attack of metallic immersion heaters, corrosion of the tank material through cracks in the lining, corrosion of anode bars, and dirt from structures above the tank and from parts that fall into the solution and are not removed. The following table lists maximum limits for metallic impurities in nickel plating baths:

Contaminant	Maximum concentration, ppm
Aluminum	60
Chromium	10
Copper	30
Iron	50
Lead	2
Zinc	20
Calcium	[a]

Note: The limits may be different when several contaminants are present at the same time, and complexing agents are a part of the solution formulation.

(a) pH-dependent; will precipitate at the saturation point

The degree of contamination by many inorganic materials may be controlled by continuous filtration and dummying, that is, by electrolysis of the plating solution at 0.2 to 0.5 A/dm^2 (2 to 5 A/ft^2). This may be accomplished on a batch basis or continuously by installing a dummy compartment and overflow dam at one end of the plating tank. Solution from the filter is pumped into the bottom of the dummy compartment, up past the corrugated cathode sheets, over the dam, into the plating section of the tank, out through a bottom outlet at the far end of the tank, and back to the filter. Solid particles and soluble metallic impurities (for example, copper, zinc, lead) are removed simultaneously by this procedure.

Organic contaminants may arise from many sources, including buffing compounds, lubricating oil dropped from overhead equipment, sizing from anode bags, weaving lubricants on plastic anode bags, uncured rack coatings or stopoff lacquers, adhesives on certain types of masking tape, decomposition products from wetting agents, organic stabilizers in hydrogen peroxide, paint spray, and new or patched rubber tank linings. Many organic contaminants can be effectively removed from nickel plating solutions by adsorption on activated carbon on either a batch or a continuous basis. On a batch basis, the solution is transferred to a spare tank, heated to 60 to 71 °C (140 to 160 °F), stirred for several hours with a slurry of 6 g/L (5 lb/100 gal) minimum of activated carbon, permitted to settle, and then filtered back into the plating tank. It is usually necessary to do a complete chemical analysis and adjust the composition of the solution after this type of treatment.

For solutions in which organic contamination is a recurring problem, continuous circulation of the solution through a filter, coated at frequent intervals with small amounts of fresh activated carbon, is recommended. When continuous carbon filtration is used, the wetting agent in the solution must be replenished and controlled more carefully, to prevent pitting of the nickel deposits.

Gaseous contamination of nickel plating solutions usually consists of dissolved air or carbon dioxide. Dissolved air in small amounts may lead to a type of pitting characterized by a teardrop pattern. Dissolved air in the plating solution usually can be traced to entrainment of air in the pumping system when the solution is circulated. If this occurs, the circulating pump and valves should be checked and modified, if necessary. Nickel plating solutions can be purged of dissolved air by heating to a temperature at least 6 °C (10 °F) higher than the normal operating temperature for several hours. The solution is cooled to the operating temperature before plating is resumed. Dissolved carbon dioxide in a nickel plating solution is usually found after nickel carbonate has been added to raise the pH, and it is liberated from warm nickel plating solutions after several hours. If solutions containing carbon dioxide are scheduled for immediate use, they should be purged by a combination of heating and air agitation for approximately 1 h at 6 °C (10 °F) or more above the normal plating temperature.

Effects of Impurities on Bright Nickel Plating. The presence of impurities is especially troublesome in decorative nickel plating. Contamination by zinc, aluminum, and copper is most often caused by the dissolution of zinc-base die castings that have fallen from racks into the plating tank and have been permitted to remain there. Inadequate rinsing before nickel plating increases the drag-in of metallic elements. The presence of cadmium and lead may be attributed to a number of sources, including lead-lined equipment and tanks, impure salts, and drag-in of other plating solutions on poorly rinsed racks. Chromium is almost always carried into the nickel solution on rack tips that have not been chromium stripped, or on poorly maintained racks that have been used in a chromium plating tank and have trapped chromium plating solution in holes, pockets, and tears in the rack coating.

Metallic contaminants affect bright nickel deposition in several ways. Aluminum and silicon produce hazes, generally in areas of medium to high current density. Aluminum and silicon may also cause a fine roughness called "salt and pepper" or "stardust." Iron produces various degrees of roughness, particularly at high pH. Calcium contributes to needlelike roughness as a result of the precipitation of calcium sulfate when calcium in solution exceeds the saturation point of 0.5 g/L (0.06 oz/gal) at 60 °C (140 °F). Chromium as chromate causes dark streaks, high-current-density gassing, and possibly peeling. After reduction to the trivalent form by reaction with organic materials in the solution or at the cathode, chromium may produce hazing and roughness effects similar to those produced by iron, silicon, and aluminum. Copper, zinc, cadmium, and lead affect areas of low current density, producing hazes and dark-to-black deposits.

Organic contaminants may also produce hazes or cloudiness on a bright deposit, or they can result in a degradation of mechanical properties. Haze defects may appear at any current density, or they may be confined to narrow current density ranges.

Mechanical defects producing hairline cracks, called *macrocracking,* may be encountered if the coating is sufficiently stressed as a result of solution contamination. These cracks usually appear in areas of heavier plating thickness (higher current density) but are not necessarily confined to those areas.

Eliminating Rejects/Troubleshooting. The production of defective plated parts or rejects may be associated with the presence in solution of soluble and insoluble impurities. The nature of the coating defect is often an indication of the source of the problem. Common defects include roughness, pitting, blistering (often associated with poor preparation of the surface prior to plating), high stress and low ductility, discoloration, burning at high-current-density areas, and failure to meet thickness specifications.

Roughness is usually caused by the incorporation of insoluble particles in the deposit. In bright nickel baths, chlorine generated at an auxiliary anode that is close to the cathode can react with organic additives to form an insoluble material that is incorporated in the deposit. Insoluble particles may enter the solution from many sources: incomplete polishing of the base metal so that slivers of metal protrude from the surface, incomplete cleaning of the surface so that soil particles remain on the surface, detached flakes of deposit from improperly cleaned racks, dust carried into the tank from metal polishing operations and other activities, insoluble salts and metallic residues from the anode, and others.

Roughness from incomplete polishing, cleaning, and inadequate rack maintenance is avoided by good housekeeping, regular inspection, and control. Roughness caused by dust can be controlled by isolating surface preparation and metal polishing operations from the plating area, by providing a supply of clean air, and by removing dirt from areas near and above the tanks. Roughness caused by the precipitation of calcium sulfate can be avoided by using demineralized water. Continuous filtration of the plating solution so as to turn over the solution at least once an hour is important for minimizing roughness problems. Anode residues must be retained within anode bags, and care should be taken not to damage the bags or allow the solution level to rise above the tops of the bags.

Pitting is caused by many factors, including adhesion of air or hydrogen bubbles to the parts being plated. Air should be expelled as already mentioned. Pitting from adherent hydrogen bubbles can result from a solution that is chemically out of balance, has too low a pH, or is inadequately agitated. Other sources of pitting include incorrect racking of complicated components, too low a concentration of wetting or antipitting agents, the use of incompatible wetting agents, the presence of organic contaminants, the presence of copper ions and other inorganic impurities, incomplete cleaning of the base material, and incomplete dissolution of organic additives that may form oily globules. Pitting is therefore avoided by maintaining the composition of the plating solution within specified limits, controlling the pH and temperature, and preventing impurities of all kinds from entering the solution.

Blistering may be associated with poor adhesion resulting from poor or incorrect surface preparation prior to plating. Nickel can be deposited adherently on most metals and alloys, plastics, and other materials by following standard methods of preparation and activation, including the proper use of intermediate deposits such as cyanide copper, acid copper, and acid nickel chloride strikes. Standard procedures for the preparation of materials prior to electroplating can be found in handbooks and in the *Annual Book of ASTM Standards,* Volume 0.205. Blistering may also be related to incomplete removal of grease, dirt, or oxides, formation of metal soaps from polishing compounds, or formation of silica films from cleaning solutions. In the case of zinc-base die castings or aluminum castings, blistering during or immediately after plating may be due to surface porosity and imperfections that trap plating solution under the coating.

High stress and low ductility usually occur when organic addition agents are out of balance, and also because of the presence of organic and inorganic impurities. Solutions must be maintained in a high state of purity.

Discoloration in low-current-density areas is most likely the consequence of metallic contamination of the plating solution. The effects can be evaluated systematically by plating over a reproducible range of current densities on a Hull cell cathode. Hull cells are available from plating supply houses and are shaped so that nickel can be deposited onto a standard panel over a predictable range of current densities. The variation in current density over the face of the panel is achieved by placing the panel at a specified angle to the anode. Bent panels that are L-shape and plated with the recessed area facing the anode can also be used to assess discoloration at low-current-density areas, and they may provide information on roughness problems.

Burning at high current densities can be caused by applying the full load on the rectifier to the lowest parts on a rack as it is lowered into the tank. This can be controlled by applying a reduced load or ramping the current during immersion of the rack. Burning can also be caused by exceeding the recommended maximum cathode current density, the presence of phosphates in solution introduced via contaminated activated carbon, or incorrect levels of organic additives.

Failure to meet thickness specifications is most frequently due to the application of too low a current and/or too short a plating time. This can be avoided by measuring the area of the parts to be plated, then calculating the total current required for a specified current density and plating for the appropriate time (see Table 1). Another major cause of failure to meet thickness requirements is nonuniform distribution of current leading to insufficient deposition in low-current-density areas. Poor electrical contacts and stray currents can also cause thin deposits, and anode and cathode bars, hooks, and contacts should be kept clean.

Controlling and Testing Deposit Properties. The requirements for testing electrodeposited nickel coatings may vary significantly, depending on the application. In almost all decorative applications, the appearance and the thickness of the deposit should be controlled and monitored on a regular basis. The plated surface must be free of defects such as blisters, roughness, pits, cracks, discoloration, stains, and unplated areas. It must also have the required finish--bright, satin, or semibright. Quality can only be maintained by checking the thickness of a specified number of plated parts. In decorative, electrodeposited multilayer coatings, it is also important to control the sulfur contents of the deposits, the relative thicknesses of individual layers, the ductility of the semibright nickel layer, and the difference in the electrochemical potentials between individual layers. Requirements for corrosion performance and adhesion may also be specified and may require additional testing.

In engineering and electroforming applications, it may be necessary to monitor the mechanical properties, including hardness, tensile strength, ductility, and internal stress, as well as wear resistance and other properties. Some of the more important test methods are briefly outlined below. Additional details can be found in the standard test methods collected in the *Annual Book of ASTM Standards.*

Thickness may be measured using a variety of techniques. The coulometric method described in ISO 2177 and ASTM B 504 can be used to measure the chromium and nickel thicknesses, as well as the thickness of copper undercoats, if present. The coulometric method measures the quantity of electrical energy required to deplate a small, carefully defined area of the component under test. A cell is sealed to the test surface and filled with the appropriate electrolyte, and a cathode is inserted. The component is made the anode, and the circuit is connected to the power supply via an electronic coulometer. By integrating time in seconds with the current passing, the electronic coulometer provides a direct reading in coulombs; modern instruments provide a direct reading of thickness. The completion of the deplating is shown by a marked change in the applied voltage. For routine control of production, it is convenient to monitor nickel thickness nondestructively by means of a magnetic gage, calibrating the gage at intervals with standard samples. Instruments for measuring thickness by beta backscatter, X-ray spectrometry, and eddy current techniques are also available. The traditional method of measuring thickness by microscopic examination of a metallographically prepared cross section of the plated part is still employed, but it is time-consuming, expensive, and destructive.

The simultaneous thickness and electrochemical potential (STEP) test was developed to measure the difference in electrochemical potential between semibright and bright nickel layers in multilayer nickel deposits on parts that are plated in production. It is similar to the coulometric method just described. By including a reference electrode in the circuit, however, it is possible to measure the electrochemical potential of the material being dissolved at the same time that the thickness of the individual layers is being measured. For example, with a double-layer nickel coating, a relatively large change in potential occurs when the bright nickel layer has dissolved and the semibright nickel layer begins to be attacked. The potential difference is related to the overall corrosion resistance of the double-layer coating and should be greater than 100 mV. Details can be found in ASTM B 764.

Corrosion testing may be specified and may require the plater to perform accelerated corrosion tests on a specified number of production parts as part of an overall quality assurance requirement. Three accelerated corrosion tests are recognized internationally: the Copper-Accelerated Acetic Acid Salt Spray (CASS), the Corrodkote, and the Acetic Acid Salt Spray tests. The CASS test is the one most widely used. The CASS and Corrodkote tests were developed when conventional chromium was the only type of chromium available; when the accelerated tests are used to evaluate microdiscontinuous chromium coatings, the surface appearance deteriorates more rapidly than in real-world environments. Details of these three tests can be found in ISO 1456 as well as in ASTM standards. The salt spray tests involve the application of the corrosive solution in the form of a spray or fog inside a fog cabinet or room made or lined with glass, rubber, or resistant plastics. The Corrodkote test involves applying a corrosive slurry to parts and exposing them to high, controlled humidity in a suitable chamber or cabinet; the slurry is formulated to simulate road mud containing corrosive salts. The CASS and Corrodkote tests were developed to control the quality of decorative, electrodeposited nickel-chromium-plated parts for exterior automotive use under severe conditions of corrosion and abrasion. CASS and other corrosion test requirements are specified in ASTM B 456 for nickel-plus-chromium coatings applied to steel, zinc alloys, or copper alloys. Similar information for nickel-plus-chromium coatings on plastics is given in ASTM B 604.

Ductility testing is used in decorative nickel plating to test that the percent elongation of semibright nickel deposits is greater than 8, and to verify that bright nickel solutions are in good working condition. The simple test described in ISO 1456 and in ASTM B 489 is based on bending a test strip of the deposit over a mandrel of specified diameter until the two ends of the strip are parallel. Other tests based on hydraulic or mechanical bulge testing are available. The percent elongation can also be determined by traditional mechanical testing by machining a test sample from relatively thick electroformed nickel and subjecting it to a tensile test. Because ductility is affected by the thickness of the coating, ductility should be measured at the actual thickness specified in a specific end use.

Other useful tests described in ASTM standards include adhesion (B 571), internal stress measurements with the spiral contractometer (B 636), and microhardness testing (B 578), among others.

Nickel Anode Materials

Most nickel plating processes are operated with soluble nickel anode materials. Nickel from the anode is converted into ions that enter the plating solution to replace those discharged at the cathode. In addition, the anode distributes current to the parts being plated and influences metal distribution.

The simplest way to satisfy anode requirements is to suspend nickel bars from hooks placed on an anode bar so that the nickel, not the hook, is immersed in the plating solution. Nickel anode materials are encased in cloth anode bags to prevent insoluble anode residues from entering the solution and causing roughness at the cathode. The use of bars or electrolytic nickel strip is still practiced but has been supplanted in most regions of the world by the use of titanium anode baskets. The baskets used in nickel plating are generally made of titanium mesh strengthened by solid strips of titanium at tops, bottoms, and edges. The baskets are encased in cloth anode bags, suspended on the anode bar by hooks that are an integral part of the baskets, and loaded with small pieces of nickel. The mesh facilitates the free flow of plating solution. Baskets that incorporate hoppers at the tops facilitate basket loading and help prevent pieces of nickel from falling into the tank.

Titanium anode baskets were quickly accepted because of their many advantages. The basket anode is large and unchanging, ensuring a uniform anode area giving constant current distribution and consistent thickness for repeat batches of the same work. Anode maintenance involves topping-up the load to keep the baskets filled. Conforming baskets can be made in virtually any size and shape. The anode-to-cathode distance can be made constant, thereby contributing to good current distribution. Lowest-cost, primary forms of nickel can be used to fill the baskets. Baskets can be semiautomatically or automatically filled with nickel, and that practice is growing in progressive plating shops. One limitation is that titanium cannot be used in concentrated fluoborate solutions or those containing fluoride ions; small amounts of fluoride in solution activate titanium, causing it to corrode.

The available forms of nickel for titanium baskets include high-purity electrolytic nickel squares about 25 × 25 mm, pure electrolytic nickel in button-like shapes about 22 mm in diameter, and sulfur-activated, electrolytic nickel button-shape pieces about 25 mm in diameter. Other popular forms of nickel for plating with baskets are made in spherical shapes by a gas-refining process; the spherical forms are also available in sulfur-free and sulfur-containing grades.

The sulfur-activated forms dissolve relatively uniformly at high current densities and at 100% anode efficiency even in the absence of chloride ions, whereas sulfur-free forms dissolve nonuniformly and require the presence of chloride ions in solution to dissolve efficiently. The need for chloride ions is due to the tendency for pure nickel to become passive in nickel sulfate solutions. Although the tendency for passivity persists even in the presence of chlorides, the chloride ion attacks the passive oxide film that forms when current flows through the anode, and nickel can be dissolved through pits on the surface. The sulfur-containing materials do not form oxide films, and they dissolve at low anode potentials. The small amount of sulfur in the nickel lowers the surface resistance to current flow, the practical effect being to reduce power costs. The unique advantage of the spherical forms of nickel is product flowability, which facilitates automatic basket loading and filling of conforming, semicylindrical, and other complicated basket shapes.

The anode affects the quality of nickel primarily through its effect on current distribution and thickness uniformity. Most anode materials available today are made to strict specifications of purity and are unlikely to introduce significant amounts of impurities into the solution.

Environmental, Health, and Safety Considerations

Strict environmental regulations are being imposed on the plating industry worldwide. The major problem facing nickel platers is to prevent nickel and other metallic ions from entering the environment via plant effluents. The most widely used method of removing metallic elements from effluents is to precipitate nickel and other metals in sludges as hydroxides or sulfides. The solid waste is then disposed of in landfills. Because the number of landfill sites is limited, and because disposal of solid waste is expensive, the recovery of metallic elements by applying reverse osmosis, ion exchange, electrotwinning, and other methods is economically appealing. Nickel producers accept nickel-containing sludges for recycling through smelters or special plants. The recovery of metallic elements is technically possible and will become important in the future.

Environmental regulations vary from state to state. Platers need to become familiar with all applicable local regulations and comply with them. Although there was great resistance to compliance in the early 1970s, most electroplaters in the United States are complying with existing regulations. In some cases, the recycling and recovery of salts and metals, coupled with the conservation of water and energy, have led to economies in plating operations that partially offset the cost of compliance.

The adoption and enforcement of strict environmental regulations arises from concern with the possible effects of metal contaminants on human health. Although the general perception is that these health effects are completely understood, the reality is that our knowledge is extremely limited. It is only when metals are present in high concentrations and in very specific forms that they are definitely known to be toxic.

In the nickel plating shop, three types of exposure are possible: Nickel and its compounds may be inadvertently ingested, nickel-containing solutions may be allowed to remain on the skin for long periods of time, and nickel and its compounds may be taken into the body by breathing. Although nickel and its compounds are not considered acutely toxic, it is advisable to avoid ingesting even small amounts of these substances by taking some simple precautions--wearing work gloves, washing one's hands before eating, and not eating in the workplace. Some workers may develop a skin rash or dermatitis after persistent contact with nickel and its salts. People who have become so sensitized should avoid contact with nickel and its compounds. To avoid becoming sensitized, one should limit skin contact with nickel and its compounds. In the plating shop, this may mean wearing work gloves and washing one's hands immediately after coming in contact with nickel plating solutions.

On the basis of available information, enhanced risk of cancer appears to be confined to the inhalation of high concentrations of dusts containing nickel subsulfides and oxides under conditions previously existing in certain nickel refineries. Although similar health problems have not been observed in plating shops and other workplaces where nickel is found, it is recommended that precautions be taken to avoid dispersing nickel-containing dusts or sprays into the air. Airborne concentrations of nickel should be kept below the permissible exposure limits established by law. This is not only the law, but good common sense. Simple housekeeping and personal hygiene can help prevent the release of toxic substances to the environment and minimize the possible effects of metallic contaminants on human health.

Iron Plating

Sue Troup-Packman, Hughes Research Laboratories

Introduction

IRON has been electrodeposited for many years. One of the earliest references to iron electroplating is in Langbein's *Electrodeposition of Metals,* published in 1894 as the English translation of a German treatise. In that translation there is a reference to "Mr. Alfred Smee (who made) many discoveries in the deposition of antimony, platinum, gold, silver, iron, copper and zinc. In publishing his experiments, in 1841, he originated the very appropriate term 'electro-metallurgy' for the process of working in metals by means of electrolysis" (Ref 1). A paper published in 1930 was titled "The Production of Electrolytic Iron Printing Plates" (Ref 2). It appears, though, that the largest body of published papers and patents were written in the 1950s and 1960s, although a small number of new papers on this topic are published every year.

Iron has been electroplated from a variety of electrolytes. These include chloride, sulfate, sulfamate, fluoroborate, sulfonate, and various combinations of these electrolytes. Perhaps the widest use of iron plating has been in electroforming, where thicknesses of 6 mm (0.25 in.) are common. The bath parameters of these electroplating solutions are as varied as the parts that are plated in them, and the resulting coatings have widely divergent characteristics according to the specific characteristics desired in the finished product.

Acknowledgements

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References

1. G. Langbein and W. Brannt, *A Complete Treatise on the Electro-Deposition of Metals,* Henry Carey Baird, 1894, p 5
2. W. Safranek, *The Properties of Electrodeposited Metals and Alloys,* 2nd ed., American Electroplaters and Surface Finishers Society, 1986, p 215

Advantages and Limitations

Iron is the least expensive metal available. This is partly because it makes up 5% of the earth's crust, making it second in abundance to aluminum among the metals and fourth in abundance behind oxygen, silicon, and aluminum among the elements. Iron, which largely constitutes the core, is the most abundant element in the Earth as a whole (about 35%). This abundance, plus the fact that iron is easily extracted from concentrated ore sources, is what makes it so inexpensive. In addition, the human body contains approximately 4.5 g of iron. The average adult human requires 10 to 20 mg of dietary iron each day to maintain good health. This human requirement, coupled with the vast abundance of iron around us, makes iron an unlikely candidate for environmental controls, at least on the metal itself. Also, the physical properties of the deposited metal can be altered very easily by adjustments in electrolyte, temperature, pH, and addition agents. The ability to "design" a coating to meet a specific need, coupled with the environmental friendliness of iron, has caused a recent upsurge in interest in this electrodeposited metal.

The primary limitations of iron electrodeposition are the innate corrosion properties that affect all iron and steel, although electrodeposited iron appears to be more corrosion resistant than ordinary iron, probably because of its higher purity. Even with better resistance, a protective coating of some kind must be applied to the deposit to prevent corrosion.

An additional limitation seems to be obtaining consistent properties from one batch of parts to another. There is evidence that iron baths function best when they are run in a full production mode. Intermittent operation creates problems in restoring the electrolyte to proper operating condition. Many baths are highly corrosive to ordinary equipment. Pitting and roughness can be a problem if the bath is not controlled properly. Extreme brittleness can result from the presence of codeposited hydrated Fe(III) or Fe(II) oxide as well as codeposition of organic additive breakdown products.

Principal Applications

Today the principal applications for electrodeposited iron are in the production of solder gun tips, the electroplating of iron onto aluminum automobile engine parts, and the electroforming of iron foils for certain magnetic applications. In the past there was a large market for electroformed stampers, engraving plates, and textile rollers, but these iron applications have been almost totally replaced by nickel plating. However, as environmental concerns about nickel increase, a return to iron plating will become increasingly probable. Interest is increasing in the use of nickel-iron alloys containing up to 40% Fe as a substitute for the more expensive and potentially toxic nickel deposits.

Process Description

Table 1 shows some typical iron plating bath parameters. It should be noted that the addition of various organic additives can change the properties of the deposit to a high degree. These are addressed in the Section "Properties of the Deposited Materials and Modified Surfaces" in this article.

Table 1 Typical iron plating solutions

Bath type	Composition	pH	Temperature, °C	Current density

	Component	g/L	Molarity		°C	A/m²	A/ft²
Sulfate	Fe^{++}	48	0.86	2.8-3.5	32-65	215-430	20-40
	(a)	240	0.86				
Double sulfate	Fe^{++}	36-51	0.64-0.92	2.5-3.5	24-65	215-645	20-60
	(b)	250-400	0.64-1.2				
Chloride	Fe^{++}	84-125	1.5-2.25	0.5-1.0	85 min	215-1075	20-100
	(c)	300-450	1.5-2.25				
	(d)	300	2.7				
Sulfate-chloride	Fe^{++}	60	1.08	2.5-3.5	27-70	215-540	20-50
	(a)	250	0.9				
	(c)	36	0.18				
	(e)	20	0.37				
Fluoborate	Fe^{++}	55	1	3.0-3.5	57-63	430-970	40-90
	(f)	227	1				
	(g)	10	0.17				
Sulfamate	Fe^{++}	75	1.35	2.5-3.5	60 max	215-430	20-40
	(h)	30-38	0.25-0.32				
Sulfonate	Fe^{++}	150	2.7	1.2-1.8	60-82	430-860	40-80
	(g)	50	0.81				
	(i)	275	2.7				

(a) Ferrous sulfate (7-hydrate).

(b) Ferrous ammonium sulfate (6-hydrate).

(c) Ferrous chloride (4-hydrate).

(d) Calcium chloride.

(e) Ammonium chloride.

(f) Ferrous fluoborate.

(g) Sodium chloride.

(h) Ammonium sulfamate.

(i) Ferrous sulfonate

In addition, there are many baths that have been reported for both the electrolytic and electroless deposition of iron alloys. Alloys are attracting more interest as replacements for nickel, but this chapter will address only electrodeposited pure iron deposits.

Processing Equipment

Because many of the electrolytes used in iron plating are very corrosive, it is necessary to choose the most corrosion-resistant materials for the processing equipment. This means at least a lined steel or stainless steel tank. However, considering the potential problems with liners, it is advisable to have tanks made out of polypropylene. The high temperatures of some of the baths make polyethylene a poor choice for tank construction.

Filters should be chlorinated polyvinyl chloride or polypropylene. Magnetically coupled pumps do not work well because of the high molar concentration of most of the solutions. Centrifugal pumps require seals, which do not hold up well in hot acidic solutions. In-tank pump and filter assemblies are highly recommended because any solution that leaves the tank and dries leaves a red-brown stain that can be a major problem in maintaining good housekeeping. There should be provision for regular carbon treatment. Care must be exercised to prevent the pump from aspirating air that aggravates the problem of oxidation.

Agitation can be mechanical or provided by the pump and filter. Air agitation should not be used because it will increase the oxidation of the ferrous to ferric iron that causes brittle, dark deposits.

Heaters should be Teflon-covered titanium except for those to be used in fluoroborate baths, which should be Teflon-coated stainless steel. Steam-heated tanks usually do not get enough for baths with higher temperatures, but they are acceptable for lower-temperature baths.

Anodes should be pure electrolytic iron (often called ARMCO iron) and should be bagged with glass fiber (except in fluoborate solutions) or Dynel anode bags to retain the sludge that comes from the anodes. In certain cases low-carbon steel anodes can be used, but these can cause incorporation of carbon into the deposit, which could cause the deposit to be very hard. This could be a problem if one of the required deposit characteristics is low hardness.

Properties of the Deposited Materials and / or Modified Surfaces

Table 2 shows some of the characteristics of deposits produced in various baths. It also shows a few instances where postplate heat treatment was used to change the stress characteristics of a deposit and some of the changes that additives can make in a deposit.

Table 2 Properties of electrodeposited iron coatings

Basic bath	Additives	Ultimate tensile strength		Elongation, %	Hardness, HV
		MPa	ksi		
Sulfate	None	572-614	83-89	3.0-3.5	250
	NaCl	354	51.4	5.5	200
	Boric acid + urea	. . .	. . .	. . .	480-720
	Oxalic acid	. . .	. . .	. . .	600-615
	NaCl + citric acid[(a)]	. . .	. . .	. . .	1000-1100
Double sulfate	NaCl + antioxidant	. . .	. . .	. . .	600-700
Chloride	None	421-434	61-63	5.0-18.0	<100
	NaCl	448-593	65-86	4.0-18.0	150-530
	Glycerol	786-883	114-128	. . .	360-380
Sulfate-chloride	Amidopyrine[(b)]	. . .	. . .	. . .	500-750
Fluoborate	Boric acid	. . .	. . .	. . .	575
Sulfamate	Formic acid[(c)]	676-1068	98-155	. . .	1200-1500
Sulfonate	Antioxidant 15 g/L	. . .	. . .	. . .	650-750
	Antioxidant 1.5 g/L	. . .	. . .	. . .	350-400

(a) Properties are for parts stress relieved by heat treatment for 1 h at 250 °C (480 °F).

(b) Properties are for parts stress relieved by heat treatment for 2 h at 200-300 °C (392-572 °F).

(c) Properties are for parts stress relieved by heat treatment for 24 h at 190 °C (374 °F).

Other additives can be used in various combinations with various baths. Organic additives (acetic acid, arginine, dextrin, glycerin, glycine, saccharin, sugar, and thiourea) are grain refiners as a general rule. They induce stress by the inclusion of their breakdown products in the coating. Inorganic additives (manganese chloride and potassium chloride) increase conductivity. A wetting agent (sodium lauryl sulfate) can be used to reduce pitting. The additive characteristics overlap each other and can change with current density, temperature, pH, and concentration.

References cited in this section

3. F. Lowenheim, *Electroplating,* McGraw-Hill Book Co., 1978, p 333-341

4. S.T. Packman, unpublished data

Environmental Considerations

Iron metal does not pose any special waste disposal considerations unless associated radicals are hazardous (Ref 3). In fact, most publicly owned treatment works (POTWs) like to see iron introduced into the sewer system because it acts as a "getter" for the sulfides in the system, thereby reducing the hydrogen sulfide that can form. The only waste treatment required for iron baths is the adjustment of the pH to a value within the operating range specified in a facility's waste disposal permit. The only exception to this rule is the fluoroborate bath, which could introduce fluorides to the waste disposal system. Most POTWs have fluoride limits that have to be considered when designing a waste disposal system. Boron also has limits in some geographical areas. Local permitting agencies can provide detailed information. Compared to other metal finishing operations, iron is very easy to keep in compliance.

Reference cited in this section

3. F. Lowenheim, *Electroplating,* McGraw-Hill Book Co., 1978, p 333-341

Health and Safety Considerations

As in all metal finishing operations, good judgment should be exercised when operating an iron plating bath. Eye protection, clothing protection, and gloves should be used. Most of the baths are highly corrosive and can have detrimental effects on surrounding equipment. This is especially true of the chloride and fluoroborate baths. High corrosion potentials coupled with current efficiencies in the range of 82 to 87% probably indicate that air emission equipment is necessary. The sulfate, sulfamate, and sulfonate baths are less corrosive and, even though they run at low pH, should require only general ventilation equipment.

Cadmium Plating

Revised by Milton F. Stevenson, Sr., Anoplate Corporation

Introduction

Electrodeposits of cadmium are used to protect steel and cast iron against corrosion. Because cadmium is anodic to iron, the underlying ferrous metal is protected at the expense of the cadmium plate even if the cadmium becomes scratched or nicked, exposing the substrate.

Cadmium is usually applied as a thin coating (less than 25 μm or 1000 μin. thick) intended to withstand atmospheric corrosion. It is seldom used as an undercoating for other metals, and its resistance to corrosion by most chemicals is low.

Besides having excellent corrosion protective properties, cadmium has many useful engineering properties, including natural lubricity. When corrosion products are formed on cadmium-electroplated parts, they are not voluminous, and there is minimal change in dimension. These two properties are responsible for the wide use of cadmium on moving parts or threaded assemblies.

Cadmium has excellent electrical conductivity and low contact resistance. Noncorrosive fluxes can be used to produce top-quality soldered sections. Steel that is coated with cadmium can be formed and shaped because of the ductility of the cadmium. Malleable iron, cast iron, powdered metals, and other hard-to-plate surfaces can be coated with cadmium, and materials used for adhesives bond very well to cadmium-coated surfaces.

Cadmium is highly toxic, and health, safety, and environmental concerns are driving the reduction or elimination of its use for many applications. See the section "Toxicity of Cadmium" in this article and the article "Cadmium Elimination" in this Volume for more information.

Plating Baths

Most cadmium plating is done in cyanide baths, which generally are made by dissolving cadmium oxide in a sodium cyanide solution. Sodium cyanide provides conductivity and makes the corrosion of the cadmium anodes possible.

Cyanide Baths. Compositions and operating conditions of four cyanide baths are given in Tables 1(a) and 1(b). Note that for each of these baths a ratio of total sodium cyanide to cadmium metal is indicated; maintenance of the recommended ratio is important to the operating characteristics of the bath.

Table 1(a) Compositions of cadmium plating cyanide solutions

Solution No.	Ratio of total sodium cyanide to cadmium metal	Composition[(a)]									
		Cadmium oxide		Cadmium metal		Sodium cyanide		Sodium hydroxide[(b)]		Sodium carbonate[(c)]	
		g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal
1	4:1	23	3	19.8	2.62	78.6	10.4	14.4	1.90	30-75	4-10
2	7:1	23	3	19.8	2.62	139	18.4	14.4	1.90	30-45	4-6
3	5:1	26	3.5	23.1	3.06	116	15.3	16.6	2.19	30-60	4-8

(a) Metal-organic agents are added to cyanide solutions to produce fine-grain deposits. The addition of excessive quantities of these agents should be avoided, because this will cause deposits to be of inferior quality and to have poor resistance to corrosion. The addition of these agents to solutions used for plating cast iron is not recommended.

(b) Sodium hydroxide produced by the cadmium oxide used. In barrel plating, 7.5 g/L (1 oz/gal) is added for conductivity.

(c) Sodium carbonate produced by decomposition of sodium cyanide and absorption of carbon dioxide, and by poor anode efficiency. Excess sodium carbonate causes anode polarization, rough coatings, and lower efficiency. Excess sodium carbonate may be reduced by freezing, or by treatment with calcium sulfate.

Table 1(b) Operating conditions of cadmium plating cyanide solutions

Solutions No.	Current density[a]				Operating temperature		Remarks
	Range		Average				
	A/m^2	A/ft^2	A/m^2	A/ft^2	°C	°F	
1	55-650	5-60	270	25	27-32	80-90	For use in still tanks. Good efficiency, fair throwing power. Also used in bright barrel plating
2	110-860	10-80	270	25	27-32	80-90	For use in still tanks and automatic plating. High throwing power, uniform deposits, fair efficiency. Not for use in barrel plating
3	55-970	5-90	380	35	24-29	75-85	Primarily for use in still tanks, but can be used in automatic plating and barrel plating. High efficiency and good throwing power
4	55-	5-	540	50	27-	80-	Used for plating cast iron. High speed and high efficiency[b]

(a) For uniform deposits from cyanide solutions, the use of a current density of at least 215 A/m^2 (20 A/ft^2) is recommended. Agitation and cooling of solution are required at high current densities.

(b) Agitation and cooling are required when current density is high (above 215 A/m^2, or 20 A/ft^2).

For still tank or automatic plating of steel, selection of a bath on the basis of cyanide-to-metal ratio depends on the type of work being plated and the results desired:

- For parts with no recesses and when protection of the basis metal is the sole requirement, Solution 1 in Table 1(a) (ratio, 4 to 1) is recommended.
- For plating parts with deep recesses and when a bright, uniform finish is required, Solution 2 in Table 1(a) (ratio, 7 to 1) is recommended.
- For all-purpose bright plating of various shapes, Solution 3 in Table 1(a) (ratio, 5 to 1) is recommended.
- For high-speed, high-efficiency plating, Solution 4 in Table 1(a) (ratio, 4.5 to 1) is recommended.

Although the use of brighteners produces maximum improvement in uniformity and throwing power (that is, the ability of an electroplating solution to deposit metal uniformly on an irregularly shaped cathode) in Solution 3 in Tables 1(a) and 1(b), brighteners also improve these properties in Solutions 1 and 2.

Normally, the sodium hydroxide content of cyanide baths is not critical. Usual limits are 7.5 to 26 g/L (1.0 to 3.5 oz/gal); the preferred concentration for best results is 15 ± 4 g/L (2 ± 0.5 oz/gal). Sodium hydroxide contributes to conductivity and, in excess, affects the current-density range for obtaining bright plate. Analytical procedures useful in the maintenance of cyanide baths are outlined in the section "Chemical Analysis of Cyanide Cadmium Plating Baths" in this article.

In recent years, the need for pollution control of cyanide solutions has led to the development of noncyanide cadmium electroplating baths, shown in Table 2. Noncyanide baths generate little hydrogen embrittlement and are used to electroplate hardened, high-strength steels. Both the sulfate and the fluoborate baths have been used for some time as a substitute for cyanide baths, and working data are available. The fluoborate bath is characterized by high cathode

efficiency, good stability, and relatively little production of hydrogen embrittlement (see the section "Selective Plating" in this article). The major disadvantage of the fluoborate bath is its poor throwing power. It is widely used in barrel plating operations. If this bath is used for still plating at high current density, air agitation is desirable. Wire and strip geometries can readily be plated in a fluoborate bath. Practically all of the other acid-type baths shown in Table 2 are supplied to electroplaters as proprietary baths. Because each proprietary bath has its own peculiarities, it is advisable to obtain all proper operating information from the supplier to obtain the desired results.

Table 2 Concentration of commercial noncyanide cadmium plating baths

Bath	Proprietary[a]		Fluoborate[b]		Acid sulfate[c]
	g/L	oz/gal	g/L	oz/gal	
Ammonium chloride	11-23	1.5-3.0	. . .	. . .	. . .
Ammonium fluoborate	. . .	. . .	60	8	. . .
Ammonium sulfate	75-115	10-15	. . .	. . .	. . .
Boric acid	. . .	. . .	27	3.6	. . .
Cadmium	4-11	0.5-1.5	95	12.6	. . .
Cadmium fluoborate	. . .	. . .	244	32.2	. . .
Cadmium oxide	. . .	. . .	. . .	. . .	7.6-11 g/L (1.0-1.5 oz/gal)

(a) Proprietary requires a current density of 22 to 160 A/m^2 (2 to 15 A/ft^2) and an operating temperature of 16 to 38 °C (61 to 100 °F).

(b) Fluoborate requires a current density of 325 to 650 A/m^2 (30 to 60 A/ft^2) and an operating temperature of 21 to 38 °C (70 to 100 °F).

(c) Acid sulfate requires a current density of 110 to 660 A/m^2 (10 to 61 A/ft^2) and an operating temperature of 16 to 32 °C (61 to 90 °F).

Brighteners. The most widely used, and probably the safest, brightening agents for cyanide baths are organics such as:

- Aldehydes
- Ketones
- Alcohols
- Furfural
- Dextrin
- Gelatin
- Milk sugar

- Molasses
- Piperonal
- Some sulfonic acids

These materials form complexes with the electrolyte in cyanide baths and influence the orientation and growth of electrodeposited crystals, resulting in the formation of fine longitudinal crystals, and hence a bright deposit. Care should be taken not to add the brighteners in too large an amount. Too much brightener can result in dullness, pitting, blistering, and general poor quality and appearance. It is difficult to remove the excess brightener. Many organic brighteners are available as proprietary materials. When these are used, manufacturers' recommendations regarding amounts and other conditions of use should be followed.

Another method of brightening consists of the use of trace quantities of metallic nickel, cobalt, molybdenum, and selenium. The concentration of these elements in the bath is much more critical than the concentration of the organic brighteners. Poor bright dipping qualities or poor ductility and corrosion resistance of the coating may result from an excess of these metals. Certain proprietary brighteners contain both metallic and organic compounds. Brighteners for the noncyanide baths are also proprietary products.

Rough or pitted deposits should not be encountered in a well-balanced, carefully operated bath. However, if the concentration of metal is too low or the ratio of metal to cyanide varies from recommended values, roughness may result. Other factors that may contribute are contamination by dust, dirt, oil, metallic particles, or soap. Excessive concentrations of sodium carbonate and too high a temperature or current density also promote surface roughness.

Pitted deposits usually are the result of metallic impurities or an excessive amount of decomposed organic addition agents. The interfering metals are antimony, lead, silver, arsenic, tin and thallium. Pitting may also result from the presence of nitrates.

Correction of roughness or pitting may require a complete solution clean-up, including removal of excess sodium carbonate, purification with zinc dust, treatment with activated carbon, and filtration.

Formation and Elimination of Carbonate. Sodium carbonate forms in the cyanide bath as a result of the decomposition of sodium cyanide and the reaction of sodium cyanide with carbon dioxide from the air. The preferred method of agitation, if used, is mechanical because air agitation accelerates the buildup of carbonates.The buildup also results from failure to keep ball anode racks full or from the use of a large area of insoluble steel anodes.

Maximum concentrations of sodium carbonate that can be present in the bath without adverse effect on operating efficiency and deposit characteristics depend on the metal content of the bath. For example, carbonate can be present in concentrations up to 60 g/L (8 oz/gal) if the metal content is 19 g/L (2.5 oz/gal), and up to 30 g/L (4 oz/gal) if metal content is 30 g/L (4oz/gal), without deleterious effects. Exceeding these concentrations results in anode polarization, depletion of the metal content of the bath, and poor, irregular, and dull deposits.

To remove carbonates, the preferred method is to freeze them out by reducing the temperature to 1 to 3 °C (35 to 40 °F) in an outside treatment tank. This lowers the solubility of the carbonates, and the resulting precipitate is allowed to settle. The next step is to pump or filter the clear solution back to the plating tank, readjust the solution based on analysis, and properly dispose of the settled precipitate and solution. It is also possible to remove carbonates by treating the solution with calcium sulfate or calcium cyanide. The equipment supplier should be consulted about which procedure should be applied. Continuous purification equipment that maintains a preset level of carbonate is now available in state-of-the-art equipment.

Purification and Filtration. Whenever it is convenient, continuous filtration is advisable. If a solution is contaminated by impurities such as copper, tin, lead, or other metals, the following treatment is recommended.

Transfer the solution to an auxiliary tank of the same size as the plating tank; stir in 0.7 to 1 kg (1.5 to 2 lb) of purified zinc dust per 400 L (100 gal). Continue to stir for about 1 h, then allow to settle for no more than 6 h. Filter through a well-packed filter. If the solution contains excess organic impurities, such as decomposed brighteners, it should be treated with activated carbon and filtered. Pumps and filter parts should be made of iron or steel for alkaline cyanide baths. The solution attacks brass or bronze, and heavy copper contamination results.

Anodes

The anode system for cadmium plating from a cyanide solution consists of ball-shape cadmium anodes in a spiral cage of bare steel (Fig. 1). The spherical shape provides a large surface area in relation to weight, without a large investment in cadmium. Ball anodes also make it possible to maintain an approximately constant anode area, and little or no anode scrap is produced. Cadmium balls are usually 50 mm (2 in.) in diameter and weigh 0.6 kg ($1\frac{1}{4}$ lb) per ball.

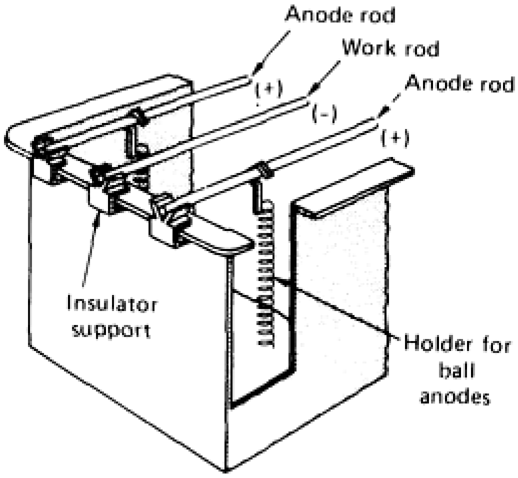


Fig. 1 Unagitated plating tank with spiral steel holders to secure cadmium ball anodes

If a cadmium cyanide solution is to be left idle for an extended period of time (a week or more), the steel anode cages should be removed from the solution, because the galvanic cell set up between the steel and the cadmium anodes will accelerate chemical dissolution of the anodes when the current is off.

When cadmium is plated from an acid solution, such as the fluoborate bath, ball anodes in uncoated steel cages cannot be used, because the steel would dissolve. Rather, bar anodes of elliptical or oval cross section, 460 to 2440 mm (18 to 96 in.) long, are used.

The use of bar anodes in a cyanide solution results in a high percentage of waste, because they must be removed and replaced when the cross-sectional area decreases, or they will dissolve preferentially at the solution level and drop to the bottom of the plating tank.

Purity of the anode is of great importance, especially if a bright deposit is to be produced. The typical composition range for cadmium anodes is as follows:

Element	Composition, %
Cadmium	99.95-99.97
Lead	0.008-0.03
Iron	0.005-0.008

Copper	0.002-0.01
Arsenic	0-0.001
Zinc	0-0.001

Anode composition complying with Federal Specification QQ-A-671 is:

Element(s)	Composition
Cadmium	99.9% min
Silver, lead, tin	0.05% max (total)
Arsenic, antimony, thallium	0.005% max

Insoluble anodes, which are made of low-carbon steel strip or wire, offer no particular advantage except where inside anodes are necessary or for special applications in which they are required because of a need to reduce metal concentration in the plating bath. When insoluble anodes are used, their total area should be 10 to 15% of the total anode area. Insoluble anodes accelerate the formation of carbonate.

Current Density

Cyanide cadmium baths may be operated over a wide range of cathode current densities, as indicated in Table 1(b). In a properly formulated bath operated within its intended current-density range, the cathode efficiency is 90% ± about 5%. Thus, to apply a 25 μ(1000 μin.) deposit of cadmium requires 120 A · h/m^2 (11 A · h/ft^2).

The ranges of current density given in Table 1(b) are suggested limiting values. Choice of current density is governed mainly by the type of work being plated; for example, low current densities are suitable for small lightweight parts, current densities up to 430 A/m^2 (40 A/ft^2) for medium-weight parts of fairly uniform shape, and high current densities for uniformly shaped heavy parts such as cylinders and shafts.

Baths containing 19 g/L (2.5 oz/gal) of cadmium are suitable for general use at current densities up to 270 A/m^2 (25 A/ft^2); higher concentrations of cadmium, up to 38 g/L (5 oz/gal), permit operation at higher current density.

A bath containing 19 g/L (2.5 oz/gal) of cadmium is suitable for barrel plating, where average current density may be about 55 A/m^2 (25 A/ft^2). Such a bath is also suitable for many still tank or automatic plating applications in which current densities do not exceed 270 A/m^2 (25 A/ft^2). At higher current densities, burning may result, with attendant dull, rough deposits that lack decorative and protective qualities. Where higher current densities are required, baths of higher metal content should be used.

Too low a current density (less than 55 A/m^2, or 5 A/ft^2) particularly in still tank or automatic plating, can result in excessively long plating times and inferior appearance of deposits.

The recommended range of current densities for plating with a fluoborate bath is 320 to 650 A/m^2 (30 to 60 A/ft^2). Even near 650 A/m^2 (60 A/ft^2), however, the bath has poor throwing power.

Deposition Rates

Among plating baths used commercially to deposit common metals (other than precious metals), cadmium cyanide baths are high in both throwing and covering power; only alkaline tin and cyanide copper have greater throwing power. Based on Haring-Blum cell measurements, the throwing power of cadmium cyanide baths is rated between 40 and 45%, with a distance ratio of 5. Therefore, the distance between the anode and the work is not critical, although as the distance is increased, current density and efficiency decrease, and current distribution is altered.

Table 3 lists the times required to plate cadmium deposits from 3 to 18 μm (120 to 720 μin.) thick. These times are predicated on 90% cathode efficiency.

Table 3 Time for plating cadmium to a given thickness at various current densities

Data based on 90% cathode efficiency, in a cyanide bath

Thickness of plate		**Plating time in minutes at current density specified**					
μm	**μin.**	**54 A/m^2 (5 A/ft^2)**	**110 A/m^2 (10 A/ft^2)**	**160 A/m^2 (15 A/ft^2)**	**215 A/m^2 (20 A/ft^2)**	**270 A/m^2 (25 A/ft^2)**	**325 A/m^2 (30 A/ft^2)**
3	120	13.0	6.5	4.3	3.2	2.6	2.2
5	200	26.0	13.0	8.6	6.4	5.2	4.4
8	320	39.0	19.5	13.9	9.6	7.8	6.6
10	400	52.0	26.0	18.2	12.8	10.4	8.8
13	520	65.0	32.5	22.5	16.0	13.0	11.0
15	600	78.0	39.0	25.8	19.2	15.6	13.2
18	720	91.0	45.5	30.4	22.4	18.2	15.4

Bath Temperature

Typical operating temperature ranges for cyanide baths are given in Table 1(b). Data for noncyanide baths are shown in Table 2. In general, satisfactory plating results are obtained by controlling bath temperature within ±3 °C (±5 °F) during plating. When greater precision is required, temperature should be controlled within ±1 °C (±2 °F).

Plating Equipment

Considerations specific to the operation of cadmium cyanide baths in conventional plating equipment are discussed here, with attention to the materials of construction used.

Still Tanks. Usually, unlined steel tanks are used for alkaline cadmium plating; however, steel tanks with plastic linings are useful in preventing stray tank currents. Another advantage is that lined tanks may satisfy the diking requirements of the Occupational Safety and Health Administration (OSHA). Double tanks and containment berms must be considered with the current regulations. Rubber and plastics used for tank linings should be tested for compatibility with the plating bath, to prevent contamination from constituents of the lining. Vinyl plastisols are compatible, commercially available, and require no further testing.

Filters and cooling coils may also be made of steel. Equipment for fume control should be used; such equipment in some cases is required by local ordinances. A typical tank arrangement is shown in Fig. 1. Equipment for baths other than the cyanide must be made acid-resistant.

Barrels may be made of hard rubber, polypropylene, acrylic resins, phenol-formaldehyde or melamine-formaldehyde laminates, or expanded or perforated sheet steel coated with vinyl plastisol. The plastisol coating is about 3.2 mm ($\frac{1}{8}$ in.) thick and is resistant to the standard barrel plating solutions and temperatures. Usually, doors and wall ends are of the same material.

Perforated cylinders for oblique barrels also have perforated bottoms and are made of the same materials used for perforated cylinders of horizontal barrels.

Anodes used for barrel plating may be bar- or ball-shape. For maximum current density, the anodes are curved to shorten the path of the current. Curved solid anodes are placed on insulated supports, whereas anode balls are placed in curved holders tied together at the lower ends.

Figure 2 illustrates schematically the use of barrel equipment for cadmium plating. Although not shown in the illustration, barrel installations are equipped with plate coils to remove the excess heat caused by the high current used in the plating bath.

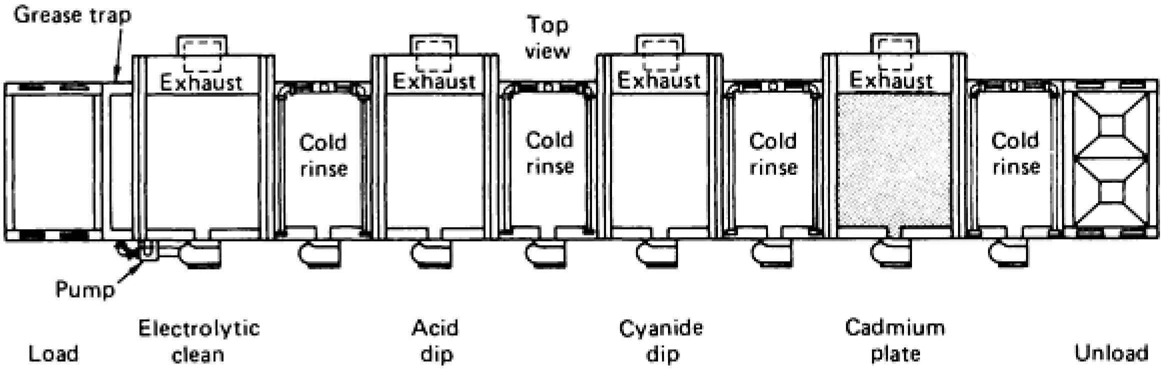


Fig. 2 Schematic showing cadmium plating installation that incorporates the barrel method

Automatic plating machines may be of either the straight-line or the return type. In straight-line plating machines, the work is loaded at one end, carried through the various phases of the cleaning and finishing cycles, and unloaded at the opposite end. Such a machine is considered a heavy-duty unit, because it can be designed for large racks and heavy loads.

Loading and unloading of the return machine is performed in the same area; the work follows an elliptical path, as indicated by the schematic layout of Fig. 3. This unit can be designed for either light or heavy loads.

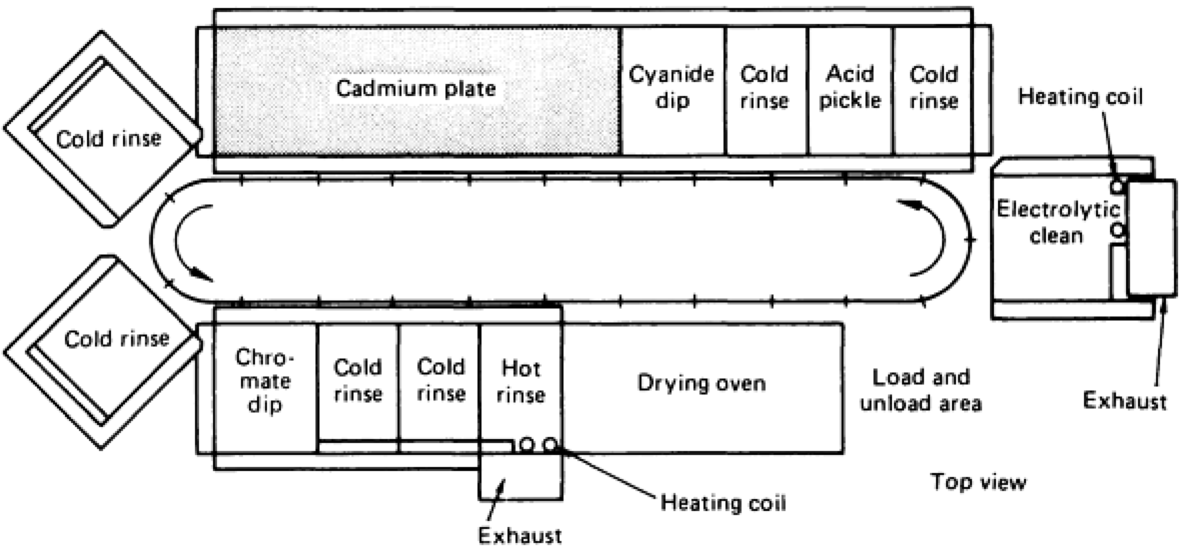


Fig. 3 Schematic showing process sequence for automatic cadmium plating installation

Both types of automatic machines may be continuous, with the work load in constant motion, or intermittent, in which case the motion of the carriers stops for a predetermined time after the work is immersed in each solution.

Power for cadmium plating is provided by rectifiers, which can be of silicon-controlled-rectifier (SCR) thyristor or tapswitch type. If the SCR type is used, attention should be paid to reducing ripple through a filter choke. This is necessary because bright cadmium is sensitive to a high-ripple current, which produces a dull finish on coatings plated in the medium- and high-current density range.

The rectifier elements are silicon. SCR rectifiers offer the advantage of remote control, finer control, computer interface, and constant current-voltage availability. Tap switch rectifiers offer the advantage of lower cost and eliminate the need for ripple filter chokes.

Rinse Tanks. Although longer tank life will be obtained if rinse tanks are lined or coated with polyvinyl chloride or rubber, all rinsing, with the exception of the rinse following hydrochloric acid pickling, may be done in unlined steel tanks. The use of unlined steel tanks for rinsing following pickling or acid plating is not recommended.

Racking of parts for cadmium plating is subject to the same considerations as in the electrodeposition of other metals. Information on design and use of plating racks is available in the article "Industrial (Hard) Chromium Plating" in this Volume.

Maintenance. Table 4 is a typical schedule of maintenance for plating and auxiliary equipment.

Table 4 Recommended maintenance schedule for plating and auxiliary equipment

Daily
Check anodes; replenish when necessary. Check all contacts, anode and cathode. Check solution levels. Check bath temperatures and controls. Check bath composition, if possible, using chemical analysis and plating cell test., Probe tank bottom for lost parts. Check motors for signs of overheating, arcing, or failure. Check amperage and voltage to work.

Check lubrication on automatic equipment.

Weekly
Probe tank bottom for lost parts, if not checked daily. Check rubber tank linings for damage. Filter plating bath, unless constant filtration is used. Check bath analysis, chemically and with plating cell, and make additions and corrections, if these functions are not performed more frequently. Oil equipment. Clean all contacts. Check for preventive-maintenance items that cannot be repaired during the week. Dump and replenish cleaning lines where necessary

Monthly
Pump plating solution to purification tank; treat for impurities, if necessary. Inspect tank linings while plating tanks are empty; repair if necessary. Inspect and clean heat exchangers or plate coils if accumulation or buildup exists. Blow out and check rectifier stacks for condition and power delivery. Check for arcing or scored armatures on generators. Blow out coils. Perform general preventive maintenance examination of all equipment.

Semiannually
Clean out exhaust systems. Repair exhaust fans. Check all motors. Repaint where necessary. Inspect and clean out all floor drains. Check for leaks and cross connections between cyanide and acid drains.

Selection of Plating Method

Selection of plating method involves both technical and economic factors. Still plating, with parts racked, is the oldest and most universally used plating method. Barrel plating, limited to smaller parts that can be tumbled in the plating bath, is popular because many parts can be plated at one time. Automatic hoist units offer a means of mechanizing the still-tank rack or the barrel.

Still tanks are suitable for all types of work. They are used for small production quantities, in general, and for all quantities of parts that cannot be plated in barrel or automatic systems, because of a need for auxiliary anodes or special handling or because plating dimensions are critical.

Example 1: Cadmium Plating of Valve Bodies and Baffle Plates in Still Tanks.

Valve bodies and baffle plates are typical of many parts that are plated in still tanks (see Table 5). To cadmium plate the production quantities of these parts given in Table 5, the equipment required is:

Equipment	Specification
Plating tank (1440 L, or 380 gal)	2.7 by 0.76 by 0.76 m (9 by 2 $\frac{1}{2}$ by 2 $\frac{1}{2}$ ft)
Other tanks (420 L, or 110 gal)	0.91 by 0.76 by 0.76 m (3 by 2 $\frac{1}{2}$ by 2 $\frac{1}{2}$ ft)
Power rectifier (600 A)	1.5 to 6 V
Dimensions of rectifier	0.76 by 0.91 by 2.1 m (2 $\frac{1}{2}$ by 3 by 7 ft)
Total floor space of equipment and access area	2.0 by 4.6 m (6 $\frac{1}{2}$ by 15 ft)
Number of racks	15

Other tanks include a cleaning tank, an acid pickle tank, a hot-water rinse tank, and three cold-water rinse tanks.

Table 5 Equipment requirements for cadmium plating of valve bodies and baffle plates in still tanks

Production requirements	Valve body	Baffle plate
Weight per piece	1.1 kg (2 $\frac{1}{2}$ lb)	0.2 kg (0.5 lb)
Pieces plated per hour	210	175
Area plated per hour	6.5 m^2 (70 ft^2)	11.1 m^2 (120 ft^2)
Minimum thickness	8 μm (320 μin.)	4 μm (160 μin.)

Barrel plating may be used for parts up to 100 mm (4 in.) long and 50 mm (2 in.) thick. Parts such as machine bolts, nuts, and washers are ideal for barrel plating. Conversely, intricate shapes, such as ornaments and complex castings of brittle metals with small sections that fracture easily, should not be barrel plated; the tumbling action may damage these parts, and variation in plating thickness and appearance may result. Intricate designs incorporating recessed or shielded

areas may present problems in plating coverage, luster, and appearance. Barrel plating is not applicable for parts requiring heavy plate. Usually, 8 to 13 μm (320 to 520 μin.) is the maximum thickness of plate applied.

Example 2: Barrel Plating of Small Coil Springs and Brush Holders.

Small coil springs and brush holders are illustrative of parts suitable for barrel plating. Production requirements for plating these parts in horizontal barrels are given in Table 6. Equipment specifications are as follows:

Equipment	**Specification**
Plating tank (1330 L, or 350 gal)	1.8 by 1.2 by 0.76 m (6 by 4 by $2\frac{1}{2}$ ft)
Other tanks (605 L, or 160 gal)	0.91 by 1.2 by 0.76 m (3 by 4 by $2\frac{1}{2}$ ft)
Power rectifier (2000 A)	9 to 15 V
Dimensions of rectifier	0.91 by 1.2 by 2.4 m (3 by 4 by 8 ft)
Centrifugal dryer	0.61 by 0.61 by 0.76 m (2 by 2 by $2\frac{1}{2}$ ft)
Baking oven	1.2 by 0.91 by 2.4 m (4 by 3 by 8 ft)
Equipment floor space	12 m^2 (125 ft^2)
Access area behind line	6.3 m^2 (68 ft^2)
Access area in front	9.3 m^2 (100 ft^2)

Other tanks in the list above refer to cleaning tanks, acid pickle tanks, hot-water tanks, and three cold-water rinse tanks.

Table 6 Production requirements for cadmium plating of coil springs and brush holders in a horizontal barrel

Production requirements	**Coil spring**	**Brush holder**

Weight per piece	14 g ($\frac{1}{2}$ oz)	9 g ($\frac{5}{16}$ oz)
Pieces plated per hour	7200	3800
Area plated per hour	22 m^2 (240 ft^2)	17 m^2 (180 ft^2)
Minimum thickness	4 μm (160 μin.)	8 μm (320 μin.)

Automatic Plating. The primary selection factor for automatic plating is cost. The volume of work must be sufficient to warrant installation of the equipment.

Example 3: Cadmium Plating of Voltage-Regulator Bases on Automatic Equipment.

Voltage-regulator bases were cadmium plated, to a minimum thickness of 3.8 μm (152 μin.), in automatic equipment at the rate of 2640 pieces/h.

Production requirements:

Factor	**Specification**
Weight per piece	170 g (0.37 lb)
Pieces plated per hour	2640
Area to be plated per hour	53 m^2 (570 ft^2)
Minimum plate thickness	4 μm (160 μin.)

Equipment requirements:

Factor	**Specification**
Dimensions of full automatic plating unit	21 by 3.4 by 2.8 m(70 by 11 by 9 ft)
Width of access space on sides of unit	0.76 m (3 ft)

Width of access space on load end of unit	3.1 m (10 ft)
Motor-generator set	15 V, 7500 A
Dimensions of motor-generator set	3.1 by 3.1 by 2.4 m(10 by 10 by 8 ft)

Example 4: Cadmium Plating of Electrical-Outlet Receptacles with Automatic Equipment.

A quantity of 12,000 to 14,000 electrical-outlet receptacles per eight-hour day were required in order to justify the use of a small automatic plating system of 3800L (1000 gal) solution capacity with a single lane of rods and workpieces and plating 4 to 5 μm (160 to 200 μin.) of cadmium. When the size and shape of the parts are such that either automatic or still-tank plating processes may be used, the racking requirement is often the most important factor in determining the relative economy of still-tank and automatic plating. Two kinds of automated plating equipment are available, the regular return machine and the programmed hoist unit, which is an automated straight-line unit. The latter equipment is much less expensive to purchase.

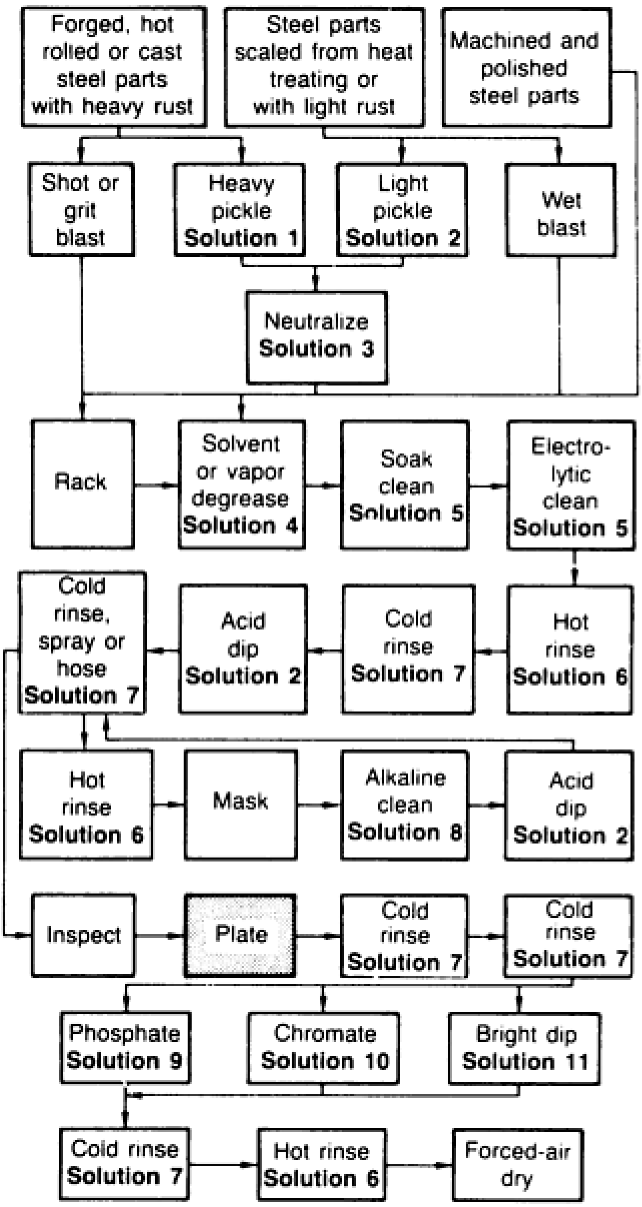
Cleaning and rinsing are essential operations in any plating sequence. Figures 2 and 3 show the number of tanks or stations required for such operations in typical barrel and automatic processes. In Fig. 4, where cleaning, rinsing, and postplating operations are indicated for various initial conditions of the work surface, the plating step itself is a rather inconspicuous item in the flow chart of the total finishing process. Table 7 shows variations in processing techniques for still-tank, barrel, or automatic plating to a thickness of less than 13 μm (520 μin.).

Table 7 Conditions for plating cadmium to a thickness of less than 13 μm (520 μin.)

Process variable	Still tank	Barrel	Automatic
Soak cleaning			
Alkali, g/L (oz/gal)	53 (6)	106 (12)	70 (8)
Temperature, °C (°F)	82 (180)	82 (180)	82 (180)
Time, min	2-3	5	3-5
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	$\frac{1}{2}$
Electrolytic cleaning			
Alkali, g/L (oz/gal)	70 (8)	. . .	70 (8)

Temperature, °C (°F)	82 (180)	. . .	82 (180)
Time, min	$\frac{1}{2}$-1	. . .	1-3
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	1
Acid dipping			
HCl, vol%	10-50	10-50	10-50
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{8}$-1	3	$\frac{1}{2}$ to >1
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	1
Cyanide dipping			
NaCN, g/L (oz/gal)	30-45 (4-6)	30-45 (4-6)	30-45 (4-6)
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	1
Plating			
Temperature, °C (°F)	29 (85)	29 (85)	29 (85)

Current density, A/m^2 (A/ft^2)	270 (25)	9-15 V	270 (25)
Time, min	10	30	10
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	$\frac{1}{2}$
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	2	$\frac{1}{2}$
Bright dipping			
HNO_3, vol%	$\frac{1}{4}$-$\frac{1}{2}$	$\frac{1}{4}$-$\frac{1}{2}$	$\frac{1}{4}$-$\frac{1}{2}$
Temperature, °C (°F)	82 (180)	Ambient	Ambient
Time, min	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{2}$
Rinsing			
Temperature, °C (°F)	. . .	71-82 (160-180)	82 (180)
Time, min	. . .	2	$\frac{1}{2}$
Drying			
Temperature, °C (°F)	82-105 (180-220)	82-105 (180-220)	82-105 (180-220)
Time, min	1-3	5	1-3



Solution No.	Composition	Amount	Temperature		Immersion time
			°C	°F	
1	H_2SO_4	8-12 vol%	71-93	160-200	10-120 s
2	HCl	20-50 vol%	RT	RT	10-120 s
3	Na_2CO_3	75-90 g/L (10-12 oz/gal)	RT	RT	15-60 s[(a)]

4	Petroleum solvent	. . .	RT	RT	$\frac{1}{2}$-3 min
5	Alkali[b]	60-75 g/L[b] (8-10 oz/gal)	82-93[b]	180-200[b]	$\frac{1}{2}$-3 min
6	Water	. . .	82-93[c]	180-200[c]	5-15 s
7	Water[d]	. . .	RT	RT	5-15 s
8	Alkali	60-75 g/L (8-10 oz/gal)	66 max	150 max	$\frac{1}{2}$-1 min
9	[e]	[e]	[e]	[e]	$\frac{1}{2}$-1 min
10	[e]	[e]	[e]	[e]	30 s
11	NaCN	45-60 g/L (6-8 oz/gal)	RT	RT	5-15 s

Note: For cast iron, the solutions, conditions, and procedure are the same as for steel, except that cast iron parts, after being thoroughly washed in cold water following the acid dip, are dipped for 5 s in a room-temperature (RT) cyanide solution (NaCN, 45 to 60 g/L, or 6 to 8 oz/gal) and then again rinsed in cold water, before proceeding to inspection, plating, and post-treatments.

(a) When solution is sprayed, time is 5 to 15 s.

(b) Heavy-duty cleaner. For electrolytic cleaning, concentration of alkali is 45 to 60 g/L (6 to 8 oz/gal), temperature is 82 °C (180 °F), and time is 1 to 3 min.

(c) When a spray rinse is used, water temperature is 71 to 82 °C (160 to 180 °F).

(d) Immersion or spray rinsing.

(e) Proprietary compounds

Fig. 4 Flow diagram showing cadmium plating operation relative to overall cleaning and post-treatment operations for steel and cast iron components

In the case of Fig. 2, 3, and 4 and Table 7, it is important to consider double or triple overflow rinses to control both water usage and pollution control costs. The use of dead rinses, following process tanks, is equally important.

Variations in Plate Thickness

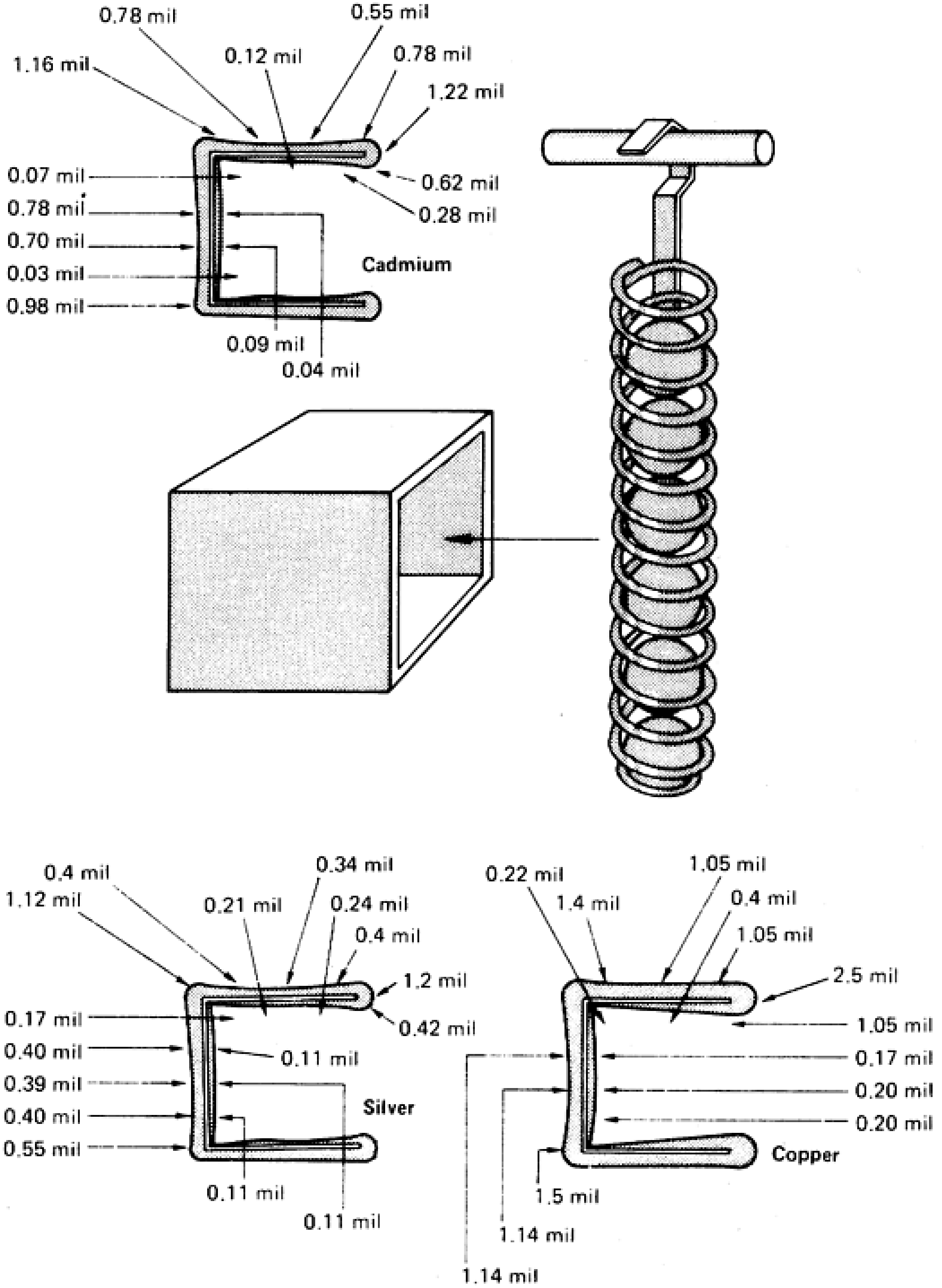
For adequate protection of steel, the thicknesses of cadmium in Table 8 are recommended. The shape of a part can markedly influence uniformity of the electrodeposit. Parts of simple design, such as socket wrenches and bathroom hardware, can be plated with a high degree of uniformity of plate thickness. On such parts, about 90% uniformity would be anticipated.

Table 8 Recommended thicknesses of cadmium

Environmental exposure	Description	Thickness		Uses
		µm	µin.	
Mild	Exposure to indoor atmospheres with rare condensation. Minimum wear and abrasion	5	200	Springs, lock washers, fasteners
Moderate	Exposure mostly to dry indoor atmospheres. Subject to occasional condensation, wear, or abrasion	8	320	Television and radio chassis, threaded parts, screws, bolts, radio parts instruments
Severe	Exposure to condensation, infrequent wetting by rain, cleaners	13	520	Washing machine parts, military hardware, electronic parts for tropical service
Very severe	Frequent exposure to moisture, saline solutions, and	25	1000	. . .

Threaded fasteners present a special problem, because of variations in contour and because of tolerance requirements. These items ordinarily are barrel plated, and thicknesses of 3 to 4 µm (120 to 160 µin.) are usually specified.

Throwing Power. The effect of shape on uniformity of deposit thickness is exemplified by the open-ended box (100 mm, or 4 in., cube) of Fig. 5. The open end of the box is pointed toward one of the anodes, to produce the most desirable condition for this shape without auxiliary thief rings, shields, bipolar anodes, insoluble anodes, or other devices. Results of plating such boxes with cadmium, silver, and copper, all deposited from cyanide baths, are shown in Fig. 5. These diagrams illustrate two facts: thickness of plate varies significantly from place to place on the simplest shape; and various plating baths have different throwing powers or abilities to plate uniformly over the surface, regardless of shape.



Plating bath	Thickness ratio[(a)]	
	Side	Bottom
Cadmium	1:4.25	1:12

Copper	1:3.0	1:6
Silver	1:2.5	1:5

(a) Ratio of average plate thickness of inside of average plate thickness on outside

Fig. 5 Plate thickness deposited on the cross section of a cube-shape workpiece to show throwing power of cadmium relative to that of silver or copper in a cyanide bath. Open ends of the 100 mm (4 in.) cubes were pointed toward ball anodes during plating.

The data on cyanide baths tabulated in Fig. 5 show that cadmium has appreciably less throwing power than silver or copper. However, cyanide cadmium has greater throwing power than nickel, chromium, iron, cyanide zinc, acid tin, acid cadmium, acid copper, or acid zinc. Normally, metals plated from cyanide or alkaline baths are more uniformly distributed than metals from acid baths. As design becomes more complex, uniform thickness of plate is more difficult to achieve without the use of special conforming anodes.

Example 5: Plate Thickness Variation in a Workpiece Plated without Use of Conforming Anodes.

A cylindrical, cup-shape production part that was plated without the use of conforming anodes is shown in Fig. 6. Thickness of plate varied from a minimum of 6 μm (240 μin.) to a maximum of 25 μm (1000 μin.).

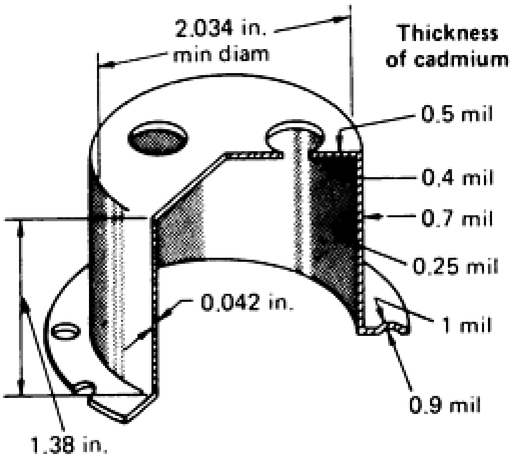


Fig. 6 Variations in plate thickness obtained on a workpiece plated without the use of conforming anodes

Conforming Anodes. Parts of complex shape with stringent dimensional requirements, such as those shown in Fig. 7 and 8, require the use of special techniques, conforming anodes, and shields, in order to obtain the required uniformity of plate thickness.

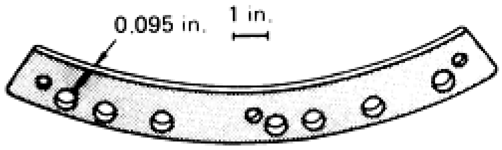


Fig. 7 Application of shields to obtain shim having a uniform cadmium plating. The 305 mm (12 in.) long and 38 mm (1 in.) wide shim was plated to the required thickness of 13 ± 5 μm (520 ± 200 μin.).

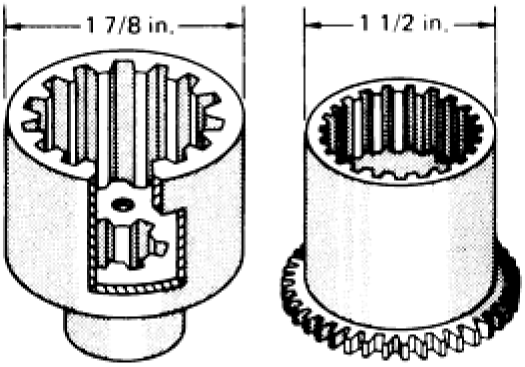


Fig. 8 Couplings that were uniformly cadmium plated with the aid of a 6.4 mm ($\frac{1}{4}$ in.) diameter anode centered in the bore during the plating operation. Plating thickness ranges from 8 to 13 μm (320 to 520 μin.).

Example 6: Application of Shields to Produce Uniform Cadmium-Plated Shim.

A shim, 305 mm (12 in.) long by 40 mm ($1\frac{1}{2}$ in.) wide by 2.4 mm (0.095 in.) thick, is shown in Fig. 7. Parallelism of all sides, as well as plate thickness, was extremely critical. When this part was plated in a simple rack, plate thickness varied from 13 μm (520 μin.) at the center to 50 to 75 μm (0.002 to 0.003 μin.) at the edges and ends.

By using shields that approximated the outline of the shim, it was possible to plate cadmium all over to a depth of 13 ± 5 μm (520 ± 200 μin.). The part was gently agitated in a still bath.

Example 7: Uniform Internal and External Cadmium Plating of Splined Couplings.

A coupling that required 8 to 13 μm (320 to 520 μin.) all over, except for the last 6.4 mm ($\frac{1}{4}$ in.) of the outside diameter of the small end, is shown in Fig. 8. The internal splines on both large and small bores were checked with plug gages and a single-tooth gage to ensure uniformity of plate thickness. To obtain the required uniformity, a 6.4 mm ($\frac{1}{4}$ in.) diameter anode was centered in the bore during plating. Although the outer surface of the large end of the coupling accumulated a heavier coating than other areas, general plate-thickness uniformity met requirements.

Example 8: Uniform Cadmium Plating of Coupling Leaving External Teeth Unplated.

A coupling that, except for the external teeth, was cadmium plated all over to a specified depth of 8 to 13 μm (320 to 520 μin.) is also shown in Fig. 8. Spline and internal bore dimensions were critical and had to be held to a tolerance of ±5 μm (±200 μin.) after plating. Again, uniformity of plate thickness was achieved by centering a 6.4 mm ($\frac{1}{4}$ in.) diameter anode in the bore during plating.

Simple cylindrical, cuboid, and channel shapes, such as those shown in Fig. 9, usually require conforming anodes in order to achieve complete coverage of plate and reasonable plating uniformity. Dimensional limits that definitely require the use of an internal anode are indicated for each geometric shape.

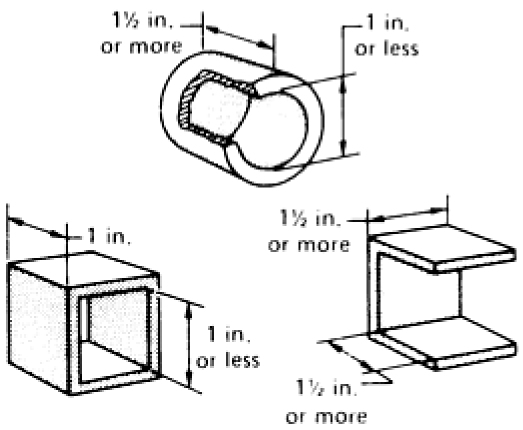


Fig. 9 Typical workpiece configurations with accompanying dimensions that require the use of conforming anodes to ensure uniform plate thickness

Normal Variations. Even under preferred production conditions, some variation in plate thickness must be anticipated. Usually, this normal scatter is acceptable and falls within the specified range of allowable variation.

In general, barrel plating produces greater variations in thickness than still plating. In barrel plating, factors such as the weight, size, and shape of the part usually exert a greater influence on uniformity of plate thickness than they do in still or automatic plating.

Screws, nuts, and other small parts of fairly regular shape will usually coat uniformly in barrel plating. Parts that are likely to nest because they have large flat areas or cup-shape recesses exhibit wide variations in coating thickness. Variations decrease somewhat as the thickness of plate increases.

Variations in plate thickness obtained on production parts are detailed in the example that follows:

Example 9: Histogram Showing Thickness Distribution of 90 Cadmium-Plated Components.

The small cylindrical part shown in Fig. 10 was plated in a horizontal barrel. The load contained about 5000 pieces. Thickness of plate was measured with a magnetic gage on 90 parts from each load. Plating thickness ranged from 5 to 14 μm (200 to 560 μin.).

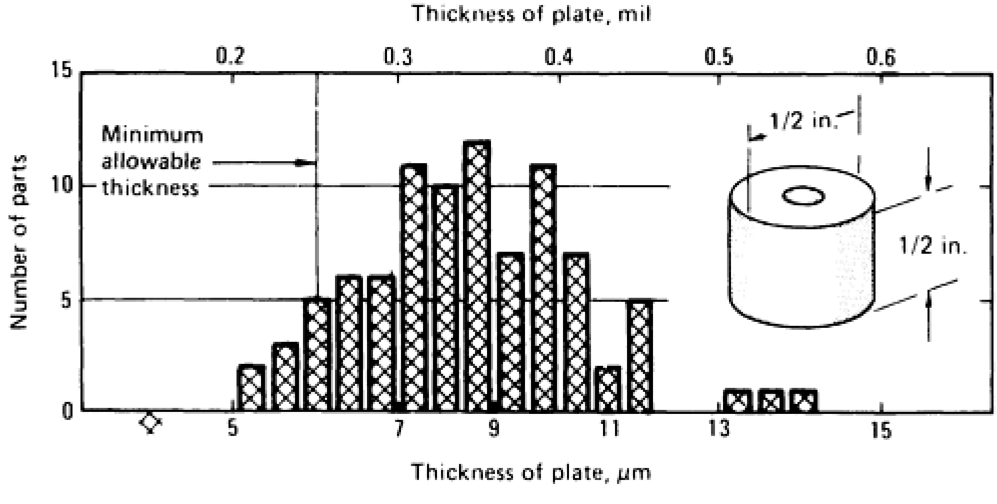


Fig. 10 Thickness distribution for cadmium plating of 90 samples that were evaluated from a 5000-piece

production lot

Other Application Factors

Aside from considerations of cost of very large plating systems, there are no size limitations on parts that can be cadmium plated, provided a tank of adequate size and other essential equipment are available. When a very large part is to be plated, jet plating methods may sometimes be used, rather than constructing a very large plating tank. In the jet technique, a steady stream of solution impinges against the part to be plated until the required thickness of plate is obtained. Because of the rapid movement of the solution, very high current densities can be used. The quality of the plate is comparable to that obtained by conventional methods.

Another technique that can be used on large parts is selective (or brush) plating. Detailed information is available in the article "Selective Plating" in this Volume.

Hardness. The hardness of the basis metal has little or no effect on the successful deposition of cadmium. However, the harder steels are likely to be more highly alloyed and may produce difficult-to-remove smuts from excessive pickling or chemical cleaning. Pickling is also a source of hydrogen embrittlement, which may be particularly harmful to hardened and stressed parts.

Springs often are electroplated with cadmium for protection against corrosion and abrasion. The following example deals with failure of a cadmium-plated compression spring that was not properly treated to release hydrogen.

Example 10: Baking of Cadmium-Plated 6150 Alloy Steel to Eliminate Hydrogen Embrittlement.

A spring used in a high-temperature relief valve under intermittent loading had dimensions and specifications as follows: wire size, 8.76 mm (0.345 in.); outside diameter of spring, 50 mm (2 in.); length, 75 mm (3 in.); six coils; 6150 alloy steel at 43 HRC; stress relieved immediately after coiling. The plating sequence was:

1. Alkaline clean.
2. Rinse in cold water.
3. Electroplate with cadmium 8 μm (320 μin.) thick.
4. Rinse in hot water.
5. Relieve hydrogen embrittlement in boiling water $\frac{1}{2}$ h.

The spring broke with a shatter fracture typical of that caused by hydrogen embrittlement. The corrective action was to bake the spring at 190 °C (375 °F) for 5 h.

For additional information on this subject, refer to the section "Hydrogen Embrittlement" in this article.

Service Temperature. Cadmium-plated, high-strength steel parts that are subjected to heavy loading should never be used at temperatures above 230 °C (450 °F). Cadmium melts at 320 °C (610 °F); at temperatures approaching 260 °C (500 °F), damage occurs that adversely affects mechanical properties.

Diffused Coatings. The aviation industry has developed an application for cadmium for low-alloy steel jet engine parts. The substrate is first plated with 10 μm (400 μin.) of nickel and then 5 μm (200 μin.) of cadmium. The alloy is diffused at 340 °C (645 °F) for about 1 h. Coverage with nickel must be complete, because cadmium can detrimentally affect the steel substrate when heated above the melting point of cadmium. In this way, an alloy with a very high melting point can be formed. Low-alloy steel parts that operate in jet engines at a temperature of 540 °C (1005 °F) were coated with this diffused alloy. After operating for 1 h at 540 °C (1005 °F), the parts withstood 100 h of salt spray without rusting. Cadmium can also be plated on copper and zinc, as well as on nickel.

Solderability. Although cadmium usually solders well with solders of the 60% tin, 40% lead type, using an inactive rosin flux, its performance may sometimes be unaccountably erratic. Solderability can be improved and made more

consistent by predepositing a thin (3 to 4 μm, or 120 to 160 μin.) layer of copper. If the final cadmium deposit is at least 4 μm (160 μin.) thick, the copper coating will not adversely affect corrosion resistance in mild indoor atmospheres. It is important for health and safety reasons to see the section "Toxicity of Cadmium" in this article.

Cadmium on Stainless. Cadmium can be successfully plated over stainless steels and heat-resisting chromium-nickel alloys if the basis metal is first activated and given a light coating of nickel in a nickel chloride-hydrochloric acid bath (U.S. Patent 2,437,409). Composition and operating conditions for this bath are as follows:

Factor	Specification
Nickel chloride	240 g/L (32 oz/gal)
Hydrochloric acid (1.16 sp gr)	120 g/L (16 oz/gal)
Temperature	Room temperature
Current density	55 to 2150 A/m^2 (50 to 200 A/ft^2)
Time	2 to 4 min
Anodes	Nickel

Plating of Cast Iron

Cast iron is difficult to plate because of the graphite flakes or nodules in the microstructure. The larger the graphite inclusions, the more difficult the plating operation. Cast iron parts with unmachined surfaces should be cleaned by mechanical methods, such as shot blasting or tumbling, before plating. Heavy pickling should be avoided if possible, because it produces smut that is difficult to remove. However, light pickling is required after abrasive cleaning, to activate the surface for plating.

Pickling should be followed by a thorough water rinse and a cyanide dip (see note in the table accompanying Fig. 4). Any carryover of acid to the cyanide dip must be avoided, because the combination of these chemicals generates a highly poisonous hydrocyanic gas. The fluoborate solution described in Tables 1(a) and 1(b) is excellent for plating cast iron parts without deep recesses. The cyanide solutions in Tables 1(a) and 1(b) also may be used, provided no metal-organic grain-refining agents have been added. Current density on the high side of the indicated ranges is recommended, to establish a continuous film of cadmium on the iron as soon as possible.

Cadmium Versus Zinc

In rural areas, cadmium and zinc are generally considered to offer equal protection. However, zinc is superior to cadmium in industrial environments (Table 9). In uncontaminated marine atmospheres, zinc and cadmium give approximately equal protection. When the comparison is made at a distance of 24 m (80 ft) from the ocean, cadmium gives significantly greater protection than zinc. Although it is used to a limited extent in the paper and textile industries, cadmium plate has poor resistance to chemicals commonly used in these processes and also to the chemicals of the petroleum and pharmaceutical industries.

Table 9 Protection against rusting imparted to steel in selected atmospheres by 25μm (1000μin.) of cadmium plate or zinc plate

Test location	Atmosphere	Time required for 5 to 10% rusting, yr	
		Cadmium	Zinc
New York, NY	Industrial	2	4
Pittsburgh, PA	Industrial	3	4
Sandy Hook, NJ	Marine, Industrial	6	5
State College, PA	Rural	>11	>11
Key West, FL	Marine	>7	>9

Source:ASTM

One reason for preferring cadmium to zinc is that cadmium plate forms a smaller amount of corrosion products than zinc, particularly in marine atmospheres. Cadmium also retains its initial appearance for a longer time. This is an important consideration in applications where a buildup of corrosion products would have a detrimental effect, such as preventing the flow of current in electrical components or the movement of closely fitting parts such as hinges. For such applications, cadmium should be chosen in preference to zinc. Cadmium is preferable to zinc for plating cast iron.

Cadmium Substitutes

There is increased pressure, both domestically and internationally, for reduced usage, or even elimination of cadmium plating for health, safety, and environmental reasons. There have been several zinc alloy baths developed that work for specific applications, but none duplicates all the properties of cadmium. There are many instances, however, where the use of cadmium plating is not essential and zinc or zinc alloy deposits could be substituted, because both give adequate anodic protection, and there was no functional purpose when cadmium was chosen in the first place.

Chemical Analysis of Cyanide Cadmium Plating Baths

Table 10 lists analytical tests that may be applied to cyanide cadmium plating baths to determine their contents of cadmium metal, sodium cyanide, sodium hydroxide, and sodium carbonate.

Table 10 Analytical tests for determining concentration of selected chemical constituents of cyanide cadmium plating baths

Test constituent	Component			
	Cadmium metal	Sodium cyanide (total)	Sodium Hydroxide	Sodium Carbonate
Reagents	Hydrochloric or sulfuric acid (concentrated) Ammonium hydroxide (concentrated) Eriochrome black "T" indicator (0.5% solution in alcohol) Formaldehyde (8% solution in water)	Ammonium hydroxide (concentrated) Potassium iodide (10% solution in water) Silver nitrate (13 g/L, or	LaMotte sulfo-orange indicator Sulfuric acid, standard (0.94	Barium chloride (10% solution in water) Methyl orange-xylene cyanole

	Disodium dihydrogen ethylenediaminetetraacetate dihydrate (EDTA), 0.575*M* solution (21.4 g/L, or 2.85 oz/gal)	1.7 oz/gal solution in water)	*N*)	indicator solution Hydrochloric acid, standard (0.7 *N*)
Procedure	1. Pipette exactly 2 mL (0.07 oz) of plating bath into a 250 mL (8.5 oz) Erlenmeyer flask, and dilute to about 100 mL (3.4 oz) with distilled water. 2. Neutralize this dilution to a faint white precipitate with hydrochloric or sulfuric acid. This can be conveniently done from the burette of standard sulfuric acid (0.94 *N* used for the caustic titration, or by the addition of a 50% solution of hydrochloric acid from an eyedropper. If no precipitate appears, as may happen with a new bath, thymolphthalein can be used as an indicator and will change from blue to colorless on neutralization. 3. Add 10 mL (0.34 oz) of concentrated ammonium hydroxide and about $\frac{3}{4}$ mL of Eriochrome indicator. 4. Zero the burette. 5. Add 8 mL (0.27 oz) of 8% formaldehyde solution. 6. Titrate immediately with EDTA solution. The color change is from red to blue, and it is sharpest when the solution is titrated as soon as possible after the formaldehyde has been added. A rapid titration will also give a sharper end point. Occasionally, the presence of impurities in the bath will prevent the attainment of a clear blue end point, but the color will prevent the attainment of a clear blue end point, but the color change is still sharp, from a red to a purplish blue.	1. Pipette a 2 mL (0.07 oz)sample of plating bath into a 250 mL (8.5 oz) flask. 2. Add to the sample about 50 mL (1.7 oz) distilled water, 5 to 7 mL (0.17 to 0.24 oz) of ammonium hydroxide, and 2 to 3 mL (0.07 to 0.10 oz) of potassium iodide solution. 3. Titrate with silver nitrate solution to the first stable faint yellowish turbidity.	1. Pipette 10 mL (0.34 oz) of the plating bath into a 250 ml (8.5 oz) flask. 2. Add to the sample about $\frac{1}{2}$ mL (0.017 oz) of indicator solution. 3. Titrate with the sulfuric acid to the color change from orange to yellow.	1. Pipette 10 mL (0.34 oz) of plating bath into a 250 mL (8.5 oz) beaker, add to it about 100 mL (3.4 oz) of water, and heat to boiling. 2. Stir into boiling bath dilution about 20 mL of barium chloride solution; cover mixture; allow to stand warm for about $\frac{1}{4}$ to $\frac{1}{2}$ h. 3. Filter, using No. 41 Whatman filter paper, and wash precipitate and flask at least 2 or 3 times with hot distilled water. 4. Place paper and precipitate in the original beaker, add about 10 mL (0.34 oz) of hot distilled water and 3 or 4 drops of indicator. 5. Titrate with the hydrochloric acid (while stirring) to the first permanent color change from green to purple.
Calculation	Milliliters of EDTA solution used × 0.432 = ounces per gallon, cadmium metal	Milliliters of silver nitrate used × 0.5 = ounces per gallon, total sodium cyanide	Milliliters of sulfuric acid used × 0.5 = ounces per gallon, sodium hydroxide	Milliliters of hydrochloric acid used × 0.5 = ounces per gallon, sodium carbonate

Methods for Measuring Thickness of Cadmium Plate

There are many nondestructive and destructive methods for measuring the thickness of cadmium deposits (Table 11). The most widely used are magnetic, coulometric, and eddy-current methods, as well as x-ray spectrometry and microscopic cross-sectioning. Other reliable methods, including the chemical drop test, may be used. Detailed information on most methods can be obtained from ASTM specification B 659-85 ("Standard Guide for Measuring Thickness of Metallic and Inorganic Coatings") (Ref 1) and ISO Standards.

Table 11 Methods applicable to measuring cadmium coating thickness on selected ferrous and nonferrous substrates per ASTM B 659

Substrates	**Measurement technique**

	Beta backscatter[(a)]	Coulometric[(b)]	Magnetic[(c)]
Magnetic steel (including corrosion-resisting steel)	X	X	X
Nonmagnetic stainless steels	X	X	. . .
Copper and alloys	X	X	. . .
Zinc and alloys	X	. . .	. . .
Aluminum and alloys	X	X	. . .
Magnesium and alloys	X	. . .	. . .
Nickel	X	X	. . .
Glass sealing nickel-cobalt-iron alloys (UNS No. K94610)	X	. . .	X
Nonmetals	X	X	. . .
Titanium	X	. . .	. . .

Source: Ref 1

(a) ASTM B 567; ISO 3543.

(b) ASTM B 504; ISO 2177.

(c) ASTM B 499; ISO 2178.

Reference cited in this section

1. 1989 Annual Book of ASTM Standards, Vol 2.05 *(Metallic and Inorganic Coatings; Metal Powders, Sintered P/M Structural Parts)*, ASTM, 1989, p 441-443

Solutions for Stripping Cadmium Plate

Electrodeposited cadmium can be stripped chemically from the basis metal by immersion in one of the following solutions: ammonium nitrate, inhibited hydrochloric acid, chromic acid with a sulfuric acid addition, and ammonium persulfate with an ammonium hydroxide addition. Electrolytic stripping is performed in a solution of sodium cyanide with an addition of sodium hydroxide. Compositions of these stripping solutions, and the immersion times to be used with them, are given in Table 12.

Table 12 Solutions for stripping electrodeposited cadmium

Solution[a]	Composition	Amount		Immersion time, min[b]
		g/L	oz/gal	
1	Ammonium nitrate	105-136	14-18	10-20
2[c]	Hydrochloric acid (1.18 sp gr), undiluted	. . .	. . .	10-20
	Antimony trioxide	15	2	. . .
3	Chromic acid	203	26.8	5-10
	Sulfuric acid (95%)	48[d]	6.4[e]	. . .
4	Ammonium persulfate	51	6.7	5-10
	Ammonium hydroxide	96.8[d]	12.8[e]	. . .
5[f]	Sodium cyanide	60-91	8-12	10-20

(a) Solutions are listed in order of preference; all solutions are used at room temperature.

(b) Immersion times are for deposits 8 to 13 μm (320 to 520 μin.) thick.

(c) Solution should not be used on stressed or hardened parts.

(d) mL/L.

(e) fl oz/gal.

(f) Solution for stripping electrolytically; 540 to 1080 A/m^2 (50 to 100 A/ft^2) and 6 to 8 V; part to be stripped is made the anode.

Toxicity of Cadmium

Two hazardous consequences attend the use of cadmium in contact with food products: acute poisoning resulting from the ingestion of cadmium dissolved from containers or from food-handling equipment; and poisoning from the inhalation of fumes of cadmium oxide, if cadmium-plated vessels or food-handling equipment is heated.

Acute poisoning has resulted from the ingestion of cadmium salts derived from cadmium-plated vessels in which any acid foods have been stored for even short periods of time; therefore, cadmium should not be used on food containers of any

kind. Fatal poisoning is more apt to result from the inhalation of dust or fumes of cadmium salts and cadmium oxide. These are the kinds of exposure encountered in industrial operations when cadmium-plated parts are heated or soldered. Exposure to dust or fumes of cadmium should be avoided and safety / OSHA regulations should be followed. The complete regulatory text of the cadmium rule and appendixes is published in the Federal Register 57 (178): 42102-42463, 14 September 1992. Among its provisions, the rule requires employers to adhere to a new personal exposure limit (5 g/ μm^3), provide medical surveillance, monitor exposure level, and maintain proper records.

Deposits of cadmium on the sides or bottom of a tank previously used for cadmium plating should not be burned off, because the fumes from this operation are highly toxic. These deposits should be removed mechanically or deplated. For high-efficiency deplating, the solution used contains 45 to 60 g/L (6 to 8 oz/gal) of sodium cyanide and 23 to 30 g/L (3 to 4 oz/gal) of sodium hydroxide in water; the tank is the anode, and steel sheets or scrap steel parts are the cathodes. Just like the production solutions presented in Table 1(a), the resulting solution must be treated with the utmost care. The proper handling of cyanide solutions should be discussed with the proper vendors, and internal safety departments must train operators in the safe use of these solutions. Disposal issues must be part of waste treatment management practices. Additional information is available in the article "Cadmium Elimination" in this Volume.

Selective Plating

When plating must be applied to only certain areas of parts, the areas not to be plated must be stopped off or masked, which means they must be covered with materials that will not conduct current, such as waxes, lacquers, or rubber tape.

Waxes. Ordinarily, a petroleum-derived wax is used for stopping off. The wax must not contain any oil or other organic materials that will dissolve in the plating solution and contaminate it. It must also be capable of adhering tightly to the part, to prevent the plating solution from coming in contact with the stopped-off area.

Before being applied, the wax is heated in a pot to about 27 °C (80 °F) above its melting point, so that it does not solidify too rapidly and will adhere more readily. Still-better adhesion is obtained if parts are warmed on a hot plate before the wax is applied.

Parts must be positioned so that only the area to be coated is placed in the molten wax. This means that, normally, only end areas or protrusions can be stopped off with wax. The wax can be applied with camel's hair brushes, but this is time-consuming if many parts are to be treated. For a large number of similar parts, a fixture can be used that will dip each part to the proper depth.

A sharp, uniform demarcation between plated and nonplated areas can be obtained by the use of pressure-sensitive tape and wax, following either of two procedures:

- Apply the tape to the part so that the trailing edge of the tape follows the demarcation line; dip that portion of the part to be left unplated in molten wax so as to overlap the trailing edge of the tape slightly; and then remove the wax when it has solidified.
- Apply the tape to the part so that the leading edge follows the demarcation; dip that portion of the part to be left unplated in molten wax so as to overlap partly the trailing edge of the tape; and then, when the wax has solidified, plate the part without removing the tape.

Waxing must be done carefully, so that areas that are to be plated have no wax on them. If wax does get on areas to be plated, it must be thoroughly removed. After plating and postplating treatments, the wax is removed from parts by placing them in hot water.

Lacquers may be used instead of wax as stop-off coatings, but their use is generally limited to instances in which the plating bath is operated at a temperature at which the wax would melt. Lacquer is applied by dipping or painting the areas to be stopped off. Normally, two to four coats of lacquer must be applied. One disadvantage of lacquer is that it is difficult and time-consuming to get all of it off. Heavier coatings prevent leakage and make stripping easier.

Plastic Tape. For stopping off irregular areas of heavy parts that cannot be dipped or that are too large to be painted (e.g., splines, large shafts, or bearing shoulders), a plastic tape is used. The tape is wound tightly and stretched over the irregular areas. To prevent leakage, each turn should overlap the preceding one at least half-way. At the edge of the stop-

off area, a pressure-sensitive tape is used to form a sharp line and prevent the leakage of plating solution under the plastic tape.

Plastic tape is expensive to use. When many similar parts are to be selectively plated, rubber sheet, held in place by pressure-sensitive tape, may be used for stopping off areas not to be plated. Rubber stoppers, plastic plugs, or corks, sealed with wax, are used for stopping off internal areas of cylindrical parts. Rubber or plastic tubing can be used to stop off areas of small cylindrical parts.

Rinsing and Drying

Although one of the simplest operations in plating, rinsing is often the most difficult to accomplish. The primary requirements are that the rinsing be effective in removing the solutions used in the preceding tank and that no contaminants be introduced into the subsequent tank. Rinse baths, whether hot or cold, usually are provided with some means for constant changing of the water, good agitation, and skimming of the surface. Agitation of both the water and part is usually necessary. The surface skimmer may consist of jets of water shooting across the surface to rinse surface films into an overflow trough at the far side of the rinse tank. Water should enter at the bottom of one side of a rinse tank and escape over a weir outlet along the top at the opposite side of the tank. Constant monitoring of the water quality versus product quality is essential with the increased demand to lower water usage. The amount of contamination in rinse tanks can be regulated by controlling the flow of fresh water into the rinse through a valve actuated by a conductivity cell.

The temperature of the postplating rinse bath depends to some extent on the mass of the work being rinsed, because the workpiece must supply all the heat of evaporation for drying. Thin-gage materials require rinse temperatures of 93 to 100 °C (200 to 212 °F); otherwise, the workpiece cools before evaporation is complete. Parts made from thicker materials may be rinsed in water at 82 to 88 °C (180 to 190 °F).

Rapid and thorough drying of the plated work is important, to prevent water marks and stains and to eliminate the moisture from residual salt that may not have been entirely removed from crevices or recesses by rinsing. Residual salt and moisture can be a source of corrosion.

Drying practice is also influenced by the shape and orientation of the workpiece as it leaves the final rinse. In many applications, hot-water rinsing is followed with oven drying, wherein hot air is blown directly against the work. In automatic installations, oven temperatures are maintained at 105 °C (220 °F) or higher and the work passes through in 3 to 5 min. Centrifuges with a hot air blast are used for barrel-plated work.

Hydrogen Embrittlement

If an electrodeposited coating is to be applied to a highly stressed part or a high-strength (over 1100 MPa, or 160 ksi) heat-treated steel part, it is important that the processing not decrease the static or fatigue strength of the part. Hydrogen embrittlement does not affect fatigue life. Coatings having high residual stresses, such as chromium, affect fatigue life; however, this is not the case with cadmium.

Cadmium deposited from a cyanide solution is more likely to produce hydrogen embrittlement than any other commonly plated metal. Heat-treated steels, particularly those plated and used at 35 HRC and above, are susceptible to hydrogen embrittlement. Most susceptible is spring steel that has not been adequately stress relieved after forming. The requirements of Federal Specification QQ-P-416F may be used as a guide for stress relief before plating and hydrogen embrittlement post-treatment (Table 13). Other guidelines vary from these, but the latest revision (F) seems to be the most stringent.

Table 13 Heat treat specifications required to stress relieve cadmium-plated components

Hardness, HRC	Stress relief before plating			Hydrogen embrittlement relief (within 4 h of plating)		
	Temperature		Minimum time, h	Temperature		Minimum time, h
	°C	°F		°C	°F	

34-54	175-205	350-400	4	. . .	. . .	. . .
36-45	. . .	. . .	. . .	175-205	350-400	8 23[(a)]
46-54	. . .	. . .	. . .	175-205	350-400	23
>55	120-150	250-300	23	120-150	250-300	23

(a) Fasteners and bearings

Although the thickness of the plated deposit appears to have no direct bearing on hydrogen embrittlement, it is always more difficult to release the hydrogen (by baking) from heavy deposits.

By adhering to the following procedures, hydrogen embrittlement can be minimized or made inconsequential:

- Use mechanical cleaning methods, such as brushing, blasting, and tumbling.
- Wherever possible, avoid the use of strong acid-pickling solutions and extended exposure to acid pickling.
- If pickling is essential to the preparation of medium-strength and high-strength steel parts, bake the parts at 175 to 205 °C (350 to 400 °F) for 3 h after pickling and before plating.
- In plating, use the higher current densities to produce a more porous deposit; 755 A/m^2 (70 A/ft$^{2)}$ in a cyanide bath without brighteners has been satisfactory for steel at 46 HRC.
- After plating, bake parts at 175 to 205 °C (350 to 400 °F) for 3 to 24 h. The shorter baking periods are generally adequate for parts with a tensile strength below about 1520 MPa (220 ksi); longer baking periods are recommended for steel of tensile strength above about 1520 MPa (220 ksi) or for lower-strength parts if sharp notches or threads exist. Parts greater than 25 mm (1 in.) thick should also be baked for 24 h. The elapsed time between plating and baking must never exceed 8 h and should be carried out as soon as possible, preferably within 4 h.
- Plate parts to a thickness of about 5 μm (200 μin.), bake for 3 h at 195 °C (385 °F), activate in cyanide, and then complete the plating to the required final thickness.

The applications of shot peening and baking, as related to the hardness of the steel to be plated, are described in Federal Specification QQ-C-320 (Amendment 1) and are summarized in the article "Industrial (Hard) Chromium Plating" in this Volume.

Tests for Adhesion of Plated Coatings

The tests used for evaluating adhesion of plated coatings are largely qualitative. A bend test, described in Federal Specification QQ-P-416, involves observation of the degree of flaking that occurs as a specimen is bent. Additional tests are scrape/scratch, short blasts from a glass bead machine (reduced pressures), and bake/cold water quench, all of which tend to show blistering or peeling. In another test, a pressure-sensitive tape, such as surgical adhesive or masking tape, is attached to the plated surface. The tape is quickly stripped from the specimen by pulling it at right angles to the surface. If adhesion is poor, loose plate or blisters will appear as flecks on the surface of the adhesive.

Another good test for adhesion, on parts that have been baked after being plated, is a visual inspection for blisters in the plate. If a good bond has not been established, the plate will most often pull away from the basis metal and form blisters.

Chromate Conversion Coatings

The corrosion of cadmium plate can be retarded by applying a supplemental chemical conversion coating of the chromate type. The chromate films are produced by immersing the plated article in a solution containing chromic acid or other chromates and catalytic agents. These films provide protection against initial corrosion through the inhibitive properties of the water-soluble chromium compounds present. However, the chromate finish must not be applied before stress relieving or baking, because its beneficial effect will be destroyed by the elevated temperature.

Chromate conversion coatings are used in some instances to improve the bond between paint and cadmium-plated surfaces and to provide the plate with resistance to corrosion if gaps should occur in the paint film. However, wash primers will not adhere to chromate finishes, and baking painted chromate finishes will produce poor bonding.

Plate Discoloration. Cadmium tarnishes easily from handling and, at a lesser rate, from normal oxidation. Both types of tarnish may be prevented by the use of chromate conversion coatings. For maximum prevention of tarnish, an unmodified chromate film should be applied, if the iridescence or the light yellow coloration it imparts is not objectionable. Such a surface film also provides resistance against salt spray and humidity, and its application for this purpose is frequently standard practice. The clear film obtained by bleaching a chromate coating affords much poorer protection, but it is superior to an as-plated cadmium surface with respect to resistance to tarnishing, humidity, and salt spray.

With a plate thickness of 13 to 18 μm (520 to 720 μin.) and a chromate conversion coating, cadmium will provide adequate service in marine and humid tropical atmospheres. When long-term exposure is anticipated, a paint coating is desirable.

If a chromate treatment is used, only two cold-water rinse tanks are necessary after plating. The first may be for reclaiming the cadmium solution or for the treatment of water. The second rinse should be provided with sufficient flow and agitation to prevent carryover of cyanide into the chromate solution. After chromate dipping, three rinse tanks are required. Again, the first tank may be for reclaiming or waste treatment.

Yellow chromate finish is obtained by dipping in acidified sodium or potassium dichromate. Excellent corrosion protection and a superior base for organic finishing are obtained.

Clear chromate finish consists of 117 g (0.258 lb) of chromic acid and 1.2 g (2.6×10^{-3} lb) of sulfuric acid per liter (gallon) of water and provides good passivation and attractive appearance. Although the protective film is very thin, it prevents the formation of a white, powdery corrosion product on cadmium-plated parts in indoor or internal-component use.

Olive green coating is obtained in an acidified dichromate solution and is easily colored by any of the acid dyes.

Other Postplating Processes

Bright Dipping. The solution for bright dipping consists of $\frac{1}{4}$ to 1% of commercial-grade nitric acid (1.41 sp gr) and is used at room temperature. The acid neutralizes any alkaline salts on the surface and provides some passivation. It is used extensively because it does not interfere with solderability. Immersion times vary from 2 to 30 s.

A solution of acidified hydrogen peroxide is also used for bright dipping. It consists of 6 to 7% commercial-grade (35%) hydrogen peroxide acidified with about 0.25% H_2SO_4. It produces a bright luster and uniform finish but adversely affects resistance to atmospheric corrosion, ultimately resulting in the formation of a white powder. The solution is rather expensive and has a short life.

Phosphate treatment produces a supplementary conversion coating. The solution consists of 3 to 4% equivalent phosphoric acid at a pH of 3.5 to 4.2. The solution is maintained at a temperature of 71 to 88 °C (160 to 190 °F); immersion time ranges from 3 to 5 min. Following the acid dip, parts are water rinsed and then passivated for 2 to 3 min in a solution of sodium dichromate (0.8 to 1.5 g/L, or 0.1 to 0.2 oz/gal) or chromic acid (pH, 3.5 to 4.0) at a temperature of 66 to 77 °C (150 to 170 °F). The coating provides a good basis for organic finishes.

Molybdenum coating is performed in a proprietary bath containing molybdenum salts dissolved in a highly concentrated solution of ammonium chloride at 54 to 66 °C (130 to 150 °F). An attractive, adherent black finish is obtained.

Zinc Plating

Revised by A. Sato, Lea Ronal Inc.

Introduction

ZINC is anodic to iron and steel and therefore offers more protection when applied in thin films of 7 to 15 μm (0.3 to 0.5 mil) than similar thicknesses of nickel and other cathodic coatings, except in marine environments where it is surpassed by cadmium (which is somewhat less anodic than zinc to iron and steel). When compared to other metals it is relatively inexpensive and readily applied in barrel, tank, or continuous plating facilities. Zinc is often preferred for coating iron and steel parts when protection from either atmospheric or indoor corrosion is the primary objective. Electroplated zinc without subsequent treatment becomes dull gray in appearance after exposure to air. Bright zinc that has been subsequently given a chromate conversion coating or a coating of clear lacquer (or both) is sometimes used as a decorative finish. Such a finish, although less durable than heavy nickel chromium, in many instances offers better corrosion protection than thin coatings of nickel chromium, and at much lower cost.

Much recent attention has been focused on the development of techniques for electroplating alloys such as zinc-iron, zinc-nickel, and zinc-cobalt. The operating parameters and applications of these coatings is very similar to those for unalloyed zinc. More detailed information about these techniques is provided in the article "Zinc Alloy Plating" in this Volume.

Plating Baths

Commercial zinc plating is accomplished by a number of distinctively different systems: cyanide baths, alkaline noncyanide baths, and acid chloride baths. In the 1970s, most commercial zinc plating was done in conventional cyanide baths, but the passage of environmental control laws throughout the world has led to the continuing development and widespread use of other processes. Today, bright acid zinc plating (acid chloride bath) is possibly the fastest growing system in the field. Approximately half of the existing baths in developed nations use this technology and most new installations specify it.

The preplate cleaning and postplate chromate treatments are similar for all zinc processes; however, the baths themselves are radically different. Each separate system is reviewed in detail in this article, giving its composition and the advantages and disadvantages.

Cyanide Zinc Baths

Bright cyanide zinc baths may be divided into four broad classifications based on their cyanide content: regular cyanide zinc baths, midcyanide or half-strength cyanide baths, low-cyanide baths, and microcyanide zinc baths. Table 1 gives the general composition and operating conditions for these systems.

Table 1 Composition and operating conditions of cyanide zinc baths

Constituent	Standard cyanide bath[a]				Mid or half-strength cyanide bath[b]			
	Optimum		Range		Optimum		Range	
	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal
Preparation								

Sodium cyanide	42	5.6	30-41	4.0-5.5	20	2.7	15-28	2.0-3.7
Sodium hydroxide	79	10.5	68-105	9.0-14.0	75	10.0	60-90	8.0-12.0
Sodium carbonate	15	2.0	15-60	2.0-8.0	15	2.0	15-60	2.0-8.0
Sodium polysulfide	2	0.3	2-3	0.3-0.4	2	0.3	2-3	0.3-0.4
Brightener	[g]	[g]	1-4	0.1-0.5	[g]	[g]	1-4	0.1-0.5
Analysis								
Zinc metal	34	4.5	30-48	4.0-6.4	17	2.3	15-19	2.0-2.5
Total sodium cyanide	93	12.4	75-113	10.0-15.1	45	6.0	38-57	5.0-7.6
Sodium hydroxide	79	10.5	68-105	9.0-14.0	75	10.0	60-90	8.0-12.0
Ratio: NaCN to Zn	2.75	0.37	2.0-3.0	0.3-0.4	2.6	0.3	2.0-3.0	0.2-0.4

Constituent	**Low-cyanide bath**[c]				**Microcyanide bath**[d]			
	Optimum		**Range**		**Optimum**		**Range**	
	g/L	**oz/gal**	**g/L**	**oz/gal**	**g/L**	**oz/gal**	**g/L**	**oz/gal**
Preparation								
Zinc cyanide	9.4[b]	1.3[e]	7.5-14[b]	1.0-1.9	[f]	[f]	[f]	[f]
Sodium cyanide	7.5	1.0	6.0-15.0	0.8-2.0	1.0	0.1	0.75-1.0	0.4-0.13
Sodium hydroxide	65	8.7	52-75	6.9-10.0	75	10.0	60-75	8-10
Sodium carbonate	15	2.0	15-60	2.0-8.0	. . .	. . .	. . .	. . .
Sodium polysulfide	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Brightener	[g]	[g]	1-4	0.1-0.5	[g]	[g]	1-5	0.1-0.7
Analysis								

Zinc metal	7.5	1.0	. . .	0.8-1.5	7.5	1.0	6.0-11.3	0.8-1.5
Total sodium cyanide	7.5	1.0	6.0-15.0	0.8-2.0	1.0	0.1	0.75-1.0	0.1-0.13
Sodium hydroxide	75	10	60-75	8.0-10.0	75	10.0	60-75	8-10
Ratio: NaCN to Zn	1.0	0.1	1.0	0.1	. . .	. . .	. . .	. . .

Note: Cathode current density: limiting 0.002 to 25 A/dm^2 (0.02 to 250 A/ft^2); average barrel 0.6 A/dm^2 (6 A/ft^2); average rack 2.0 to 5 A/dm^2 (20 to 50 ft^2). Bath voltage: 3 to 6 V, rack; 12 to 25 V, barrel.

(a) Operating temperature: 29 °C (84 °F) optimum; range of 21 to 40 °C (69 to 105 °F).

(b) Operating temperature: 29 °C (84 °F) optimum; range of 21 to 40 °C (69 to 105 °F).

(c) Operating temperature: 27 °C (79 °F) optimum; range of 21 to 35 °C (69 to 94 °F).

(d) Operating temperature: 27 °C (79 °F) optimum; range of 21 to 35 °C (69 to 94 °F).

(e) Zinc oxide.

(f) Dissolve zinc anodes in solution until desired concentration of zinc metal is obtained.

(g) As specified

Cyanide baths are prepared from zinc cyanide (or zinc oxide sodium cyanide), and sodium hydroxide, or from proprietary concentrates. Sodium polysulfide or tetrasulfide, commonly marketed as zinc purifier, is normally required in standard, midcyanide, and occasionally low-cyanide baths, to precipitate heavy metals such as lead and cadmium that may enter the baths as an anode impurity or through drag-in.

Standard cyanide zinc baths have a number of advantages. They have been the mainstay of the bright zinc plating industry since the early 1940s. A vast amount of information regarding standard cyanide bath technology is available, including information on the technology of operation, bath treatments, and troubleshooting.

The standard cyanide bath provides excellent throwing and covering power. The ability of the bath to cover at very low current densities is greater than that of any other zinc plating system. This capability depends on the bath composition, temperature, base metal, and proprietary additives used, but it is generally superior to that of the acid chloride systems. This advantage may be critical in plating complex shapes. This bath also tolerates marginal preplate cleaning better than the other systems.

Cyanide zinc formulas are highly flexible, and a wide variety of bath compositions can be prepared to meet diverse plating requirements. Zinc cyanide systems are highly alkaline and pose no corrosive problems to equipment. Steel tanks and anode baskets can be used for the bath, substantially reducing initial plant investment.

The cyanide system also has a number of disadvantages, including toxicity. With the possible exception of silver or cadmium cyanide baths, the standard cyanide zinc bath containing 90 g/L (12 oz/gal) of total sodium cyanide is

potentially the most toxic bath used in the plating industry. The health hazard posed by the high cyanide content and the cost for treating cyanide wastes have been the primary reasons for the development of the lower-cyanide baths and the switch to alkaline noncyanide and acid baths. Although the technology for waste treatment of cyanide baths is well developed, the cost for the initial treatment plant may be as much as or more than for the basic plating installation.

Another disadvantage is the relatively poor bath conductivity. The conductivity of the cyanide bath is substantially inferior to that of the acid bath, so substantial power savings may be had by using the latter.

The plating efficiency of the cyanide system varies greatly, depending on such factors as bath temperature, cyanide content, and current density. In barrel installations at current densities up to 2.5 A/dm^2 (25 A/ft^2), the efficiency can range within 75 to 90%. In rack installations, the efficiency rapidly drops below 50% at current densities above 6 A/dm^2 (60 A/ft^2).

Although the depth of brilliance obtained from the cyanide zinc bath has increased steadily since 1950, none of the additives shows any degree of the intrinsic leveling found in the acid chloride baths. The ultimate in depth of color and level deposits reached in the newer acid baths cannot be duplicated in the cyanide bath.

Midcyanide Zinc Baths. In an effort to reduce cyanide waste as well as treatment and operating costs, most cyanide zinc baths are currently at the so-called midcyanide, half-strength, or dilute cyanide bath concentration indicated in Table 1. Plating characteristics of midcyanide baths and regular cyanide baths are practically identical. The only drawback of the midcyanide bath, compared with the standard bath, is a somewhat lower tolerance to impurities and poor preplate cleaning. This drawback is seldom encountered in practice in the well-run plant. Greater ease of rinsing, substantially less dragout, and savings in bath preparation, maintenance, and effluent disposal costs are responsible for the prominence of this type of bath.

Low-cyanide zinc baths are generally defined as those baths operating at approximately 6 to 12 g/L (0.68 to 1.36 oz/gal) sodium cyanide and zinc metal. They are substantially different in plating characteristics from the midcyanide and standard cyanide baths. The plating additives normally used in regular and midstrength cyanide baths do not function well with low metal and cyanide contents. Special low-cyanide brighteners have been developed for these baths.

Low-cyanide zinc baths are more sensitive to extremes of operating temperatures than either the regular or midcyanide bath. The efficiency of the bath may be similar to that of a regular cyanide bath initially, but it tends to drop off more rapidly (especially at higher current densities) as the bath ages. Bright throwing power and covering power are slightly inferior to those of a standard midcyanide bath. However, most work that can be plated in the higher cyanide electrolytes can be plated in the low-cyanide bath. Despite the fact that low-cyanide baths have significantly lower metal and cyanide contents, they are less sensitive to impurity content than the standard or midcyanide bath. Heavy metal impurities are much less soluble at lower cyanide contents. The deposit from a low-cyanide bath is usually brighter than that from a regular or midcyanide system, especially at higher current densities. These baths are used extensively for rack plating of wire goods. Unlike the other cyanide systems, low-cyanide baths are quite sensitive to sulfide treatments to reduce impurities. Regular sulfide additions may reduce the plating brightness and precipitate zinc.

Microcyanide zinc baths are essentially a retrogression from the alkaline noncyanide zinc process discussed in the following section. In the early history of alkaline baths it was often difficult to operate within its somewhat limited parameters; many platers used a minimal amount of cyanide in these baths, 1.0 g/L (0.13 oz/gal), for example. This acted essentially as an additive, increasing the overall bright range of the baths. However, it negated the purpose of the alkaline noncyanide bath, which is to totally eliminate cyanide.

Preparation of Cyanide Zinc Baths

Bath may be prepared with cyanide zinc liquid concentrates that are diluted with water, and to which sodium hydroxide is normally added, or they may be prepared as follows:

1. Fill the makeup and/or plating tank approximately two-thirds full of tap water.
2. Slowly stir in the required amount of sodium hydroxide.
3. Add the required amount of sodium cyanide and mix until dissolved.
4. Prepare a slurry of the required amount of zinc oxide or zinc cyanide and slowly add to the bath. Mix until completely dissolved. Instead of zinc salts, the bath may be charged with steel baskets of zinc

anode balls that are allowed to dissolve into the solution until the desired metal content is reached.
5. Add an initial 15 g/L (2.0 oz/gal) sodium carbonate for rack plating baths.
6. Add approximately 0.25 to 0.50 g/L (0.03 to 0.06 oz/gal) of sodium polysulfide or zinc purifier for regular and midcyanide baths.
7. Run plating test panels and add the necessary amount of brightener to the bath. If a satisfactory deposit is obtained, place anodes for production.

Zinc baths prepared from impure zinc salts may require treatment with zinc dust and/or low-current-density dummying (the process of plating out bath impurities). Zinc dust should be added at the rate of 2 g/L (0.26 oz/gal) and the bath should be agitated for about 1 h. After settling, the bath should be filtered into the plating tank. Dummying is preferably done on steel cathode sheets at low current densities of 0.2 to 0.3 A/dm^2 (2 to 3 A/ft^2) for 12 to 24 h.

Cyanide Zinc Plating Brighteners

Zinc plating bath brighteners are almost exclusively proprietary mixtures of organic additives, usually combinations of polyepoxyamine reaction products, polyvinyl alcohols, aromatic aldehydes, and quaternary nicotinates. These materials are formulated for producing brightness at both low- and high-density areas and for stability at elevated temperatures. Metallic brighteners based on nickel and molybdenum are no longer commercially used in zinc systems, because their concentration in the deposit is highly critical. Proprietary additives should be used following the manufacturer's recommendations for bath operation. Some incompatibility between various proprietary additives may be encountered, and Hull Cell plating tests should always be used to test a given bath and evaluate new brighteners.

Alkaline Noncyanide Baths

Alkaline noncyanide baths are a logical development in the effort to produce a relatively nontoxic, cyanide-free zinc electrolyte. Approximately 15 to 20% of zinc plated at present is deposited from these baths. Bath composition and operating parameters of these electrolytes are given in Table 2. The operating characteristics of an alkaline noncyanide system depend to a great extent on the proprietary additives and brightening agents used in the bath, because the zinc deposit may actually contain 0.3 to 0.5 wt % C, which originates from these additives. This is ten times as much carbon as is found in deposits from the cyanide system.

Table 2 Composition and operating characteristics of alkaline noncyanide zinc baths

Constituent	Optimum[a]		Range[b]	
	g/L	oz/gal	g/L	oz/gal
Preparation				
Zinc oxide	9.4	1.3	7.5-21	1-2.8
Sodium hydroxide	65	8.6	65-90	8.6-12
Proprietary additive	[c]	[c]	3-5	0.4-0.7
Analysis				
Zinc metal	7.5	1.0	6.0-17.0	0.8-2.3

Sodium hydroxide	75.0	10.0	75-112	10.0-14.9

(a) Operating conditions: temperature, 27 °C (81 °F) optimum; cathode current density, 0.6 A/dm^2 (6 A/ft^2); bath voltages, 3 to 6 rack.

(b) Operating conditions: temperature, 21 to 35 °C (69 to 94 °F) range; cathode current density, 2.0 to 4.0 A/dm^2 (20 to 40 A/ft^2); bath voltages, 12 to 18 barrel.

(c) As specified

Alkaline noncyanide baths are inexpensive to prepare and maintain, and they produce bright deposits and cyanide-free effluents. An alkaline noncyanide zinc bath with a zinc metal content of 7.5 to 12 g/L (1.0 to 1.6 oz/gal) used at 3 A/dm^2 (30 A/ft^2) produces an acceptably bright deposit at efficiencies of approximately 80%, as shown in Fig. 1. However, if the metal content is allowed to drop 2 g/L (0.26 oz/gal), efficiency drops to below 60% at this current density. Raising the metal content much above 17 g/L (2.3 oz/gal) produces dull gray deposits, lower-current-density plating areas, and poor distribution; however, additives have been developed to address this problem. Increasing sodium hydroxide concentration increases efficiency, as shown in Fig. 2. However, excessively high concentrations will cause metal buildup on sharp-cornered edges. Alkaline noncyanide zinc is a practical plating bath having hundreds of thousands of gallons in use in large captive plating installations.

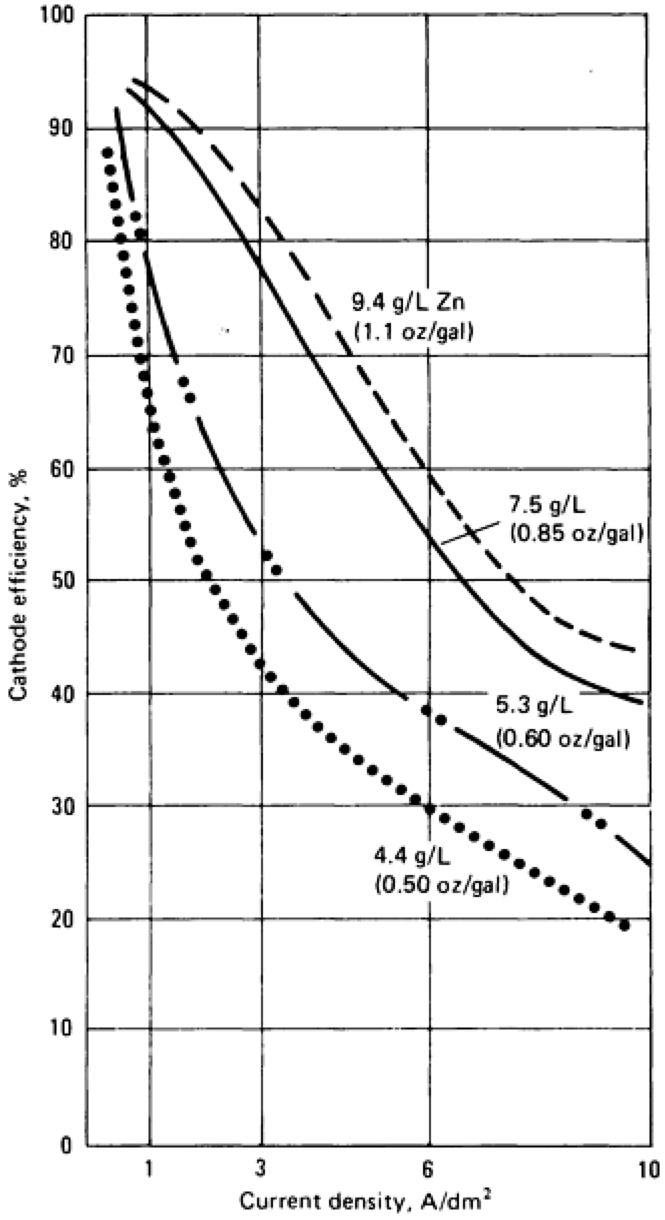


Fig. 1 Cathode current efficiency of alkaline noncyanide zinc baths as related to zinc metal contents. NaOH, 80 g/L (11 oz/gal); Na_2CO_3, 15 g/L (2 oz/gal)

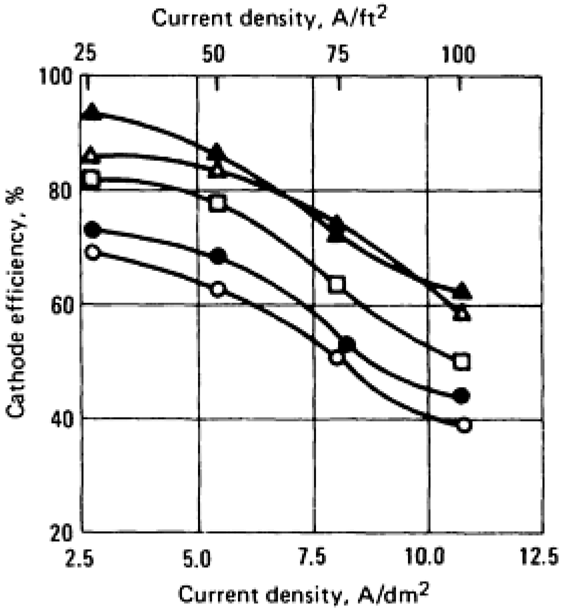


Fig. 2 Effect of zinc and sodium hydroxide concentration on the cathode efficiency of noncyanide zinc solutions. Temperature: 26 °C (77 °F). d : 7.5 g/L (1 oz/gal) Zn, 75 g/L (10 oz/gal) NaOH; •: 7.5 g/L (1.0 oz/gal) Zn, 150 g/L (20 oz/gal) NaOH; V : 11 g/L (1.5 oz/gal) Zn, 110 g/L (15 oz/gal) NaOH; ▲: 15 g/L (2.0 oz/gal) Zn, 150 g/L (20 oz/gal) NaOH; W : 11 g/L (1.5 oz/gal) Zn, 150 g/L (20 oz/gal) NaOH.

Operating Parameters of Standard Cyanide and Midcyanide Zinc Solutions

Anodes. Almost every physical form of zinc anode material has been used in cyanide zinc plating, the type and prevalence varying from country to country. In the United States, cast zinc balls approximately 50 mm (2 in.) in diameter, contained in spiral steel wire cages, are by far the most common anode material. A practical variation of this is the so-called flat top anode, with a flat surface to distinguish it from cadmium ball anodes. The use of ball anodes provides maximum anode area, ease of maintenance, and practically complete dissolution of the zinc anodes with no anode scrap formation.

One of the most economical forms of anode material is the large cast zinc slabs that form the prime material for subsequent ball or elliptical anode casting. Although these have the disadvantage of bulky handling and the need for specially fabricated anode baskets, their lower initial cost makes their use an important economic factor in the larger zinc plating shop.

Three grades of zinc for anodes are conventionally used for cyanide zinc plating: prime western, intermediate, and special high-grade zinc. The zinc contents of these are approximately 98.5%, 99.5%, and 99.99%, respectively. The usual impurities in zinc anodes are all heavy metals, which cause deposition problems unless continuously treated. Nearly troublefree results can consistently be obtained through the use of special high-grade zinc. A typical composition of special high-grade zinc is:

Constituent	Amount, %
Zinc	99.9930
Lead	0.0031

Cadmium	0.0017
Iron	0.0010
Copper	Trace

Control of Zinc Metal Content. Zinc anodes dissolve chemically as well as electrochemically in cyanide baths, so effective anode efficiency will be above 100%. This causes a buildup in zinc metal content, because cathode efficiencies are usually substantially less than 100%. A number of procedures have been developed to control this tendency.

In a conventional new zinc cyanide installation, approximately ten spiral anode ball containers should be used for every meter of anode rod. These should be filled initially, and after 1 or 2 weeks of operation they should be adjusted to compensate for anode corrosion and dragout losses so that the metal content remains as constant as possible. During shutdown periods in excess of 48 h, most cyanide zinc platers remove anodes from the bath. In large automatic installations, this may be done by using a submerged steel anode bar sitting in yokes that can be easily lifted by hoist mechanisms.

One of the prime causes of zinc metal buildup is the very active galvanic cell between the zinc anodes and the steel anode containers. This is evidenced by intense gassing in the area of anodes in a tank not in operation. Zinc buildup from this source can be eliminated by plating the anode containers with zinc before shutdown, which eliminates the galvanic couple.

Temperature. Probably no operating variable is as important and as often overlooked in the operation of cyanide zinc baths as operating temperature. Cyanide zinc solutions have been reported operating between the rather wide limits of 12 to 55 °C (54 to 130 °F), with the vast majority of baths operating between 23 to 32 °C (73 to 90 °F). The exact operating temperature for a given installation depends on the type of work processed, the finish desired, and the engineering characteristics of the plating system. Bath temperature has an effect on a great many variables in the cyanide zinc systems, so the optimum temperature is generally a compromise. Increasing the bath temperature:

- Increases cathode efficiency
- Increases bath conductivity
- Increases anode corrosion
- Produces duller deposits over a broad range of current densities
- Reduces covering power
- Reduces throwing power
- Increases breakdown of cyanide and addition agents

Lowering the bath temperature has the opposite effects. Thus, if a plater is primarily concerned with plating of pipe or conduit where deposit brilliance is not of great importance and covering and throwing power are not critical, operating the bath at the highest practical temperature to give optimum conductivity and plating efficiency would be preferred. For general bright plating of fabricated stampings, a lower bath temperature should be used, permitting the required excellent covering and throwing power and bright deposits.

The effects of higher bath temperature can be compensated to a substantial extent by increasing the total-cyanide-to-zinc ratio of the solution. The exact optimum ratio varies slightly for a given proprietary system, as shown in Table 3.

Table 3 Effect of bath temperature on total-cyanide-to-zinc ratio

Temperature	Total-NaCN-to-Zn ratio	Total-NaCN-to-Zn ratio

°C	°F	(standard cyanide bath)	(midcyanide bath)
22	72	2.6	2.2
26	79	2.7	2.3
30	86	2.8	2.4
34	93	2.9	2.5
38	100	3.0	2.6
42	108	3.2	2.7
46	115	3.3	3.0

Cathode Current Densities. Bright cyanide zinc solutions operate at wide-ranging cathode current densities varying from extremely low, less than 0.002 A/dm^2 (0.02 A/ft^2), to above 25 A/dm^2 (250 A/ft^2) without burning (i.e., the formation of dark, coarse electrodeposits). Current density limits depend on bath composition, temperature, cathode film movement, and addition agents used.

Average current densities vary but are approximately 0.6 A/dm^2 (6 A/ft^2) in barrel plating and 2 to 5 A/dm^2 (20 to 50 A/ft^2) in still or rack plating. Barrel zinc plating is a complex phenomenon in which a large mass of parts is constantly tumbled in the plating cylinder at varying distances from the cathode contact surfaces. At any given time, a part may have an infinitesimally low current density or it may even be deplating, and in another instant, near the outer surface of the tumbling mass, current density may approach 20.0 A/dm^2 (200 A/ft^2). In general, the bulk of deposition takes place in the lower current density range of 0.2 to 1 A/dm^2 (2 to 10 A/ft^2).

Average cathode current densities are generally easier to maintain in rack and still line operations and range from approximately 2 to 5 A/dm^2 (20 to 50 A/ft^2). However, the actual current density of any particular area of a given part will vary greatly, depending on part configuration, anode-to-cathode distance, bath shape, and other factors affecting the primary and secondary current distribution characteristics. In most cases, with proper attention to racking and work shape, current density variations can be kept within practical limits on fabricated parts so that if a minimum average thickness of 4 µm (0.15 mil) is required on a specific part, variations from approximately 2.5 to 8 µm (0.09 to 0.3 mil) occur at various areas on the part.

Cathode current efficiencies in barrel cyanide zinc plating vary between 75 and 93%, depending on temperature, formulation, and barrel current densities. In rack or still plating, however, there is quite a wide variation in current efficiencies when higher current densities are used, especially above 3 A/dm^2 (30 A/ft^2). The effects of zinc metal content, sodium hydroxide content, and the cyanide-to-zinc ratio on cathode current efficiency are shown in Fig. 3. As can be seen from the graphs, the current efficiency in the most commonly used baths drops dramatically from approximately 90% at 2.5 A/dm^2 (25 A/ft^2) to 50% at 5 A/dm^2 (50 A/ft^2). An improvement in current efficiency can be obtained by using a high-strength bath; however, this is offset by the relatively poor throwing power of the solution, higher brightener consumption, higher operating costs, and maintenance difficulties. The lower standard bath concentration, which gives practically identical results, is used for practically all plating installations except a selected few rack tanks that plate conduit or large flat surfaces with no critical recessed areas.

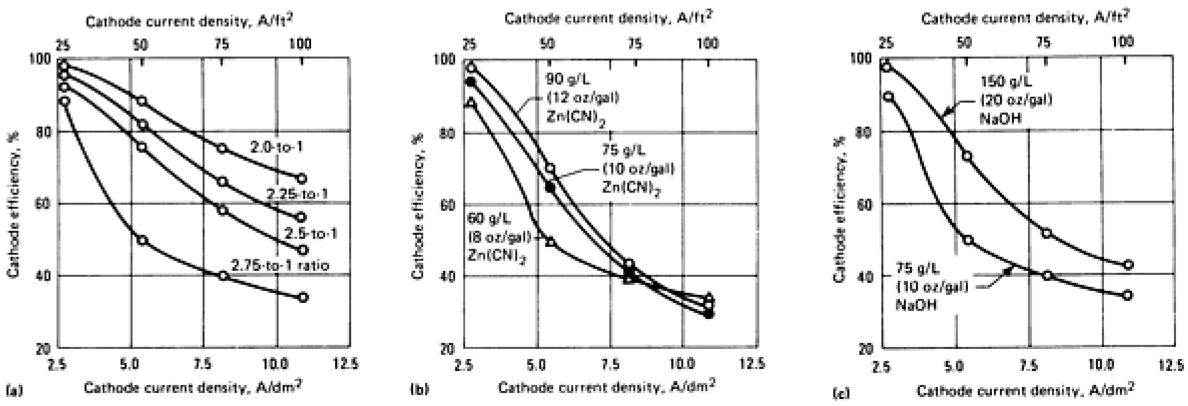


Fig. 3 Effects of bath composition variables and cathode current density on cathode efficiency in cyanide zinc plating. (a) Effect of NaCN/Zn ratio. 60 g/L (8 oz/gal) Zn (CN); 17.5 to 43.7 g/L (2.33 to 5.82 oz/gal) NaCN; 75.2 g/L (10 oz/gal) NaOH; 2.0-to-1 to 2.75-to-1 ratios of NaCN to zinc. Temperature: 30 °C (86 °F). (b) Effect of zinc metal content. 60.1, 75.2, and 90.2 g/L (8, 10, and 12 oz/gal) Zn (CN); 43.7, 54.6, and 65.5 g/L (5.82, 7.27, and 8.72 oz/gal) NaCN; 75.2 g/L (10 oz/gal) NaOH; 2.75-to-1 ratio of NaCN to zinc. Temperature: 30 °C (86 °F). (c) Effect of NaOH content. 60.1 g/L (8 oz/gal) Zn(CN); 43.6 g/L (5.8 oz/gal) NaCN; 150.4 and 75.2 g/L (20 and 10 oz/gal) NaOH; 2.75-to-1 ratio of NaCN to zinc. Temperature: 30 °C (86 °F)

Sodium carbonate is present in every cyanide and alkaline zinc solution. It enters the bath as an impurity from the makeup salts (sodium hydroxide and sodium cyanide may contain anywhere from 0.5 to 2% sodium carbonate) or as a deliberate addition to the initial bath (15 to 30 g/L, or 2.0 to 4 oz/gal).

The harmful effects of sodium carbonate in cyanide zinc plating are not as critical as in cyanide cadmium plating. Sodium carbonate does not begin to affect normal bath operation until it builds to above 75 to 105 g/L (10 to 14 oz/gal). Depending on overall bath composition and the type of work being done, a carbonate content in this range results in a slight decrease in current efficiency, especially at higher current densities, decreased bath conductivity, grainier deposits, and roughness, which becomes visible when the carbonate crystallizes out of cold solutions.

The carbonate content of zinc baths builds up by decomposition of sodium cyanide and absorption of carbon dioxide from the air reacting with the sodium hydroxide in the bath. Carbonates are best removed by one of the common cooling or refrigeration methods rather than by chemical methods, which are simple in theory but extremely cumbersome in practice. When an operating cyanide zinc bath has reached the point that excessive carbonates present a problem, it undoubtedly is contaminated with a great many other dragged-in impurities, and dilution is often a much quicker, although expensive, method of treatment. Alkaline noncyanide baths do not suffer from the effects of carbonate buildup.

Operating Parameters of Low-Cyanide Zinc Systems

Temperature control is as critical, if not more critical, in the low-cyanide bath as in the regular or midcyanide bath. The optimum operating temperature for most proprietary baths is 29 °C (84 °F), and the permissible range is more restricted than for the standard cyanide bath. Adequate cooling facilities are therefore mandatory and are more critical for low-cyanide than for the standard system.

Cathode Current Density. The average cathode current densities used in most low-cyanide processes are the same as in the standard cyanide bath. However, some proprietary baths do not have the extreme high-current-density capabilities of the standard cyanide bath, and burning on extremely high-current-density areas may be more of a problem with the low-cyanide bath than with the conventional baths.

Agitation. Unlike the standard cyanide bath, where agitation is usually nonexistent, air or mechanical agitation of the low-cyanide bath is common and is often quite useful in obtaining the optimum high-current-density plating range of the bath.

Filtration. Most low-cyanide baths appear to operate much more cleanly than the standard or midcyanide bath. The bath is a poor cleaner, and soils that may be removed and crystallized out of high-cyanide baths are not as readily affected by the low-cyanide bath.

Efficiency. The efficiency of the low-cyanide bath on aging is much more dependent on the particular addition agent used than the standard cyanide bath, because there is a substantial difference in various proprietary systems. In a new low-cyanide bath, current efficiency is slightly higher than that of a standard or midcyanide system. However, as the bath ages, current efficiency tends to drop, possibly because of the formation of additive breakdown products, and the efficiency of a bath after 2 or 3 months of operation may be as much as 30% below that of a higher cyanide system, especially at higher current densities. As in the standard cyanide bath, increasing the sodium hydroxide content, zinc metal content, and operating temperature increases the efficiency of the low-cyanide bath. However, increasing these variables has markedly harmful effects on the bright operating range of a low-cyanide bath that usually override the benefit of increased efficiency. The effects of bath constituents and temperature on the plating characteristics of the bright low-cyanide zinc systems are given in Table 4. Figure 4 shows the effect of sodium cyanide concentration on cathode efficiency.

Table 4 Effect of bath constituents and temperature on plating characteristics of bright, low-cyanide zinc plating

Variable	Cathode efficiency	Bright plating range	Bright low-current-density throwing power
Increasing sodium hydroxide	Increases	Slightly decreases	Negligible
Increasing zinc metal	Increases	Decreases	Decreases
Increasing sodium cyanide	Decreases	Increases	Increases
Increasing brightener	Increases	Increases	Increases
Increasing temperature	Increases	Decreases	Decreases

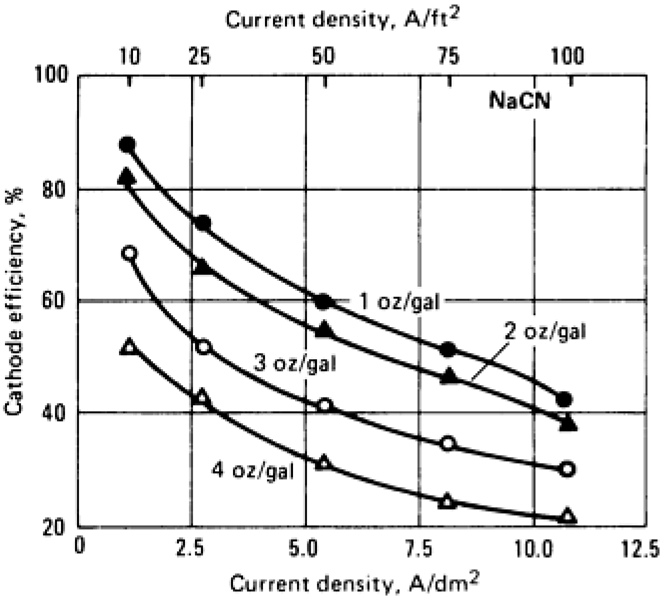


Fig. 4 Effect of sodium cyanide concentration on the cathode efficiency of low-cyanide zinc solutions. d :20 g/L

(2.5 oz/gal) NaCN; •:8 g/L (1 oz/gal) NaCN; ∨:30 g/L (4 oz/gal) NaCN; ▲:15 g/L (2 oz/gal) NaCN

Bright Throwing Power and Covering Power. The bright covering power of a low-cyanide bath operated at low current density is intrinsically not as good as that of a standard or midcyanide bath. In most operations, however, the difference is negligible except on extremely deep recessed parts. The vast majority of parts that can be adequately covered in a standard cyanide bath can be similarly plated in a low-cyanide bath without any production problems, such as excessively dull recessed areas or stripping by subsequent bright dipping.

Increasing the brightener and cyanide contents, within limits, improves the bright low-current-density deposition to a visible degree. Problems with bright throwing power at extremely low current densities are often solved by raising the cyanide content to approximately 15 g/L (2 oz/gal), which in effect returns the system to the lower range of the midcyanide bath.

Operating Parameters of Alkaline Noncyanide Zinc Baths

Temperature control is more critical in noncyanide zinc baths than in cyanide baths. The optimum temperature for most baths is approximately 29 °C (84 °F). Low operating temperatures result in no plating or, at most, very thin, milky white deposits. High operating temperatures rapidly narrow the bright plating current range, cause dullness at low current densities, and result in very high brightener consumption. However, because these temperature limitations for noncyanide zinc are within those commonly used in regular cyanide zinc, no additional refrigeration or cooling equipment is required for conversion to the process.

Operating Voltages. Normal voltages used in standard cyanide zinc plating are adequate for the noncyanide zinc bath, in both rack and barrel range. Normal voltage will be approximately 3 V with a range of 2 to 20 V, depending on part shape, anode-to-cathode relationship, temperature, barrelhole size, and variables that are unique to each operation.

Cathode Current Densities. The maximum allowable cathode current densities of the noncomplexing noncyanide bath closely approximate those of a standard cyanide bath. Current density ranges from 0.1 to more than 20 A/dm^2 (1 to 200 A/ft^2) can be obtained. This extremely wide plating range permits operation at an average current density of 2 to 4 A/dm^2 (20 to 40 A/ft^2) in rack plating, which makes a noncyanide system practical for high-production work.

Anodes. Standard zinc ball or slab anodes in steel containers are used in the noncyanide electrolyte. During the first 2 or 3 weeks of installation of noncyanide zinc baths, the anode area should be watched carefully to determine the appropriate anode area to maintain a stable analysis of zinc in the system. Whenever possible, zinc anodes should be removed during weekend shutdown periods to avoid excessive metal buildup.

Filtration of noncyanide baths is not an absolute necessity. However, the occurrence of roughness in these baths presents a greater potential problem than in regular cyanide baths. This is due to the nature of the deposit, which may become amorphous at very high current densities if the brightener is not maintained at an optimum level, and to anode polarization problems, which result in sloughing off of anode slimes, a more common occurrence in these baths. Carbon filtration may be required to remove organic contamination caused by marginal preplate cleaning practices. Filtration is also the preferred method for removing zinc dust used to treat metallic impurities in the system.

The bright plating range of the alkaline, noncyanide zinc bath is totally dependent on the particular additive used. Without any additive, the deposit from an alkaline, noncyanide bath is totally useless for commercial finishing, with a powdery, black amorphous deposit over the entire normal plating range.

Proper maintenance of the addition agent at the recommended level is extremely important in noncyanide alkaline zinc baths. A plater does not have the liberty of maintaining low levels of brightener in the bath and still obtaining passably bright deposits, as is the case in cyanide systems. Low brightener content rapidly leads to high- and medium-current-density burning, because in the noncyanide bath, as in the low-cyanide bath, burning and brightness are interdependent.

Cathode current efficiency of a noncyanide bath is a very critical function of the metal content (Fig. 1). At lower metal concentrations of approximately 4 g/L (0.5 oz/gal), efficiency is less than that of a standard cyanide bath, whereas at a metal content of approximately 9 g/L (1.2 oz/gal), efficiency is somewhat higher than in either regular or low-cyanide baths. Thus, if a plater can maintain metal content close to the 9 g/L (1.2 oz/gal) value, there will be no problem in obtaining deposition rates similar to those obtained with cyanide baths.

Acid Baths

The continuing development of acid zinc plating baths based on zinc chloride has radically altered the technology of zinc plating since the early 1970s. Acid zinc plating baths now constitute 40 to 50% of all zinc baths in most developed nations and are the fastest growing baths throughout the world. Acid zinc formulas and operating limits are given in Table 5. Bright acid zinc baths have a number of intrinsic advantages over the other zinc baths:

- They are the only zinc baths possessing any leveling ability, which, combined with their superb out-of-bath brightness, produces the most brilliant zinc deposits available.
- They can readily plate cast iron, malleable iron, and carbonitrided parts, which are difficult or impossible to plate from alkaline baths.
- They have much higher conductivity than alkaline baths, which produces substantial energy savings.
- Current efficiencies are 95 to 98%, normally much higher than in cyanide or alkaline processes, especially at higher current densities, as shown in Fig. 5.
- Minimal hydrogen embrittlement is produced than in other zinc baths because of the high current efficiency.
- Waste disposal procedures are minimal, consisting only of neutralization, at pH 8.5 to 9, and precipitation of zinc metal, when required.

The negative aspects of the acid chloride bath are that:

- The acid chloride electrolyte is corrosive. All equipment in contact with the bath, such as tanks and superstructures, must be coated with corrosion-resistant materials.
- Bleedout of entrapped plating solution occurs to some extent with every plating process. It can become a serious and limiting factor, prohibiting the use of acid chloride baths on some fabricated, stamped, or spot welded parts that entrap solution. Bleedout may occur months after plating, and the corrosive electrolyte can ruin the part. This potential problem should be carefully considered when complex assemblies are plated in acid chloride electrolytes.

Table 5 Composition and operating characteristics of acid chloride zinc plating baths

Constituent	**Ammoniated bath Barrel**		**Ammoniated bath Rack**	
	Optimum	**Range**	**Optimum**	**Range**
Preparation				
Zinc chloride	18 g/L (2.4 oz/gal)	15-25 g/L (2.0-3.8 oz/gal)	30 g/L (4.0 oz/gal)	19-56 g/L (2.5-7.5 oz/gal)
Ammonium chloride	120 g/L (16.0 oz/gal)	100-150 g/L (13.4-20.0 oz/gal)	180 g/L (24.0 oz/gal)	120-200 g/L (16.0-26.7 oz/gal)
Potassium chloride	. . .	. . .	. . .	. . .
Sodium chloride	. . .	. . .	. . .	. . .
Boric acid	. . .	. . .	. . .	. . .

Carrier brightener[a]	4 vol%	3-5%	3.5%	3-4%
Primary brightener[a]	0.25%	0.1-0.3%	0.25%	0.1-0.3%
pH	5.6	5.5-5.8	5.8	5.2-6.2
Analysis				
Zinc metal	9 g/L (1.2 oz/gal)	7.5-25 g/L (1.0-3.8 oz/gal)	14.5 g/L (1.9 oz/gal)	9-27 g/L (1.2-3.6 oz/gal)
Chloride ion	90 g/L (1.2 oz/gal)	75-112 g/L (10.0-14.9 oz/gal)	135 g/L (18.0 oz/gal)	90-161 g/L (12.0-21.5 oz/gal)
Boric acid	. . .	. . .	. . .	. . .
Operating conditions				
Temperature	24 °C (75 °F)	21-27 °C (69-79 °F)	24 °C (75 °F)	21-27 °C (69-79 °F)
Cathode current density	. . .	0.3-1.0 A/dm^2 (3-10 A/ft^2)	. . .	2.0-5 A/dm^2 (20-50 A/ft^2)
Voltage	. . .	4-12 V	. . .	1-5 V

Constituent	**Potassium bath**		**Mixed sodium ammonium Barrel bath**	
	Optimum	**Range**	**Optimum**	**Range**
Preparation				
Zinc chloride	71 g/L (9.5 oz/gal)	62-85 g/L (8.3-11.4 oz/gal)	34 g/L (4.5 oz/gal)	31-40 g/L (4.1-5.3 oz/gal)
Ammonium chloride	. . .	. . .	30 g/L (4.0 oz/gal)	25-35 g/L (3.3-4.7 oz/gal)
Potassium chloride	207 g/L (27.6 oz/gal)	186-255 g/L (24.8-34.0 oz/gal)	. . .	. . .
Sodium chloride	. . .	. . .	120 g/L (16.0 oz/gal)	100-140 g/L (13.3-18.7 oz/gal)
Boric acid	34 g/L (4.5 oz/gal)	30-38 g/L (4.0-5.1 oz/gal)	. . .	. . .

Carrier brightener[(a)]	4%	4-5%	4%	3-5%
Primary brightener[(a)]	0.25%	0.1-0.3%	0.2%	0.1-0.3%
pH	5.2	4.8-5.8	5.0	4.8-5.3
Analysis				
Zinc metal	34 g/L (4.5 oz/gal)	30-41 g/L (4.0-5.5 oz/gal)	16.5 g/L (2.2 oz/gal)	15-19 g/L (2.0-2.5 oz/gal)
Chloride ion	135 g/L (18.0 oz/gal)	120-165 g/L (16.0-22.0 oz/gal)	110 g/L (14.7 oz/gal)	93-130 g/L (12.4-17.4 oz/gal)
Boric acid	34 g/L (4.5 oz/gal)	30-38 g/L (4.0-5.1 oz/gal)	. . .	. . .
Operating conditions				
Temperature	27 °C (79 °F)	21-35 °C (69-94 °F)	27 °C (79 °F)	25-35 °C (76-94 °F)
Cathode current density	. . .	2.0-4 A/dm^2 (20-40 A/ft^2)	. . .	0.3-1 A/dm^2 (3-10 A/ft^2)
Voltage	. . .	1-5 V	. . .	4-12 V

(a) Carrier and primary brighteners for acid chloride are proprietary, and exact recommendations of manufacturer should be followed. Values given are representative.

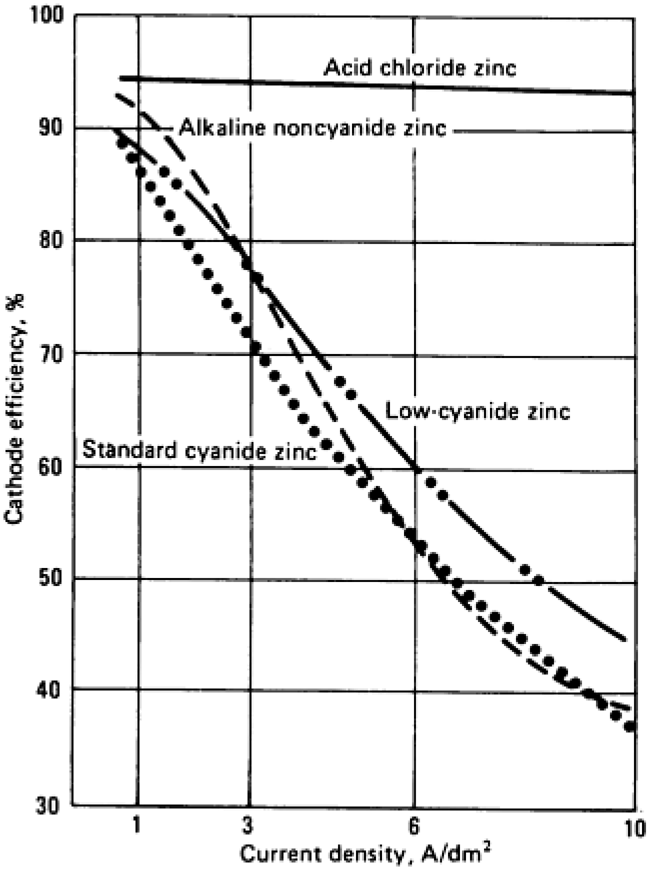


Fig. 5 Comparison of cathode current efficiencies of bright zinc plating electrolytes

Acid chloride zinc baths currently in use are principally of two types: those based on ammonium chloride and those based on potassium chloride. The ammonium-based baths, the first to be developed, can be operated at higher current densities than potassium baths. Both systems depend on a rather high concentration of wetting agents, 4 to 6 vol%, to solubilize the primary brighteners. This is more readily accomplished in the ammonia systems, which makes bath control somewhat easier. Ammonium ions, however, act as a complexing agent in waste streams containing nickel and copper effluents, and in many localities they must be disposed of by expensive chlorination. This was the essential reason for the development of the potassium chloride bath.

All bright acid chloride processes are proprietary, and some degree of incompatibility may be encountered between them. Conversion from an existing process should be done only after a Hull Cell plating test evaluation. Preplate cleaning, filtration, and rack designs for acid chloride baths should be equivalent to those required for nickel plating.

The latest acid chloride zinc baths to become available to the industry are those based on salt (sodium chloride) rather than the more expensive potassium chloride. In many of these baths, salt is substituted for a portion of either ammonium or potassium chloride, producing a mixed bath. Sodium acid chloride baths at present are generally restricted to barrel operation, because burning occurs much more readily in these baths at higher current densities. However, with the continuing development of additive technology, sodium acid chloride baths may challenge the widely used nonammoniated potassium bath in the near future.

Acid chloride zinc baths are now being explored as the basis of zinc alloy plating incorporating metals such as nickel and cobalt, to improve corrosion for specific applications and possibly eliminate standard chromate treating.

A number of zinc baths based on zinc sulfate and zinc fluoborate have been developed, but these have very limited applications. They are used principally for high-speed, continuous plating of wire and strip and are not commercially used for plating fabricated parts. Table 6 shows the compositions and operating conditions for some typical fluoborate and sulfate baths.

Table 6 Fluoborate and sulfate electroplating bath compositions

Constituent	Fluoborate[(a)]		Sulfate[(b)]	
	g/L	oz/gal	g/L	oz/gal
Zinc	65-105	9-14	135	18
Zinc fluoborate	225-375	30-50	. . .	. . .
Zinc sulfate	. . .	. . .	375	50
Ammonium fluoborate	30-45	4-6	. . .	. . .
Ammonium chloride	. . .	. . .	7.5-22.5	1-3
Addition agent	(c)	(c)	(c)	(c)

(a) At room temperature; 3.5 to 4 pH; at 20 to 60 A/dm^2 (200 to 600 A/ft^2).

(b) At 30 to 52 °C (85 to 125 °F); 3 to 4 pH; at 10 to 60 A/dm^2 (100 to 600 A/ft^2).

(c) As needed

Operating Parameters of Acid Chloride Zinc Baths

Anodes for acid chloride zinc should be special high grade, 99.99% Zn. Most installations use zinc ball or flat top anodes in titanium anode baskets. Baskets should not be used if the applied voltage on an installation exceeds 8 V, because there may be some attack on the baskets. Baskets should be kept filled to the solution level with zinc balls. Slab zinc anodes, drilled and tapped for titanium hooks, may also be used. Any areas of hooks or splines exposed to solution should be protective coated. Anode bags are optional but recommended for most processes, especially for rack plating where they are useful to minimize roughness. Bags may be made of polypropylene, Dynel, or nylon. Before being used they should be leached for 24 h in a 5% hydrochloric acid solution containing 0.1% of the carrier or wetting agent used in the particular plating bath.

Chemical Composition. Zinc, total chloride, pH, and boric acid, when used, should be controlled and maintained in the recommended ranges (see Table 5) by periodic replenishment using chemically pure materials. Excess zinc causes poor low-current-density deposits, and insufficient zinc causes high-current-density burning. Excess chloride may cause separation of brighteners, and insufficient chloride reduces the conductivity of solutions. Excessively high pH values cause the formation of precipitates and anode polarization, and excessively low pH values cause poor plating. Insufficient boric acid reduces the plating range.

Brighteners also have to be replenished by periodic additions. Because the chemical compositions of brighteners are proprietary, the suppliers specify concentrations and control procedures.

Agitation is recommended in acid chloride baths to achieve practical operating current densities. Solution circulation is recommended in barrel baths to supplement barrel rotation. In rack baths, solution circulation is usually accomplished by locating the intake and discharge of the filter at opposite ends of the plating tank. Cathode rod agitation is suitable for many hand-operated rack lines.

Air agitation is the preferred method for most installations. A low-pressure air blower should be used as a supply source.

Temperature control is more critical in acid zinc baths than in cyanide zinc baths, and auxiliary refrigeration should be provided to maintain the bath at its maximum recommended operating temperature, usually 35 °C (95 °F). Cooling coils in the bath itself should be Teflon or Teflon-coated tubing. Titanium coils may be used if they are isolated from the direct current source.

Operating an acid chloride bath above its maximum recommended temperature causes low overall brightness, usually beginning at low current densities and rapidly progressing over the entire part. High temperatures may also bring the bath above the cloud point of the brightener system. As the acid bath gets hot, additives start coming out of solution, giving the bath a milky or cloudy appearance and causing bath imbalance. Conversely, low temperatures, usually below 21 °C (70 °F), cause many baths to crystallize and cause organic additives to separate out of solution. This produces roughness and, in extreme cases, a sticky globular deposit on the bath and work, which clogs filters and completely curtails operations.

Cathode Current Efficiency. The high cathode current efficiency exhibited by acid chloride zinc baths is one of the most important properties of these baths. As shown in Fig. 5, the average cathode current efficiency for these baths is approximately 95 to 98% over the entire range of operable current densities. No other zinc plating system approaches this extremely high efficiency at higher current densities, which can lead to productivity increases of 15 to 50% over those obtainable with cyanide baths. In barrel plating, barrel loads can often be doubled in comparison with those for cyanide baths, and equivalent plating thickness can often be achieved in half the time.

pH control of acid zinc baths is usually monitored on a daily basis. Electrometric methods are preferred over test papers. The pH of a bath is lowered with a hydrochloric acid addition; when required, the pH may be raised with a potassium or ammonium hydroxide addition.

Iron contamination is a common problem in all acid chloride zinc baths. Iron is introduced into the bath from parts falling into the tank during operation, from attack by the solution on parts at current densities below the normal range, such as the inside of steel tubular parts, and from contaminated rinse waters used before plating. Iron contamination usually appears as dark deposits at high current densities; in barrel plating it appears as stained dark spots reproducing the perforations of the plating barrel. A high iron content turns the plating solution brown and murky.

Iron can be readily removed from acid chloride baths by oxidizing soluble ferrous iron to insoluble ferric hydroxide. This is accomplished by adding concentrated hydrogen peroxide to the bath, usually on a daily basis. Approximately 10 mL (0.34 fl oz) of 30% hydrogen peroxide should be used for every 100 L (26.4 gal.) of bath. The peroxide should be diluted with 4 to 5 parts water and dispersed over the bath surface. Dissolved potassium permanganate can be used instead of peroxide. The precipitated iron hydroxide should then be filtered from the bath using a 15 μm (0.6 mil) or smaller filter coated with diatomaceous earth or a similar filter aid.

Control of Plate Thickness

This section discusses the thicknesses of zinc specified for service in various indoor and outdoor atmospheres. Many combinations of variables must be considered in attempting to plate to a given thickness. To hold each variable at a steady value is virtually impossible under production conditions, so as one variable changes spontaneously, others must be adjusted to maintain uniformity of plate thickness. In automatic plating this is impractical, so the process is set up to give a certain minimum thickness under a great variety of conditions. This accounts for much of the thickness variation normally encountered in automatic plating of a run of identical pieces.

The shape and size of parts that may be plated all over, with or without the use of conforming anodes to attain uniformity of plate thickness, are essentially the same in zinc plating as in cadmium plating (see the article "Cadmium Plating" in this Volume).

Normal Variations. Preferred thicknesses in automatic zinc plating are usually minimum specified thicknesses, and there is little concern regarding the maximum thicknesses obtained. Thickness variations encountered should therefore be over the established minimum thickness.

For example, as shown in Fig. 6, tests were made on 75 samples, over a one-week period, of parts 100 mm (4 in.) long and 39 g (1.375 oz) that were automatically plated to a minimum specified thickness of 3.8 μm (0.15 mil). Although actual plate thicknesses ranged from 2.5 to 7.5 μm (0.1 to 0.3 mil), over 80% of the parts examined exceeded the target minimum.

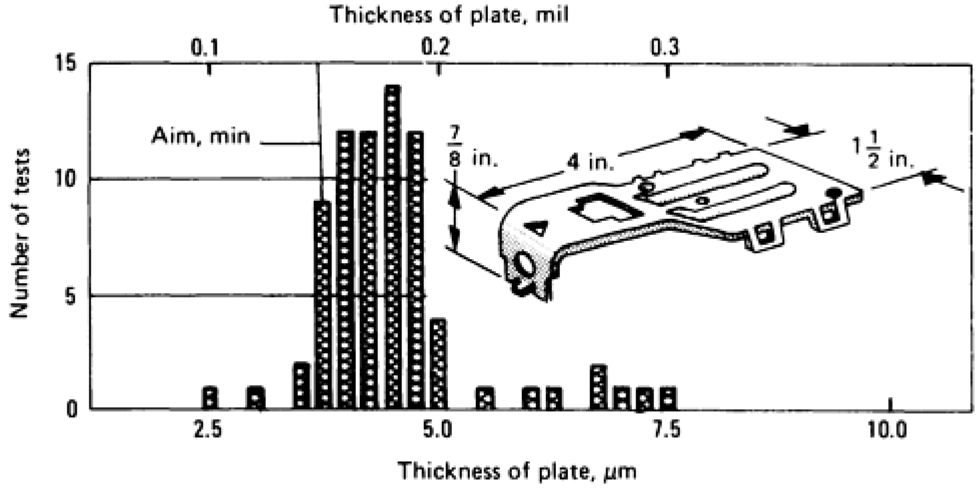


Fig. 6 Variation in thickness of zinc plate obtained in automatic plating in cyanide zinc bath, 75 tests

Thickness variations obtained in barrel plating are markedly affected by the tumbling characteristics of the part and by the density of the load in the plating barrel. Parts that can be tumbled readily are more likely to develop a uniform coating. As shown in Fig. 7, a minimum plate thickness of 12.5 μm (0.5 mil) was the target in barrel plating a 0.12 kg (0.26 lb) S-shape part made of 3 mm (0.125 in.) flat stock. Of 75 parts examined, all were found to be plated to thicknesses that exceeded the target minimum, and a few had thicknesses in excess of 34 μm (0.9 mil).

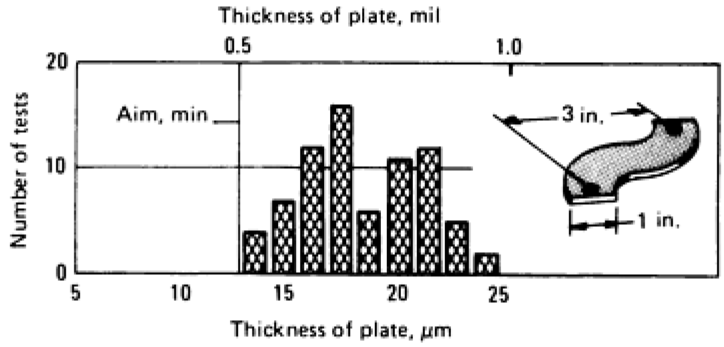


Fig. 7 Variation in thickness of zinc plate obtained in barrel plating a 3.2 mm ($\frac{1}{8}$ in.) thick part in a cyanide zinc

Similarities Between Cadmium and Zinc Plating

Except for differences in plating baths and in such operational details as current density and rates of deposition, alkaline cadmium and zinc plating are essentially similar processes. See the article "Cadmium Plating" in this Volume for a

detailed discussion of plating methods, equipment, and processing. Exceptions with respect to equipment and processing are described below.

Plating Equipment. The equipment requirements for zinc plating are the same as those noted for cadmium plating, except for the following:

- In barrel plating, zinc solutions require higher voltage and current density and therefore must be provided with greater cooling capacity to prevent overheating. Also, because the cyanide zinc bath generates much larger amounts of hydrogen, barrel design should incorporate safety features to prevent explosions.
- Fume hoods should be used on cyanide, low-cyanide, and, especially, alkaline noncyanide baths to exhaust caustic spray and toxic fumes.
- Barrels, tanks, and all superstructures coming into contact with acid chloride zinc plating baths should be coated with material able to resist acid corrosion. Polypropylene, polyethylene, polyvinyl chloride, and fiberglass are commonly used materials. Lead-lined tanks should never be used in these systems. Heating and cooling coils should be built of titanium that is electrically isolated from the tank, or of high-temperature Teflon.

Hydrogen embrittlement of steels is a major problem in all types of cyanide zinc plating. These formulas should not be used for spring tempered parts or other parts susceptible to this type of embrittlement. Spring-tempered parts and other susceptible parts should be plated in acid chloride electrolyte. When no embrittlement whatsoever can be tolerated, mechanically deposited zinc is the preferable alternative.

Processing Steps. Time requirements for various operations involved in still tank, barrel, and automatic methods of plating zinc to a thickness of less than 12.5 μm (0.5 mil) are given in Table 7.

Table 7 Process steps and time requirements for zinc plating operations

Times listed are for plating zinc to a thickness of less than 12.5 μm (0.5 mil).

Processing cycle	Time for each operation
Hand- or hoist-operated still tank	
Electrolytic cleaning	1-3 min
Cold water rinse	10-20 s
Acid pickle	30 s-2 min
Cold water rinse	10-20 s
Cold water rinse	10-20 s
Zinc plate	6-8 min
Cold water rinse	10-20 s

Cold water rinse	10-20 s
Chromate conversion coat	15-30 s
Cold water rinse	10-20 s
Hot water rinse	20-30 s
Air dry	1 min
Hand- or hoist-operated barrel line	
Soak clean	4 min
Electroclean	4 min
Cold water rinse	1-2 min
Acid pickle	2-3 min
Zinc plate	20-30 min
Cold water rinse	1-2 min
Cold water rinse	1-2 min
Chromate conversion coat	30 s-1 min
Cold water rinse	1-2 min
Hot water rinse	2-3 min
Centrifugal dry	3-5 min
Automatic barrel line	
Soak clean	6 min
Electroclean	3 min
Cold water rinse	2 min

Cold water rinse	2 min
Acid pickle	1 min
Neutralize dip	3 min
Cold water rinse	2 min
Zinc plate	30-40 min
Dragout rinse	2 min
Neutralize rinse	2 min
Cold water rinse	2 min
Nitric acid dip	30 s
Cold water rinse	2 min
Chromate dip	30 s
Cold water rinse	2 min
Hot water rinse	2 min
Centrifugal dry	3 min

Applications

In the presence of moisture, zinc becomes a sacrificial protecting agent when in contact with iron and other metals that are below zinc in the galvanic series. Attack is most severe when the electrolyte has high electrical conductivity (as in marine atmospheres) and when the area ratio of zinc to the other metals is small.

Plate Thickness. The life of a zinc coating in the atmosphere is nearly proportional to the coating thickness. Its rate of corrosion is highest in industrial areas, intermediate in marine environments, and lowest in rural locations. Corrosion is greatly increased by frequent dew and fog, particularly if the exposure is such that evaporation is slow.

Table 8 gives the estimated life of different thicknesses of unprotected zinc coatings on steel in different outdoor atmospheres. The majority of zinc-plated parts are coated with a thickness of 7.5 to 12.5 μm (0.3 to 0.5 mil). Typical applications employing thicknesses less than or greater than usual are given in Table 9.

Table 8 Estimated average service life of unprotected zinc coatings on steel in outdoor service

Condition	Coating thickness	Service, yr

	µm	mil	
Rural	5	0.2	3
	13	0.5	7
	25	1.0	14
	38	1.5	20
	50	2.0	30
Temperate marine	5	0.2	1
	13	0.5	3
	25	1.0	7
	38	1.5	10
	50	2.0	13
Industrial marine	5	0.2	1
	13	0.5	2
	25	1.0	4
	38	1.5	7
	50	2.0	9
Severe industrial	5	0.2	0.5
	13	0.5	1
	25	1.0	3
	38	1.5	4
	50	2.0	6

Table 9 Applications of zinc plating at thicknesses below or above 7 to 13 µm (0.3 to 0.5 mil)

Application	**Plate thickness**	
	µm	**mil**
Less than 7 µm (0.3 mil) of zinc		
Automobile ashtrays[(a)]	5-7	0.2-0.3
Birdcages[(b)]	5	0.2
Electrical outlet boxes[(c)]	4-13	0.15-0.5
Tacks	5	0.2
Tubular rivets[(d)]	5	0.2
More than 13 µm (0.5 mil) of zinc		
Conduit tubing[(e)]	30	1.2

(a) Chromated after plating.

(b) Chromated after plating; some parts dyed and lacquered.

(c) Bright chromated after plating.

(d) Chromated, clear or colored, after plating.

(e) Dipped in 0.5% HNO_3 or chromated after plating

Supplementary Coatings. Because corrosion is rapid in industrial and marine locations, zinc-plated parts that must endure for many years are usually protected by supplementary coatings. Steel with 5 µm (0.2 mil) of electroplated zinc is often painted to obtain a coating system for general outdoor service; a phosphate or chromate post-plating treatment ensures suitable adherence of paint to zinc.

In uncontaminated indoor atmospheres, zinc corrodes very little. A 5 µm (0.2 mil) coating has been known to protect steel framework on indoor cabinets for more than 20 years. Atmospheric contaminants accelerate corrosion of zinc if condensation occurs on cooler parts of structural members inside buildings. In 10 years or less, 12.5 µm (0.5 mil) of zinc may be dissipated. Zinc-plated steel in such locations is usually given a protective coating of paint.

A satisfactory coating for parts such as those on the inside of an office machine must afford protection in storage, assembly, and service. The cost is also important. Gears, cams, and other parts of the working mechanism can be plated with 3.8 to 6.3 μm (0.15 to 0.25 mil) of zinc to meet these requirements.

Chromate conversion coatings, colored or clear, are almost universally applied to zinc-plated parts for both indoor and outdoor use to retard corrosion from intermittent condensation, such as may occur in unheated warehouses. Chromate films minimize staining from fingerprints and provide a more permanent surface appearance than bare zinc.

Limitations. Zinc-plated steel is not used for equipment that is continually immersed in aqueous solutions. It must not be used in contact with foods and beverages because of dangerous health effects. Although zinc may be used in contact with gases such as carbon dioxide and sulfur dioxide at normal temperatures if moisture is absent, it has poor resistance to most common liquid chemicals and to chemicals of the petroleum and pharmaceutical industries.

Fasteners. Steel fasteners, such as screws, nuts, bolts, and washers, are often electroplated for corrosion resistance and appearance. If protection against atmospheric corrosion is the sole objective, zinc is the most economical coating metal. Coatings of 5 to 7.5 μm (0.2 to 0.3 mil) give protection for 20 years or more for indoor applications in the absence of frequent condensation of moisture. Chromate coatings are used to retard corrosion from condensates, provide a more permanent surface appearance, and prevent staining from fingerprints. For indoor use in industrial areas and in locations where condensation is prevalent, as in unheated buildings, corrosion may be rapid, and the zinc surface should be phosphated and then painted to extend its service beyond the few years that would be obtained by the unpainted coating. Unprotected zinc-plated screws should not be used to fasten bare parts if the service is to include marine exposure.

The dimensional tolerance of most threaded articles, such as nuts, bolts, screws, and similar fasteners with complementary threads, does not permit the application of coatings much thicker than 7.5 μm (0.3 mil). The limitation of coating thickness on threaded fasteners imposed by dimensional tolerance, including class or fit, should be considered whenever practicable, to prevent the application of thicker coatings than are generally permissible. If heavier coatings are required for satisfactory corrosion resistance, allowance must be made in the manufacture of the threaded fasteners for the tolerance necessary for plate buildup. If this is not practicable, phosphating before assembly and painting after assembly will increase service life. The approximate durability of 5 μm (0.2 mil) untreated coatings is given in Table 8.

Appearance. The appearance of electrodeposited zinc can be varied over a wide range, depending on bath composition, current density, the use of brighteners, and postplating treatments. The appearance of electroplated zinc is bright and silvery, and the deposit from the acid chloride baths is often initially indistinguishable from bright nickel chrome when plated.

Currently, nearly all zinc plating is followed by some type of chromate dip. These preserve the appearance of the part and vastly increase the bright shelf life of the surface. The cost of chromating is so minimal that its use has become practically universal. Presently, bright zinc deposits are used for a wide variety of low-cost consumer goods such as children's toys, bird cages, bicycles, and tools. Refrigerator shelves are commonly bright zinc plated, chromated, and lacquered. Without lacquer protection, even chromated bright zinc will tarnish and discolor quite rapidly when handled, and unlacquered bright zinc plate is not a good substitute for nickel chrome when a longlasting bright finish is desired. However, the vast majority of zinc plate is deposited primarily to impart corrosion resistance; brightness is not the primary factor for these applications.

Additional information about applications of electroplated zinc is provided in the article "Surface Engineering of Carbon and Alloy Steels" in this Volume.

Indium Plating

Allen W. Grobin, Jr., Grobin Associates, Inc.

Introduction

INDIUM is a soft, low-melting-point, silvery white metal with a brilliant metallic luster and a color resembling that of platinum. It alloys with most other metals to form a series of unique alloys, many of which are used as solders. It is soft enough to be readily marked by light fingernail pressure. Indium can be easily extruded at very low pressures: solders containing 50% In can be extruded as 1 mm (0.04 in.) wire at a pressure of 83 MPa (12 ksi). The hardness of indium is

0.9 to 1.0 on the modified Brinell scale, and it has a melting point of 156.7 °C (314.1 °F), a boiling point of 2000 °C (3632 °F), and a low vapor pressure.

Indium is ductile, malleable, crystalline, and diamagnetic. The pure metal gives a high pitched "cry" when bent. It wets glass and finds application in low-melting alloys and solders. It is used in making alkaline batteries, automotive trim, bearing alloys, electronic assemblies, germanium transistors, photoconductors, rectifiers, thermistors, vacuum seals, and group III-V compound semiconductors such as indium phosphide and indium arsenide. When rubbed together, two indium-plated parts will "cold weld" (autogenously join). This can be easily accomplished with freshly plated parts, but as surface oxides build up with time, more vigorous rubbing is required. This cold welding phenomenon is being explored for use in the surface mount technology of the electronics industry. Indium is electropositive to iron and steel and electronegative to tin. In an aqueous 3% sodium chloride solution of pH 6.7 to 7.2, indium has a half-cell static potential of -0.56 V referenced to that of a silver electrode given the value of zero. This places indium between cadmium and tin in the electromotive series of metals, which is used by materials and design engineers to identify and avoid potential galvanic corrosion problems.

Indium is particularly useful in making reliable electrical contact to aluminum. When indium-plated steel wire terminals are secured to aluminum, the high-resistance surface aluminum oxide cracks under the pressure and the indium extrudes into the oxide cracks, making direct metal-to-metal contact with the underlying aluminum. This application, which was widely used in the telephone industry, has diminished in use with that industry's switch to fiber optics. However, it is used for aluminum wire terminals in the electronics industry, particularly where the use of terminal fluids is undesirable. One relatively new use is for the plating of steel internal dished-tooth star-washer-ring-lug terminals for attachment to aluminum capacitors.

Acknowledgements

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Indium Electrodeposits

Indium electrodeposits provide excellent solderability, low electrical contact resistance, friction resistance, and atmospheric corrosion resistance when plated on aluminum, copper-base alloys, and steel, which are typically selected for their engineering properties. Indium can be readily electrodeposited from either acid or alkaline solutions. It is particularly useful for coating aluminum and other amphoteric metals; its alkaline corrosion resistance provides a wider measure of corrosion protection for these metals than that provided by cadmium, tin, or zinc.

Indium can be plated without special apparatus. Any shop or laboratory that has plating equipment can set up an indium plating tank without costly equipment. Any technician familiar with the plating of silver, copper, and so on finds indium plating quite easy to handle. However, barrel plating of small, lightweight items (e.g., ring lugs, wire terminations, and threaded fasteners and washers) may present a problem on occasion. This type of part may cold weld during the tumbling action of the barrel and end up as a solid indium-plated mass. The problem is easily overcome by adding gelatin or glue to the bath to increase its viscosity.

Plating Baths. The four most commonly used indium plating baths are indium cyanide, indium fluoborate, indium sulfamate, and indium sulfate. Table 1 compares these processes. The details of the processes are shown in Tables 2, 3, 4, and 5.

Table 1 Comparison of indium plating baths

Parameter	Bath salt			
	Cyanide	Fluoborate	Sulfamate	Sulfate
Throwing power	Excellent	Good	Excellent	Poor

Quality of plate	Excellent	Good	Excellent	Passable
Ease of solution analysis	Difficult	Easy	Easy	Easy
Critical temperature	No	21-32 °C (70-90 °F)	No	Controlled
Color of solution	Clear	Clear	Clear	Clear
Wettability	Easy	Difficult	Easy	Difficult
Anode	Insoluble	Indium	Indium	Indium
Cathode efficiency	40-50%	40-50%	90%	30-70%
Tendency to pit	No	No	No	Yes
Control of solution	Cyanide and metal	Metal and pH	Metal and pH	Metal and pH

Table 2 Indium cyanide plating bath

Constituent or parameter	**Value or condition**
Indium as metal	33 g/L (4.4 oz/gal)
Dextrose	33 g/L (4.4 oz/gal)
Total cyanide (KCN)	96 g/L (12.7 oz/gal)
Potassium hydroxide (KOH)	64 g/L (8.5 oz/gal)
Temperature (static)	Room temperature
Cathode efficiency	50-75%
Anodes	Plain steel
Throwing power	Excellent
Quality of plate	Excellent
Ease of solution analysis	Difficult

Critical temperature (working)	None, with or without agitation
Color of solution	Clear, pale yellow to dark amber
Wettability	Easy
Tendency to pit	None
Control of solution	Cyanide and metal by additions
Use	General
Current	162-216 A/m^2 (15-20 A/ft^2)
pH	High

Notes: (1) Because insoluble anodes are used, it is necessary to replace the indium metal content of this alkaline bath. Under normal conditions, addition of cyanide will not be required; however, it is best to keep the cyanide concentration at about 100 g/L (13.4 oz/gal) for efficient operation. (2) Plating efficiency of the bath will be maintained within a range suitable for normal plating until the indium content is reduced. The plating rate should be checked at regular intervals, because as the bath is depleted a decrease in rate of deposition is to be expected.

Table 3 Indium fluoborate plating bath

Constituent parameter	**Value or condition**
Indium fluoborate	236 g/L (31.5 oz/gal)
Boric acid	22-30 g/L (2.9-4.0 oz/gal)
Ammonium fluoborate	40-50 g/L (5.3-6.7 oz/gal)
pH (colorimetric)	1.0
Temperature (static)	21-32 °C (70-90 °F)
Cathode efficiency	40-75%
Anode efficiency	Indium, 100%
Throwing power	Good
Quality of plate	Good

Ease of solution analysis	Easy
Critical temperature (working)	21-32 °C (70-90 °F), with or without agitation
Color of solution	Clear
Wettability	Difficult
Tendency to pit	None
Control of solution	Metal and pH
Use	Experimental
Current density	540-1080 A/m^2 (50-100 A/ft^2)

Notes: (1) The pH of this bath is controlled by the addition of 42% fluoboric acid. (2) Some insoluble anodes (platinum or graphite) should be used because the anode and cathode efficiency are not in good relation.

Table 4 Indium sulfamate plating bath

Constituent or parameter	**Value or condition**
Indium sulfamate	105.36 g/L (14 oz/gal)
Sodium sulfamate	150 g/L (20 oz/gal)
Sulfamic acid	26.4 g/L (3.5 oz/gal)
Sodium chloride	45.84 g/L (6 oz/gal)
Dextrose	8.0 g/L (1 oz/gal)
Triethanolamine	2.29 g/L (0.3 oz/gal)
pH	1-3.5[a]
Temperature (static)	Room temperature
Cathode efficiency	90%
Anode efficiency	Indium, 100%

Throwing power	Excellent
Quality of plate	Excellent
Ease of solution analysis	Easy
Critical temperature (working)	None, with or without agitation
Color of solution	[b]
Wettability	Fairly easy
Tendency to pit	None
Control of solution	Metal and pH[a]
Use of solution	Experimental
Current density	108-216 A/m^2 (10-20 A/ft^2)[c]

(a) 1.5-2 preferred. The pH of this bath is controlled by the addition of sulfamic acid.

(b) Clear when new; after use will darken due to organic material breakdown. This has no effect on deposit. Filtering of bath can be done through activated charcoal to maintain clarity of bath.

(c) Optimum. If metal is increased, current density can be increased up to 1080 A/m^2 (100 A/ft^2).

Table 5 Indium sulfate plating bath

Constituent or parameter	**Value or condition**
Indium (as sulfate)	20 g/L (2.67 oz/gal min)
Sodium sulfate	10 g/L (1.3 oz/gal)
pH	2.0-2.5
Temperature (static)	Room temperature
Cathode efficiency	30-70%

Anode efficiency	Indium, 100%
Throwing power	Poor
Quality of plate	Passable
Ease of solution analysis	Easy
Critical temperature (working)	Controlled, with or without agitation
Color of solution	Clear
Wettability	Difficult
Tendency to pit	Yes
Control of solution	Metal and pH
Use	Experimental
Current density	216-432 A/m^2 (20-40 A/ft^2)

Notes: (1) The pH of this bath is controlled by the addition of sulfuric acid or sodium hydroxide as needed. (2) Some insoluble anodes (platinum or graphite) should be used because the anode and cathode efficiency are not in good relation.

Diffusion Treatment. The plating of indium on a clean, nonferrous surface does not necessarily end the operation. For some applications, such as bearing plating, the indium deposit is diffused into the base metal, forming a surface alloy. This is accomplished by placing the plated part in an oven or hot oil bath and heat treating it for about 2 h at a temperature slightly above the melting point of indium. Indium melts at 156.7 °C (314.1 °F), and the diffusion treatment is carried out at about 175 °C (350 °F). The processing time may be shortened by increasing the temperature, but only after the diffusion has actually begun. Failure to observe the proper temperature at the beginning of the diffusion process may lead to the formation of surface bubbles or droplets of indium, which are undesirable, particularly on a decorative finish. A number of factors govern the depth of diffusion:

- The amount of indium plated on the surface
- Temperature of heat treatment
- Time of diffusion treatment
- The diffusion coefficient for indium in the base metal

Indium Alloy Electrodeposits

A variety of indium alloy deposits have been reported in the literature. Included are alloys with antimony, arsenic, bismuth, cadmium, copper, gallium, lead, tin, and zinc. Of these, only indium-lead has had any degree of commercial importance.

Indium-lead electroplated alloy was developed as an improvement over the diffusion alloy that is formed by plating a thin layer of indium over lead on lead-containing bearings and diffusing the indium into the lead in a hot, 150 °C (300 °F) oil bath. The alloy reduces the corrosion of the lead-containing bearings by lubricating oils. An alloy containing an average

of about 4% In had high resistance to corrosion and was harder and had better antifriction properties than lead. However, the composition of the thermally diffused alloy was nonuniform. The electrodeposited indium-lead alloy provided greater uniformity of composition and showed only one-fourth the corrosion compared to the thermally diffused alloy.

Plating Baths. The two most successful indium-lead plating baths are indium-lead fluoborate and indium-lead sulfamate. Table 6 compares these processes. The details of the processes are shown in Tables 7 and 8.

Table 6 Comparison of indium-lead plating baths

Parameter	Bath salt	
	Fluoborate	Sulfamate
Indium content of deposit	11%	5%
Microhardness of deposit	2.5 kg/mm^2	(a)

(a) Not reported

Table 7 Indium-lead fluoborate plating bath

Constituent or parameter	Value or condition
Indium fluoborate	25 g/L (3.4 oz/gal)
Lead fluoborate	90 g/L (12.0 oz/gal)
Free fluoboric acid	15 g/L (2.0 oz/gal)
Glue	1.5 g/L (0.2 oz/gal)
Current density	100-300 A/m^2 (9-28 A/ft^2)
Temperature	20 °C (70 °F)

Table 8 Indium-lead sulfamate plating bath

Constituent or parameter	Value or condition
Indium sulfamate	20 g/L (2.67 oz/gal)
Lead sulfamate	1 g/L (0.13 oz/gal)

Soluble coffee[(a)]	5 g/L (0.67 oz/gal)
pH	1.5
Current density	100-300 A/m^2 (9-28 A/ft^2)

(a) Regular instant coffee powder

Nonaqueous Indium Plating Baths

The literature has reported the electrodeposition of indium and alloys such as indium-antimony, indium-gallium, and indium-bismuth from solutions of the metals dissolved in distilled ethylene glycol or glycerin. High-quality deposits have been reported with good current efficiencies.

Stripping Indium Plating

Diffused indium plate cannot be stripped from bronze. Undiffused indium on bronze can be removed with hydrochloric acid. Lead-indium plating, either diffused or undiffused, can be removed by immersion in a mixture of 9 parts glacial acetic acid and 1 part 30% hydrogen peroxide at room temperature. Indium and silver-indium alloy can be removed from steel by reversing the current in 30 g/L (4 oz/gal) solution of sodium cyanide at approximately 50 to 55 °C (122 to 131 °F). The silver-indium alloy can be removed in 1:1 nitric acid, but care must be taken to remove it from the bath before the steel is etched.

Specifications and Standards

No ASTM, ISO, or U.S. government specifications exist for indium plating. ASTM initiated a draft standard several years ago, but work was suspended due to lack of interest. The thickness ranges initially proposed were identical to those for tin (ASTM B 545). The SAE/AMS series has a specification for indium-lead plating, AMS 2415.

Hazards

The toxicity of indium and its compounds has not been extensively investigated. Animal tests indicate some degree of hazard, but for normal electroplating applications, usual good housekeeping practices should be sufficient. Indium should not be used in contact with food products because its solubility in food acids is high.

Tin Plating

Revised by Arthur J. Killmeyer, Tin Information Center of North America

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Introduction

TIN IS A VERSATILE, low-melting point, nontoxic metal that has valuable physical properties. It alloys readily with most other metals, and it forms many useful inorganic and organic chemical compounds because it is amphoteric. It has the largest melting point to boiling point range (from 232 to 2370 °C, or 450 to 4300 °F) of any metal. In conventional metallurgical applications, evaporation from a pot of liquid tin does not occur. Tin is used in a multitude of products, although the amount in which it is present is usually relatively small as a percentage of the total. Most manufacturers use some tin, and it is an essential material in industries such as communications, transportation, agriculture, food processing, and construction.

Electrodeposits

A thin coating of electrodeposited tin provides beneficial properties, such as excellent solderability, ductility, softness, and corrosion or tarnish resistance. In this way, the stronger materials that are required for their engineering properties can be enhanced by the desirable properties of tin on their surfaces. A tin deposit provides sacrificial protection to copper, nickel, and many other nonferrous metals and alloys. Tin also provides good protection to steel. However, because tin is normally cathodic to iron, the coating must be continuous and effectively pore-free. (This requirement does not apply to tinplate used for food packaging because the absence of oxygen inside tin-plated food containers prevents the electrochemical cell reactions that lead to corrosion.)

Thick, nonporous coatings of tin provide long-term protection in almost any application. The required coating thickness is established by the application. Thickness recommendations for tin coatings on metallic materials are given in Table 1. Tin coatings can be applied at thicknesses of less than 1 to 250 μm or greater.

Table 1 Recommended thicknesses for typical applications of tin deposits on metal substrates (ASTM B 545-92)

Class	Minimum thickness		Typical applications
	μm	μin.	
A	2.5	100	Mild service conditions, particularly where the significant surface is shielded from the atmosphere (as in electronic connector housings). Provides corrosion and tarnish resistance where greater thicknesses may be detrimental to the mechanical operation of the product (for example, small electrical spring contacts and relays). Class A often used for tin coatings that are not to be soldered, but must function as low-resistance electrical contact surfaces.
B	5	200	Mild service conditions with less severe requirements than grade C. Used as a precoating on solderable base metals to facilitate soldering of electrical components, surface preparation for protective painting, antigalling agent, and a stopoff in nitriding. Also found on baking pans after reflow.
C	8[a]	320[a]	Moderate exposure conditions, usually indoors, but more severe than class B. Used on electrical hardware (such as cases for relays and coils, transformer cans, screened cages, chassis, frames, and fittings) and for retention of the solderability of solderable articles during storage.
D	15[b]	600[b]	Severe service conditions, including exposure to dampness and mild corrosion from moderate industrial environments. Used with fittings for gas meters, automotive accessories (such as air cleaners and oil filters), and in some electronic applications.
E	30	1200	Very severe service conditions, including elevated temperatures, where underlying metal diffusion and intermetallic formation processes are accelerated. Thicknesses of 30 to 125 μm (0.0012 to 0.005 in.) may be required if the coating is subjected to abrasion or is exposed to slowly corrosive liquids or to corrosive atmospheres or gases. Thicker coatings are used for water containers, threaded steel couplings of oil-drilling

(a) 10 μm (400 μin.) for steel substrates.

(b) 20 μm (800 μin.) for steel substrates

Applications. The largest use of tin electrodeposits occurs at steel mills that produce tinplate, primarily as food-preservation containers. A thin tin coating protects the steel inside a tin can, as long as an oxygen-free environment is maintained. The second largest use of tin electrodeposits occurs in the electronics industry, where coatings are applied to the surfaces that require good solderability and corrosion or tarnish resistance.

These include radio and television chassis, computer frames, integrated circuit chip leads, tags, connectors, lead frames, printed wiring boards, and copper wire. Electrodeposited tin is also used on food handling equipment, such as steel baking pans, sieves, can openers, and fasteners. In general, tin electrodeposits are used to protect surfaces and render them usable in applications for which they would otherwise be unsuited.

Types of Electrolytes

Tin can be deposited from either alkaline or acid solutions. Electrolyte compositions and process operating details are provided in Ref 1, 2, and 3, as well as in publications of the International Tin Research Institute. Table 2 gives the basic details of electrolyte composition and operating conditions for alkaline solutions, and Tables 3 and 4 provide this information for acid solutions. Tin ions in the alkaline electrolytes have a valence of +4, whereas those in the acid electrolytes have a valence of +2. Consequently, the alkaline systems require the passage of twice as much current to deposit one gram-molecule of tin at the cathode.

Table 2 Composition and operating conditions for stannate (alkaline) tin plating electrolytes

Values of composition are for electrolyte startup; operating limits for the electrolyte composition are approximately -10 to + 10% of startup values

Solution	Composition										Operating conditions			
	Potassium stannate		Sodium stannate		Potassium hydroxide		Sodium hydroxide		Tin metal[(a)]		Temperature		Cathode current density	
	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	°C	°F	A/dm^2	A/ft^2
A	105	14	. . .	. . .	15[(b)]	2[(b)]	. . .	. . .	40	5.3	66-88	150-190	3-10	30-100
B	210	28	. . .	. . .	22	3	. . .	. . .	80	10.6	77-88	170-190	0-16	0-160
C	420	56	. . .	. . .	22	3	. . .	. . .	160	21.2	77-88	170-190	0-40	0-400
D	. . .	. . .	105[(c)]	14	. . .	. . .	10[(b)]	1.3[(b)]	42	5.6	60-	140-	0.5-3	6-30

(a) As stannate.

(b) Free alkali may need to be higher for barrel plating.

(c) $Na_2SnO_3 \cdot 3H_2O$; solubility in water is 61.3 g/L (8.2 oz/gal) at 16 °C (60 °F) and 50 g/L (6.6 oz/gal) at 100 °C (212 °F)

Table 3 Composition and operating conditions for sulfate (acidic) tin plating electrolyte

Constituent	Amount	Operating limits

	g/L	oz/gal	g/L	oz/gal
Stannous sulfate	80	10.6	60-100	8-13
Tin metal, as sulfate	40	5.3	30-50	4-6.5
Free sulfuric acid	50	6.7	40-70	5.3-9.3
Phenolsulfonic acid[(a)]	40	5.3	30-60	4-8
β-naphthol	1	0.13	1	0.13
Gelatin	2	0.27	2	0.27

Note: Temperature range for sulfate electrolytes is 21 to 38 °C (70 to 100 °F), and they do not require heating. Cooling can be considered if temperature rises to reduce adverse effects of heat on the electrolyte constituents. Cathode current density is 1 to 10

(a) Phenolsulfonic acid is most often used. Cresolsulfonic acid performs equally well and is a constituent of some proprietary solutions.

Table 4 Composition and operating conditions for fluoborate tin (acidic) plating electrolyte

Constituent or condition	Standard	High-speed	High throwing power
Electrolyte, g/L (oz/gal)			
Stannous fluoborate	200 (26.7)	300 (39.7)	75 (9.9)
Tin metal[(a)]	80 (10.8)	120 (16.1)	30 (4.0)
Free fluoboric acid	100 (13.4)	200 (26.8)	300 (40.2)
Free boric acid	25 (3.35)	25 (3.35)	25 (3.35)
Peptone[(b)]	5 (0.67)	5 (0.67)	5 (0.67)
β-naphthol	1 (0.13)	1 (0.13)	1 (0.13)
Hydroquinone	1 (0.13)	1 (0.13)	1 (0.13)
Temperature, °C (°F)	16-38[(c)] (60-100)[(c)]	16-38 (60-100)	16-38 (60-100)

Cathode current density, A/dm^2 (A/ft^2)	2-20 (20-200)	2-20 (20-200)	2-20 (20-200)

Note: The standard electrolyte composition is generally used for rack or still plating, the high-speed composition for applications like wire plating, and the high-throwing-power composition for barrel plating or applications where a great variance exists in cathode current density as a result of cathode configuration.

(a) As fluoborate.

(b) Dry basis.

(c) Electrolytes do not require heating. Cooling may be considered if temperature rises to reduce adverse effects of heat on the electrolyte constituents.

Alkaline electrolytes usually contain only a metal stannate and the applicable hydroxide to obtain satisfactory coatings. Unlined mild steel tanks are satisfactory. These can be heated by electrical immersion heaters, steam coils, or external gas burners. If steam coils are used, they should be supported 5 to 10 cm (2 to 4 in.) above the bottom of the tank to allow sediment to remain undisturbed. It is not necessary to filter still baths of this type, except at infrequent intervals. The electrical equipment is the same as that used in other plating operations. A rectifier for converting alternating current to direct current or a pulse-plating rectifier, which allows more precise control of electrical parameters, can be used. Factors such as operating temperature, solution constituent concentration, and operating current density all affect the efficiency and plating rate of the system and must be properly balanced and controlled.

Unusual operating conditions of the alkaline electrolytes involve:

- Tin anode control and electrochemical solution mode (discussed below)
- Cathodic deposition occurring from Sn^{+4}
- Solubility of the alkaline stannate in water

Ninety percent of the problems encountered in alkaline tin plating result from improper anode control. Conversely, operating the alkaline electrolytes is simple if one understands anode behavior, because there are no electrolyte constituents except the applicable stannate and hydroxide.

Tin anodes must be properly filmed, or polarized, in alkaline solutions to dissolve with the tin in the Sn^{+4} state. Once established, the anode film continues to provide the tin as Sn^{+4}. The anodes can be filmed either by subjecting them for about 1 min to a current density considerably above that normally used, or by lowering them slowly into the bath with the current already flowing.

Three reactions are possible at tin anodes in alkaline solutions:

$$Sn + 6OH^- \rightarrow Sn(OH)_6^{2-} + 4e^- \quad \textbf{(Eq 1)}$$

$$Sn + 4OH^- \rightarrow Sn(OH)_4^{2-} + 2e^- \quad \textbf{(Eq 2)}$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad \textbf{(Eq 3)}$$

Equation 1 represents the overall process occurring at the anodes when the film is intact and the tin is dissolving as stannate ion, with tin in the Sn^{+4} state. Film formation is confirmed by a sudden increase in the electrolyte cell voltage, a drop in the amperage passing through the cell, and the observation of a yellow-green film for pure tin anodes. High-speed anodes (containing 1% Al), used for tinplate production, turn darker. Because the anodes do not function at 100% efficiency when filmed, moderate gassing occurs as the result of the generation of oxygen, as in Eq 3.

Equation 2 is the process occurring if there is no film and the tin is dissolving as stannite ion, with tin in the Sn^{+2} state. The presence of stannite in the electrolyte produces unsatisfactory plating conditions, and the deposit becomes bulky, rough, porous, and nonadherent. The addition of hydrogen peroxide to the electrolyte oxidizes the Sn^{+2} to Sn^{+4}, returning it to a usable condition. If this remedy is required frequently, it indicates other problems that must be addressed. The concentration of caustic may be too high. This can be remedied with the addition of acetic acid.

Equation 3 shows the decomposition of hydroxyl ion with the formation of oxygen. While this is a normal reaction at the anode, it should not be permitted to become the dominant reaction, as occurs when the anode current density is too high. Under this condition, no tin dissolves and the anodes take on a brown or black oxide film. The anode current density should be reduced until the normal film color returns. If this is allowed to become thick enough, it is removable only by the action of strong mineral acids. Stannate baths normally appear colorless to straw colored, and clear to milky, depending on the quantity of colloidal material present. If an appreciable quantity of stannite builds up in the bath, it will appear light to dark gray, depending on the quantity of stannite that has formed. The gray color is caused by the precipitation of colloidal tin as a result of the disproportionation of stannite:

$$2Sn(OH)_4^{2-} \rightarrow Sn(OH)_6^{2-} + Sn + 2OH^-$$

This tin will codeposit with tin from the stannate ions, causing the rough spongy deposits mentioned above.

In the alkaline systems, two factors tend to restrict the usable current density range and limit the deposition rate. One factor is the solubility of the stannates in hydroxide solutions. With the sodium formula, the normal increase is not possible, because sodium stannate is one of the unusual salts that have a reverse temperature coefficient of solubility. An example of this process is given in Table 2. Less sodium stannate dissolves as the electrolyte temperature increases, which reduces the usable current density and the plating rate. Potassium stannate is more soluble with increasing temperature, but as the stannate increases, the potassium hydroxide must also increase. Stannate solubility decreases as the hydroxide content increases.

The second factor is that cathode efficiency decreases as current density increases. Eventually, a point is reached at which these factors become offset, and a further increase in current density does not increase the deposition rate. This limits the rate at which tin can be deposited.

In specialized applications, such as plating the inside of oil-well pipe, it is not possible to have an anode surface sufficient enough to avoid passivity. A higher current density can be used if insoluble anodes are utilized, but tin deposited on the cathode must then be replaced by the addition of chemicals. The addition of stannate to provide the tin cations also adds sodium or potassium hydroxide to the electrolyte. Although the resulting additional alkalinity can be neutralized by adding a calculated amount of an acetic acid, the sodium or potassium ion concentration continues to increase and the alkaline stannate solubility is reduced. This, in turn, reduces the available Sn^{+4} ion to a low enough concentration that the plating rate decreases rapidly, and the electrolyte must be discarded. A potassium-base composition has been developed, in which the necessary Sn^{+4} ions are added to the electrolyte as a soluble, colloidal, hydrated tin oxide (Ref 2). Because the potassium ion concentration builds up more slowly in this composition, electrolyte life is nearly indefinite. The throwing power of alkaline stannate solutions is quite high, allowing the coating of intricate shapes and interior parts of cathodes.

Acid Electrolytes. Several acid electrolytes are available for tin plating. Two of these--stannous sulfate and stannous fluoborate--are general systems that are adaptable to almost any application. Electrolytes such as halogen (a chloride-fluoride base system) and Ferrostan (a special sulfate-base system) have been developed for tin coating cold-rolled steel strip traveling at high speed for the production of tinplate. The acid electrolytes differ from alkaline electrolytes in many respects. A stannous salt that is dissolved in a water solution of the applicable acid does not produce a smooth, adherent deposit on a cathode. Therefore, a grain-refining addition agent (such as gelatin or peptone) must be used. Usually, such materials are not directly soluble in a water solution, and a wetting-agent type of material (such as β-naphthol) is also necessary.

Organic brighteners can be added if a bright-as-coated electrodeposit is desired. This produces a coating that looks the same as a reflowed tin coating. Over time, these brighteners will decompose in the bath and must be replenished. The composition of these organic brighteners has been the subject of considerable research over the years. The earliest substance studied, in the 1920s, was wood tar dispersed with a wetting agent. Other materials were studied in later years, especially pure compounds such as cresol sulfonic acid and various aromatic sulfonates. These were seen to have more of

a stabilizing effect, preventing the hydrolysis and precipitation of tin as tin(II) and tin(IV) salts. Later work has shown that a "cruder" material is more effective as a brightener. Such a material is obtained by the sulfonation of commercial cresylic acid. The implication here is that by-products of the sulfonation and not the cresol sulfonic acid itself are responsible for the brightening of the tin coating. Various proprietary brightening systems have been produced over the years. Very little of the development work on brightening agents has been published outside the patent literature. A comprehensive discussion of the topic is beyond the scope of this article. It is usually most convenient to purchase a packaged system from a plating supply house.

The organic materials will co-deposit with the tin, resulting in a higher than normal carbon content in the electrodeposit. This does not create a problem, unless the tin coating is to be soldered or reflowed. The supplier of the proprietary bath should be consulted for directions on controlling this problem.

To retard the oxidation of the stannous tin ions to the stannic form, either phenolsulfonic or cresolsulfonic acid is added to a sulfate-base system, and hydroquinone is added to a fluoboric acid-base system. Although the acid electrolytes can contain large amounts of stannic ions without affecting the operation of the system, only the stannous ions are deposited at the cathode. As a result, oxidation depletes the available stannous ions, which must be replaced by adding the corresponding stannous salt to the bath. To limit the oxidation of stannous ions, a sufficient anode area must be maintained, and the operating temperature must be kept as low as possible. In addition, one must avoid introducing oxygen into the solution, either by a filter leak or air agitation. Usually, an antioxidant is added to the solution.

In terms of operating characteristics, the basic differences between acid and alkaline electrolytes are related to the type of tin ion that is present in the electrolyte. In acid systems, the stannous ions must not be oxidized to the stannic form, and operation must occur at lower temperatures. The acid electrolytes require only half as much current to deposit one gram-molecule of tin. The tin dissolves directly from the metallic anodes, and the control of an anode film is not involved. Acid electrolytes are nearly 100% efficient, both anodically and cathodically, which avoids the necessity of regularly adding chemicals for tin. The problems of oxygen gas evolution at the anode surface and hydrogen gas at the cathode surface are reduced. Some particulate matter is produced as sludge from three sources: anode slime products, the precipitation of addition agents and their breakdown products, and basic tin compounds formed by oxidation. These materials must be removed during operation. In a still tank, the precipitates gradually settle, but agitated solutions require continuous filtration.

Acid-resistant equipment must be used. Lead-lined plating tanks were formerly used, but stoneware, rubber- or plastic-lined steel, or plastic tanks are now more common. Filtration equipment should be available, because solid particles of precipitated matter in the solution will cause deposit porosity and roughness. With still baths, suspended matter can be allowed to settle without filtration, but with agitated baths, continuous filtration is advisable. Cathode bar movement is often recommended.

The stannous sulfate electrolyte is most popular because of its general ease of operation. The rate of deposition is somewhat limited by optimum metal concentration in the electrolyte. A still bath is operated at a cathode current density of 1 to 2 A/dm^2 (10 to 20 A/ft^2). Current densities of up to 10 A/dm^2 (100 A/ft^2) are possible with suitable electrolyte agitation. Higher current densities will result in burned deposits. The anode surface area must be increased when higher current densities are used, otherwise the anodes will become passive. Addition agent control is not quantitative in nature, but deficiencies are easily recognized by the experienced plater. An electrolyte can be prepared from readily available chemicals, or a proprietary system can be purchased from suppliers. Most commercial bright acid tin processes and the more recent matte acid tin systems are based on the stannous sulfate solution. Precise information on operation and control should be obtained directly from the specific supplier.

The stannous fluoborate electrolyte is a good general-purpose electrolyte. It can operate at higher current densities because of the conductivity provided by the fluoboric acid. Cathode current densities of 20 A/dm^2 (200 A/ft^2) and higher are possible with suitable solution agitation. The need to increase anode surface area at high current densities and the control of the addition agents parallel the requirements associated with using stannous sulfate. Table 4 gives standard, high-speed, and high-throwing-power electrolyte compositions, because each meets a specific need. The solution conductivity that is lost because of the lower metal content in the high-throwing-power bath is compensated for by the higher concentration of fluoboric acid. The lower total metal in the solution reduces the variance in deposit thickness that is usually associated with varying areas of cathode current density. Boric acid is listed as a constituent of the fluoborate solutions because of its presence in the stannous fluoborate and fluoboric acid used to prepare the solutions. It is not a necessary ingredient in the electrolyte.

References cited in this section

1. F.A. Lowenheim, Ed., *Modern Electroplating,* 3rd ed., Wiley-Interscience, 1974
2. S. Hirsch, Tin-Lead, Lead, and Tin Plating, *Metal Finishing Guidebook and Directory Issue,* Vol 91 (No. 1A), Jan 1993, p 269-280
3. J.W. Price, *Tin and Tin Alloy Plating,* Electrochemical Publications Ltd., Ayr, Scotland, 1983

Lead Plating

Revised by George B. Rynne, Novamax Technology

Introduction

LEAD has been deposited from a variety of electrolytes, including fluoborates, fluosilicates, sulfamates, and methane sulfonic acid baths. Fluoborate baths are the most widely used because of the availability of lead fluoborate and the simplicity of bath preparation, operation, and stability. Fluoborate baths provide finer grained, denser lead deposits. Fluosilicate baths, although less costly to use for large operations, are difficult to prepare for small-scale plating. They are not suitable for plating directly on steel and are subject to decomposition, which produces silica and lead fluoride. Use of sulfamate baths is almost nonexistent in the United States, because neither lead silicofluoride nor lead sulfamate is available commercially. These salts must be prepared by the plater using litharge (PbO) and the corresponding fluosilicic or sulfamic acids. Sulfamate baths are subject to decomposition, which produces lead sulfate.

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Applications

The appearance and properties of lead limit its commercial use in electroplating largely to corrosion protection and bearing applications-two fields in which the physical and chemical properties of lead render it unique among the commercially plated metals. Lead has not been extensively electroplated because its low melting point of 325 °C (620 °F) facilitates application by hot dipping. Electrodeposited lead has been used for the protection of metals from corrosive liquids such as dilute sulfuric acid; the lining of brine refrigerating tanks, chemical apparatus, and metal gas shells; and barrel plating of nuts and bolts, storage battery parts, and equipment used in the viscose industry.

Electroplated lead has been used for corrosion protection of electrical fuse boxes installed in industrial plants or where sulfur-bearing atmospheres are present. Lead is also codeposited with tin for wire plating, automotive crankshaft bearings, and printed circuits.

Nonporous lead deposits with thicknesses of 0.01 to 0.025 mm (0.4 to 1 mil) give good protection against corrosion, although the coating may be subject to breaking during abrasion due to the soft nature of lead. Better mechanical properties and improved durability are obtained with coating deposits with thicknesses greater than 0.025 mm (1 mil). Depositing more than 0.08 mm (3 mils) of lead is relatively easy, in that a deposit of about 0.1 mm (4 mils) can be produced in about 1 h at 2 A/dm^2 (19 A/ft^2) (Ref 1).

Reference cited in this section

1. H. Silman, G. Isserlis, and A.F. Averill, *Protective and Decorative Coatings for Metals,* Finishing Publications Ltd., 1978, p 443-448

Process Sequence

Low-Carbon Steel. Lead can be plated directly on steel from the fluoborate bath using the following cycle:

- Degrease with solvent (optional)
- Alkali clean (anodic)
- Water rinse
- Dip in 10% fluoboric acid (*Caution: Hydrochloric or sulfuric acid should not be used because they can precipitate insoluble lead sulfate or chloride on the work in the event of poor rinsing*)
- Water rinse
- Lead plate
- Rinse

Lead can be plated on steel from fluosilicate and sulfamate baths using the following cycle:

- Degrease with solvent (optional)
- Alkali clean (anodic)
- Rinse
- Dip in 5 to 25% hydrochloric acid
- Rinse thoroughly
- Dip in 30 to 75 g/L (4 to 10 oz/gal) sodium cyanide
- Rinse
- Copper cyanide strike
- Rinse thoroughly
- Dip in 10% fluoboric acid (see caution above)
- Rinse
- Lead plate
- Rinse

Copper. Lead can be plated directly on copper from fluoborate, fluosilicate, or sulfamate baths using the following cycle:

- Alkali clean (anodic or cathodic/anodic)
- Rinse
- Dip in 10% fluoboric acid (see caution above)
- Rinse
- Lead plate
- Rinse

Fluoborate Baths

Lead fluoborate baths are prepared by adding the required amount of lead fluoborate concentrate and fluoboric acid to water followed by peptone as the preferred addition agent.

Until methane sulfonic acid (MSA) baths became widely used in the past few years, fluoroborate baths were the most important bath for lead plating. Good lead deposits up to 1.5 mm (60 mils) in thickness can be achieved with a fluoroborate bath of the following composition:

Basic lead carbonate, $2PbCO_3 \cdot Pb(OH_2)$	300 g/L (40 oz/gal)

Hydrofluoric acid (50% HF)	480 g/L (64 oz/gal)
Boric acid, H_3BO_3	212 g/L (28 oz/gal)
Glue	0.2 g/L (0.03 oz/gal)

A bath of half the above concentration is suitable for thinner deposits at low current densities, but the lead concentration should be kept high if smooth deposits and good throwing power are required (Ref 1). More detailed information on fluoroborate formulations and performance for lead plating is covered in Ref 2, 3, 4, and 5.

Many different types of glue and gelatin additives are available, but no one type is manufactured specifically for lead plating. Depending on the method of manufacture, each can exhibit different levels of solubility and impurities that may be of concern to the plater.

Glue and gelatin addition agents must be swelled and dissolved in water by the plater just prior to addition to the bath. The resultant colloidal solution has a limited shelf-life and is prone to bacterial degradation on standing. Glue and hydroquinone are relatively expensive. Often, it is a by-product of an industrial process and can contain organic and inorganic impurities detrimental to the lead plating process. No grade is manufactured and sold specifically for lead plating.

Concentrates of lead fluoborate and fluoboric acid contain free boric acid to ensure bath stability. An anode bag filled with boric acid in each corner of the plating tank is recommended to maintain a stable level of boric acid in the bath solution. The concentration of boric acid in the bath is not critical and can vary from 1 g/L (0.13 oz/gal) to saturation. The water used in the bath preparation must be low in sulfate and chloride, as these lead salts are insoluble.

Table 1 provides the compositions and operating conditions of high-speed and high-throwing-power fluoborate plating baths. The high-speed bath is useful for plating of wire and strip where high current densities are used. The high-throwing-power formulation is used in applications such as barrel plating of small parts or where thickness distribution on intricate or irregularly shaped parts is important. The high-throwing-power bath should be operated at a lower current density because of the lower lead content of the bath.

Table 1 Compositions and operating conditions of lead fluoborate baths

Anode composition, pure lead; anode/cathode ratio, 2:1

Bath	Bath composition							Temperature		Cathode current density[(a)]	
	Lead		Fluorobic acid (min)		Peptone solution, vol%	Free boric acid					
	g/L	oz/gal	g/L	oz/gal		g/L	oz/gal	°C	°F	A/dm^2	A/ft^2
High-speed	225	30	100	13.4	1.7	1 to saturation	0.13 to saturation	20-41	68-105	5	50
High-throwing-	15	2	400	54	1.7	. . .	. . .	24-71	75-	1	10

(a) Values given are minimums. Current density should be increased as high as possible without burning the deposit; this is influenced by the degree of agitation.

Fluoborate baths rank among the most highly conductive plating electrolytes and thus require low voltage for the amperage used.

Maintenance and Control. The very high solubility of lead fluoborate in solution with fluoboric acid and water accounts for its almost universal use for lead plating. In the high-speed bath formulation of Table 1, neither the lead nor acid content is critical, and the bath can be operated over a wide range of lead and acid concentrations.

The high-throwing-power bath formulation of Table 1 must be operated fairly close to the guidelines given. Lowering the lead concentration improves the throwing power characteristics; however, a reduction in lead concentration must be followed by a corresponding decrease in the cathode current density. On the other hand, an increase in lead content above the optimum permits the use of higher current densities, with a corresponding decrease in throwing power.

Sludge may form in the fluoborate bath as a result of the use of impure lead anodes that contain bismuth or antimony or as a result of the drag-in of sulfates. Fluoborate baths should be constantly filtered through dynel or polypropylene filter media to remove any sludge that may form. Anodes must be bagged in dynel or polypropylene cloth. Absence of gas bubbles at the cathode or anode while plating indicates all electric energy is theoretically being used to transfer lead from the anode to the workpiece; in other words, the process is operating at 100% anode and cathode efficiency. The plating bath concentration therefore remains unchanged except for changes due to evaporation and dilution from placing wet parts in the bath in combination with dragout when the parts are removed from the bath.

Methods are available for analyzing lead and fluoboric acid concentrations. Additive concentration can be adequately evaluated through the use of the Hull cell. Low concentration of additive results in loss of throwing power, coarse-grained deposits, and treeing. (*Treeing* is the formation of irregular projections on a cathode during electrodeposition, especially at edges and other high-current-density areas).

References cited in this section

1. H. Silman, G. Isserlis, and A.F. Averill, *Protective and Decorative Coatings for Metals,* Finishing Publications Ltd., 1978, p 443-448
2. S. Hirsch, Tin-Lead, Lead and Tin Plating, *Metal Finishing Guidebook and Directory,* Elsevier Science, 1992, p 262-278
3. F.A. Lowenheim, *Modern Electroplating,* 2nd ed., John Wiley & Sons, 1963, p 242-249
4. A. Graham, *Electroplating Engineering Handbook,* 3rd ed., Van Nostrand Reinhold, 1971, p 238, 246, 266
5. *The Canning Handbook,* 23rd ed., Canning, 1982, p 742-746

Fluosilicate Baths

Fluosilicic acid is formed by the action of hydrofluoric acid on silicon dioxide. The lead fluosilicate ($PbSiF_6$) electrolyte is formed when fluosilicic acid is treated with litharge. No great excess of silicic acid can be held in solution; therefore, the fluosilicate solution is less stable than the fluoborate solution. Table 2 lists compositions and operating conditions for two lead fluosilicate baths.

Table 2 Compositions and operating conditions of lead fluosilicate baths

Temperature, 35-41 °C (95-105 °F); cathode current density, 0.5-8 A/dm^2 (5-80 A/ft^2); anode current density, 0.5-3 A/dm^2 (5-30 A/ft^2); anode composition, pure lead

Bath	Lead		Animal glue		Peptone equivalent		Total fluosilicate	
	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal
1	10	1.3	0.19	0.025	5	0.67	150	20

2	180	24	5.6	0.75	150	20.1	140	18.75

Although at low current densities it is possible to secure smooth deposits of lead from the fluosilicate bath without additive agents, higher current densities are likely to produce treeing, especially in heavy deposits. Therefore, an additive agent, such as peptone glue or other colloidal materials or reducing agents, is always used. The use of excess glue in lead plating baths, however, may result in dark deposits. Maintenance and control procedures for the fluosilicate baths are similar to those described for the fluoborate baths.

Sulfamate Baths

Sulfamate baths consist essentially of lead sulfamate with sufficient sulfamic acid to obtain a pH of about 1.5. Sulfamic acid is stable and nonhygroscopic, and is considered a strong acid. Compositions and operating conditions of two typical sulfamate baths are given in Table 3.

Table 3 Compositions and operating conditions of lead sulfamate baths

pH, 1.5; temperature, 24-49 °C (75-120 °F); cathode current density, 0.5-4 A/dm^2 (5-40 A/ft^2); anode current density, 0.5-4 A/dm^2 (5-40 A/ft^2); anode/cathode ratio, 1:1; anode composition, pure lead

Bath	Lead		Animal glue		Peptone equivalent		Free sulfamic acid	
	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal
1	140	18.75	5.6	0.75	150	20.1	. . .	. . .

Because the acid and the salt used in the solutions in Table 3 are highly soluble in water, sulfamate baths can be prepared either by adding constituents singly or as formulated salts to water. Solutions are usually formulated to concentrations that allow bath operation over a wide range of current densities. Lead concentration can vary from 112 to 165 g/L (15 to 22 oz/gal), while the pH is held at about 1.5. As in other lead plating solutions, additive agents (peptone gelatin or other colloids, alkyl or alkyl aryl polyethylene glycols) are required to produce smooth, fine-grained deposits.

Spongy deposits are obtained if the lead concentration is too low, the current density is too high, or the concentration of additive agent is too low. At low pH or high temperature, sulfamate ions hydrolyze to ammonium bisulfate to form insoluble lead sulfate. Ordinarily, this hydrolysis presents no problem, provided the bath is correctly operated.

Maintenance and Control. Sulfamate baths do not require much attention other than maintenance of the correct proportion of additive agents to produce the desired deposit quality. Additive agent content is evaluated by the use of the Hull cell. The pH is easily adjusted with sulfamic acid or ammonia and can be measured with a glass electrode. Lead concentration can be determined with sufficient accuracy by hydrometer readings or an occasional gravimetric analysis.

Methane Sulfonic Acid Baths

Methane sulfonic acid (MSA) baths consist essentially of MSA-lead concentrate mixed with MSA to arrive at a total acid concentration of 300 mL/L. The overall system is stable and is considered to be a strong acid. Compositions and operating conditions for two MSA baths are given in Table 4.

Table 4 Compositions and operating conditions of lead methane sulfonic acid (MSA) baths

Temperature, 45 °C (110 °F); anode composition, pure lead; anode/cathode ratio, 1:1

Bank	Lead		MSA, mL/L	Additive, vol%	Cathode current density	
	g/L	oz/gal			A/dm^2	A/ft^2
Rack/barrel	30	4	300	4	0.5-5	5-50
High-current	100	13.3	300	4	0.5-20	5-200

The materials used to formulate MSA baths are highly soluble liquids. The baths listed in Table 4 are metal concentrations and, as such, are sensitive to current density. A lead concentration of 30 g/L (4 oz/gal) supports a maximum current density of 5 A/dm^2 (50 A/ft^2); an increase in the lead concentration to 100 g/L (13.3 oz/gal) allows a corresponding increase in the maximum current density to 20 A/dm^2 (200 A/ft^2). The use of a proprietary additive (4% of bath composition) is required to produce the smooth, fine-grained deposits usually provided by colloidal agents in fluoborate systems.

The principal advantage of MSA baths, in addition to their overall chemical stability, is the absence of the fluoride and borate ions present in other lead plating baths. These ions are heavily regulated or prohibited in many states because of their deleterious effects on fruit-bearing trees when released to the environment. An additional advantage of MSA baths is that when they are applied to 60Pb-40Sn solder alloys, these eutectic alloys can be plated over an extremely broad range of current densities. MSA baths are easily operated and controlled, but they are more expensive to make up.

Maintenance and Control. The MSA system is extremely stable and requires little or no maintenance other than control of the metal, acid, and additive concentrations within relatively broad ranges. Of these, it is of greatest importance to control the acid concentration in actual production situations. Additive concentration is evaluated using the Hull cell; metal and acid concentrations can be evaluated through simple titrations. Deionized water must be used for rinsing the part prior to immersion in the plating bath because MSA is sensitive to chloride ions in the makeup water.

Anodes

Lead of satisfactory purity for anodes may be obtained either as corroding lead or chemical lead. Chemical lead anodes generally are preferred. Impurities in the anodes such as antimony, bismuth, copper, and silver cause the formation of anode slime or sludge and can cause rough deposits if they enter the plating solution. These impurities can also cause anode polarization if present in the anode, especially at higher anode current densities. Small amount of tin and zinc are not harmful. Anode efficiency in acid baths is virtually 100%.

Anodes should be bagged in dynel or polypropylene cloth to prevent sludge from entering the plating bath. These bags should be leached in hot water to remove any sizing agents used in their manufacture before use in the plating bath. Nylon and cotton materials deteriorate rapidly and should not be used in any of the baths.

Equipment Requirements

Fluoborate and fluosilicate baths attack equipment made of titanium, neoprene, glass, or other silicated material; thus, these materials should not be used in these solutions. Anode hooks should be made of Monel metal.

Tanks or tank linings should be made of rubber, polypropylene, or other plastic materials inert to the solution. Pumps and filters of type 316 stainless steel or Hastelloy C are satisfactory for intermittent use; for continuous use, however, equipment should be made from or lined with graphite, rubber, polypropylene, or other inert plastic. Filter aids used for the fluoborate solution should be made of cellulose rather than asbestos or diatomaceous earth.

Stripping of Lead

Table 5 identifies solutions and operating conditions for stripping lead from steel. Method C, at about 16 °C (60 °F), strips 25 μm (1 mil) of lead in 6 or 7 min with very slight etching of the steel. With Method B, voltage increases suddenly when the lead coating has been removed; at room temperature and 9.3 A/dm^2 (92 A/ft^2), the voltage may be about 2.7 V during stripping, but increases to 4.6 V when stripping is complete.

Table 5 Solutions and operating conditions for stripping lead from steel

Method A	
Sodium hydroxide	100 g/L (13.4 oz/gal)
Sodium metasilicate	75 g/L (10 oz/gal)
Rochelle salt	50 g/L (6.7 oz/gal)
Temperature	82 °C (180 °F)
Anode current density	1.9-3.7 A/dm^2 (18.5-37 A/ft^2)
Method B	
Sodium nitrite	500 g/L (67 oz/gal)
pH	6-10
Temperature	20-82 °C (68-180 °F)
Anode current density	1.9-18.5 A/dm^2 (18.5-185 A/ft^2)
Method C[(a)]	
Acetic acid (glacial)	10-85 vol%
Hydrogen peroxide (30%)	5 vol%
Method D[(a)(b)]	
Fluoboric acid (48-50%)	4 parts
Hydrogen peroxide (30%)	1 part
Water	2 parts

Temperature	20-25 °C (68-77 °F)

(a) Formulations should be made up fresh daily.

(b) Alternate method for stripping lead or lead-tin deposits. Work must be removed as soon as the lead is stripped; otherwise, the base metal will be attacked.

With the solutions used in Method A or B, a stain occasionally remains on the steel after stripping. The stain can be removed by immersion for 30 s in the solution used in Method C, leaving the steel completely clean and unetched (unless the nitrate solution of Method B was used at less than about 2 V).

Silver Plating

Alan Blair, AT&T Bell Laboratories

ELECTROPLATED SILVER--which was developed primarily for use on holloware, flatware, and tableware--has proven its usefulness in both decorative and functional applications in both engineering and electrical/electronic applications. Decorative applications of silver plating still predominate; however, silver has been successfully substituted for gold in some functional uses in electronics. Its greatest success has been the virtually complete replacement of gold on metallic leadframes, the devices that support the majority of silicon chips. Here the development of new silicon-to-silver bonding techniques and ultimate encapsulation of the silver allow for the replacement of a much more expensive precious metal without loss of performance. In electrical contact applications, where the long-term integrity of the surface is of paramount importance, silver has been less successful as a gold substitute due to its tendency to form oxides and sulfides on its surface and the resultant rise in contact resistance. Silver has been employed as a bearing surface for many decades. It is particularly useful where the load-bearing surfaces are not well lubricated (e.g, in kerosene fuel pumps on gas turbine engines.)

Solution Formulations. The first patent concerning electroplating was filed in 1840 and reported a process for plating silver from a cyanide solution. To this day, silver is plated almost exclusively with cyanide-based solutions, despite the considerable research effort that has been expended on evaluating less toxic alternatives. A formulation for such a solution is given in Table 1. This type of electrolyte would be used for plating decorative or functional deposits of silver in a conventional way (i.e., on a rack or in a barrel). It is possible to produce fully bright deposits that require no further buffing or polishing. This is achieved by including a brightening agent in the solution formula, (one of several sulfur-bearing organic compounds, or selenium or antimony added as soluble salts). Antimony containing silver deposits are harder than pure silver. A typical antimony content might be 0.1 to 0.2% by weight. However, it should be noted that antimony content will vary with the current density employed during deposition; lower current densities will produce a deposit with higher antimony content.

Table 1 Plating solutions for silver

Component/Parameter	Rack	Barrel
Silver as $KAg(CN)_2$, g/L (oz/gal)	15-40 (2.0-2.5)	5-20 (0.7-2.5)
Potassium cyanide (free), g/L (oz/gal)	12-120 (1.6-16)	25-75 (3.3-10)
Potassium carbonate (min), g/L (oz/gal)	15 (2.0)	15 (2.0)

Temperature, °C (°F)	20-30 (70-85)	15-25 (60-80)
Current density, A/dm^2 (A/ft^2)	0.5-4.0 (5-40)	0.1-0.7 (1-7.5)

Anodes of pure silver are readily soluble in the excess or "free"cyanide of these solutions. Carbonate is a natural byproduct of atmospheric oxidation of cyanide, but this adds to the solution conductivity, and some carbonate is included when preparing a new solution. Silver metal concentration is normally maintained by anode dissolution, but occasional small additions of the metal salt may be needed. This is facilitated by adding either silver cyanide (80% silver) or potassium silver cyanide (54% silver, sometimes referred to as the double salt). Additions of the former will lower the free cyanide concentration, whereas additions of the double salt will not.

Silver is usually more noble than the metal over which it is being plated, and because of this it has a tendency to form "immersion deposits." These are poorly adherent films of silver that form due to a chemical reaction between the base metal substrate and the silver ions in solution before true electrodeposition can commence. In order to avoid this phenomenon a silver strike should always be used. (A *strike* is a low-concentration bath operated at high cathode current density.) The following gives a typical silver strike solution formulation.

Component/Parameter	**Value**
Silver, as $KAg(CN)_2$, g/L (oz/gal)	1.0-2.0 (0.13-0.27)
Potassium cyanide (free), g/L (oz/gal)	80-100 (10-13)
Potassium carbonate (minimum), g/L (oz/gal)	15 (2.0)
Temperature, °C (°F)	15-25 (60-80)
Current density, A/dm^2 (A/ft^2)	0.5-1.0 (5-10)

Stainless steel anodes should always be used in a silver strike solution to avoid an increase in silver metal concentration.

High-speed, selective plating of leadframes or similar electronic components requires the use of extremely high current densities and short plating times. Typical thicknesses range from 1.5 to 5.0 μm deposited in less than 2 s. Under these conditions, solutions containing free cyanide decompose very rapidly, the cyanide polymerizes and codeposits through electrophoresis, and the deposits cease to provide the desired properties. Solutions that use phosphate or nitrate salts as conducting media and use insoluble platinum or platinized titanium or niobium anodes have been developed to meet this requirement. Silver is present as potassium silver cyanide, and its concentration must be maintained by making periodic additions of this double salt. Careful attention must be paid to buffering because of the tendency to produce low pH values at the insoluble anodes. If this occurs, an insoluble silver salt will rapidly coat the anode and plating will cease. A typical formula is shown below.

Component/Parameter	Value
Silver, as KAg(CN)2,g/L (oz/gal)	40-75 (5-10)
Conducting/buffering salts,g/L (oz/gal)	60-120 (8-16)
pH	8.0-9.5
Temperature, °C (°F)	60-70 (140-160)
Current density, A/dm^2(A/ft^2)	30-380 (275-3500)

Noncyanide formulas that have been reported include those based on simple salts such as nitrate, fluoborate, and fluosilicate; inorganic complexes such as iodide, thiocyanate, thiosulfate, pyrophosphate, and trimetaphosphate; and organic complexes such as succinimide, lactate, and thiourea. A succinimide solution and a thiosulfate/metabisulfite solution have been commercialized, but the volumes used are very small compared with the cyanide solutions.

Specifications. Federal specification QQ-S-365D gives general requirements for silver plating. Using this specification it is possible to define the type of finish needed: matte (type I), semibright (type II), or bright (type III), and with chromate film for added tarnish resistance (grade A), or with no film (grade B). A minimum thickness of 13 μm (0.0005 in.) is required for functional coatings.

ASTM B 700 specifies electrodeposited coatings of silver for engineering uses and defines purity (types 1, 2, and 3: 99.9, 99.0, and 98.0%, respectively); degree of brightness or mechanical polish (grades A, B, and C: matte, plated bright, and mechanically polished, respectively); and absence or presence of a chromate film (class N or S). Thickness must be specified by the purchaser.

The aerospace industry refers to four aerospace material specifications: AMS 2410G, AMS 2411D, and AMS 2412F, each of which applies to specific undercoats and bake temperatures; and AMS 2413C, which defines requirements for silver and rhodium plating on microwave devices.

International standard ISO 4521 defines silver coatings on metallic and nonmetallic substrates. Thicknesses are not specified but preferred thicknesses are quoted.

Users of silver plating for decorative purposes will find guidance in "Guides for the Jewelry Industry," originally issued by the Federal Trade Commission.

Gold Plating

Alfred M. Weisberg, Technic Inc.

Introduction

GOLD PLATING is similar to other metal plating in most chemical and electrochemical ways. Gold differs from other metals primarily in that it is much more expensive. Within recent memory, the price of gold metal has gone from $35 per ounce to $850 per ounce and at the time of this writing is characteristically unstable at about $375 per ounce. Thus the cost of a gallon of gold plating solution is quite high.

This price level and the daily variability of its price have required chemists and engineers to severely limit the concentration of gold in the plating solution. Nickel, alkaline copper, and silver are typically plated from solutions that contain 37 g of metal per liter of plating bath. Acid copper is plated from a solution that contains 60 g of metal per liter,

and a chromium solution can contain over 240 g of metal per liter. Gold, because of its price and the cost of the dragout losses, is rarely plated from a solution that contains more than 1 troy ounce per gallon (8.2 g/L). Some gold baths used for striking, decorative use, and barrel plating use as little as 0.8 or 0.4 g/L of gold.

These very low metal concentrations, or "starved" solutions, present problems to the gold plater that are quite different from those of other metal plating solutions. With a starved solution, every control parameter in the plating process becomes more critical. Gold concentration, electrolyte concentration, pH, impurity level, and additive level must all be monitored and controlled. Temperature, current density, agitation, and the current efficiency must be accurately known and controlled beyond the degree necessary for copper, nickel, or even silver plating. If any factor changes, even 2 to 3%, the cathode gold deposition efficiency changes. If the efficiency decreases, items being plated under standard conditions will be underplated and the specified thickness will not be attained. Similarly, if the cathode efficiency increases, the plate will be too thick and result in increased cost because of using excess gold.

The engineer and plater of gold must tread the narrow line between not depositing enough gold and giving away too much gold. In addition, those concerned with gold plating must not only keep the chemistry of the process and the peculiarities of electrodeposition in mind, as do other platers, but also be aware of the market price of gold. The plater must be an economist in order to realize when the operating conditions of the solution should be altered or the entire process changed to reflect the changes in the price of gold. Economics also determines the total consumption of gold. In the recent past, when the price of gold vaulted above $500 per troy ounce, many electronics companies replaced some of the total thickness of gold with undercoats of palladium or palladium-nickel alloys. Others abandoned gold completely. Economics is a more important factor in the plating and metallurgy of gold than in the plating of nonprecious metals.

General Description

Gold electroplating was invented in 1840. During the first 100 years electrodeposited gold was used primarily for its aesthetic appeal as a decorative finish. Because decorative appeal is a matter of fashion and personal whim, hundreds of different formulations are recorded in the literature. Each was the favorite color and finish of a master plater. In their time and place, each was good. Today, however, many factors have changed, especially the price, and the old formulas should be used for historical reference only.

With the development of electronics and radar during World War II, gold had to become a functional utilitarian coating. Low voltages, milliamp currents, dry circuits, and microwave frequencies required the very best low resistance surfaces for contacts, connectors, and waveguides. The stability of the contact resistance was of paramount importance. Nontarnishing and low-resistance 24K gold surfaces were the logical choice for connectors. Later, as the demands on the gold surface increased, it was found necessary to change the metallurgy of the gold deposit. Initially, wear resistance was increased by hardening the deposit to 150 to 250 HK. Later, wear resistance was increased by altering the crystal orientation of the gold deposit from the (100) plane to the slip plane, (111). Both of these results were achieved by the addition of controlled amounts of metallic and nonmetallic additives.

At virtually the same time, transistors required high-purity gold that could be doped with antimony or indium to give n- or p-type junctions. The printed circuit industry required gold electroplates that could be produced from solutions of lower pH (actually on the acid side) and from solutions that contained no free cyanide. The alkalinity of free cyanide lifted the resist and sometimes even lifted the laminate itself. It was rediscovered that potassium gold cyanide was stable at acidic pH. Under these conditions of mild acidity, hard, bright, and even solderable coatings could be achieved. This led to the development of perhaps another 100 formulations that could meet all of the requirements mentioned above as well as the different purities and hardnesses of the military gold plating standard MIL-G-45204 with its various modifications. The multiplicity of gold electroplating formulations was further augmented by the addition of baths for high-speed deposition that were used for continuous strip, stripe, or spot plating. Some of these plated at up to 215 A/dm^2 (2000 A/ft^2). Recently, numerous formulations have been developed to allow immersion and/or electroless gold plating. As additional requirements develop, there will be a continuing introduction of new gold plating formulations to meet these needs. All of the many formulations work, and each one has its own special advantages, but care must be taken to pick the best one for a particular application.

Decorative Plating

The traditional gold electroplating solution (Table 1) for decorative use required:

- A source of gold

- A complexing agent for the gold
- A conducting salt to help carry the current and broaden the conditions of operation
- An alloying metal or metals for color and/or hardness

The source of gold was historically gold cyanide. The complexing agent was sodium or potassium cyanide (Table 1). The conducting salts were cyanides, phosphates, carbonates, hydroxides, and occasionally but rarely citrates, tartrates, and so forth.

Table 1 Typical flash formulations for decorative gold plating

Component or parameter	Type of jewelry plating						
	English (24K)	**Hard (18K)**	**Hamilton[(a)]**	**White**	**Rose**	**Green**	**Barrel flash**
Gold as potassium gold cyanide, g/L (oz/gal)	2 (0.3)	1.6 (0.2)	1.25 (0.15)	0.4 (0.05)	4.1 (0.5)	2 (0.3)	0.8 (0.1)
Free potassium cyanide, g/L (oz/gal)	7.5 (1)	7.5 (1)	7.5 (1)	15 (2)	3.75 (0.5)	7.5 (1)	7.5 (1)
Dipotassium phosphate, g/L (oz/gal)	15-30 (2-4)	15-30 (2-4)	15-30 (2-4)	15-30 (2-4)	. . .	15-30 (2-4)	60-90 (8-12)
Sodium hydroxide, g/L (oz/gal)	. . .	. . .	. . .	. . .	15 (2)	. . .	. . .
Sodium carbonate, g/L (oz/gal)	. . .	. . .	. . .	. . .	30 (4)	. . .	. . .
Nickel as potassium nickel cyanide,g/L (oz/gal)	. . .	0.15-1.5 (0.02-0.2)	0.3 (0.04)	1.1 (0.15)	. . .	. . .	0.3 (0.04)
Copper as potassium copper cyanide, g/L (oz/gal)	. . .	. . .	1.5 (0.2)	. . .	. . .	. . .	. . .
Silver as potassium silver cyanide, ppm	. . .	. . .	. . .	. . .	. . .	200	. . .
Temperature, °C (°F)	60-70 (140-158)	60-70 (140-158)	65-70 (150-158)	. . .	65-82 (150-180)	54-65 (130-150)	49-60 (120-140)
Current density, A/dm^2 (A/ft^2)	1-4 (10-40)	1-4 (10-40)	1-3 (10-30)	. . .	2-5.5 (20-55)	1-2 (10-20)	0.5-10 (5-10)

(a) *Hamilton* is a term that has been applied to white, pink, green, and brown golds. It is practically meaningless today, but is still widely used.

If any four numbers are randomly assigned to the concentrations of the four constituents of the gold electroplating solution, plating conditions can be found that will yield a satisfactory deposit. The four numbers chosen would determine

the necessary temperature of operation, the degree of agitation, the current density for producing a good deposit, and the time of plating needed for different thicknesses. The fact that any four numbers could be used explains why hundreds of formulations appear in the literature. Given the proper operation conditions, any of the formulas will work, and at one time or another each cited formula was optimum and economic for a given plant and a given plater. Variations in the price of gold, the size of the item to be plated, the necessary rate of production, the desired deposit thickness, and the desired color resulted in almost every plater designing the "best bath."

Today, most jewelry is flash plated or strike plated from a hot-cyanide alloy (color) bath. The deposit is usually applied over a bright nickel deposit. Occasionally, the gold is flash plated over a palladium deposit over a bright acid-copper deposit, where nickel-free deposits are desired. (The European Common Market is concerned about nickel dermatitis from costume jewelry, snap fasteners, and other items that contact the skin.) Occasionally, the flash gold deposit is applied over a karat gold or rolled-gold plated item. This is done to give an even color to jewelry items made of several different findings. (Some jewelry is flashed from an acid bath directly over stainless steel for hypoallergenic jewelry.)

Typical flash formulations are given in Table 1. Although broad ranges are given for the decorative flash baths, it is absolutely essential that each parameter be closely and tightly controlled within its range if consistency of color is desired. The time of plating is quite short, usually 5 to 30 s. For minimum porosity and subtle color matches, even a 30 s plate may be duplex plated from two different solutions. For flash barrel plating the gold concentration can be as low as 0.8 g/L, the free cyanide is 7.5 g/L, the dipotassium phosphate should be 75 g/L or above, and nickel, as a brightener, should be added at 2 g/L or higher as potassium nickel cyanide.

The deposit is generally 0.05 to 0.1 μm (2 to 4 μin.) and *cannot*be marketed as gold electroplate. If the jewelry is to be marketed as gold electroplate the deposit must be 0.175 μm (7 μin.). If the jewelry is to be marketed as heavy gold electroplate the deposit must be 2.5 μm (100 μin.). Most deposits in this range are plated from an acid gold formulation (Table 2) or from a sulfite gold bath (Table 3).

Table 2 Acid gold color plating baths for heavy deposits

Component or parameter	1N Color[(a)]	2N Color[(a)]	Yellow 24K	Yellow 22K
Gold, g/L (oz/gal)	0.4-0.8 (0.05-0.1)	0.4-0.8 (0.05-0.1)	0.4-0.8 (0.05-0.1)	0.4-0.8 (0.05-0.1)
Conducting salt[(b)], g/L (oz/gal)	120 (16)	120 (16)	120 (16)	120 (16)
Nickel as chelate, g/L (oz/gal)	11 (1.5)	3.7-6 (0.5-0.8)	. . .	200 ppm
Cobalt as chelate, ppm	. . .	. . .	250	1000
pH	4-4.5	4-4.5	4.4-4.8	4.5
Temperature, °C (°F)	50-60 (120-140)	38-50 (100-120)	26-32 (80-90)	32-38 (90-100)
Current density, A/dm^2 (A/ft^2)	1-2 (9-19)	1-2 (9-19)	1-2 (9-19)	1-2 (9-19)
Agitation	Yes	Yes	Yes	Yes

(a) European color standards.

(b) The conducting salt can be a phosphate or an organic acid such as citric or malic.

Table 3 Sulfite gold decorative plating baths

Component or parameter	24K	Flash green	Pink	Heavy plating
Gold as sulfite, g/L (oz/gal)	1.25-2 (0.17-0.27)	1.25-2 (0.17-0.27)	1.25-2 (0.17-0.27)	8-12 (1.0-1.6)
Conducting sulfite salt, g/L (oz/gal)	90 (12)	90 (12)	90 (12)	45-75 (6-10)
Nickel as chelate, g/L (oz/gal)	. . .	1.1 (0.15)	0.5 (0.07)	. . .
Copper as chelate, g/L (oz/gal)	. . .	. . .	0.5 (0.07)	. . .
Cadmium as chelate, ppm	. . .	760	. . .	. . .
Brightener, often arsenic, ppm	20	20	20	20
Current density, A/dm^2 (A/ft^2)	3-5 (28-46)	3-5 (28-46)	3-5 (28-46)	0.1-0.4 (1-4)
Temperature, °C (°F)	50-65 (120-150)	50-65 (120-150)	50-65 (120-150)	50-60 (120-140)
Time, s	10-20	15-30	10-20	(a)

(a) 12.5 min at 0.3 A/dm^2 (3 A/ft^2) gives 100 μin.

As with cyanide gold plating, to achieve consistent good color control it is necessary to regulate each chemical and physical variable within its range given in Table 2. It is also necessary to analyze for metallic impurities and control their concentrations. Drag-in of metallic impurities can have a disastrous effect on color control.

Sulfite gold plating solutions (Table 3) have several unique and advantageous characteristics. First, they contain no cyanide, so the normal safety precautions used when working with or handling cyanide are not necessary when using sulfite gold. In addition, of course, there is no cyanide to destroy in the dragout, rinse stream or old solutions shipped for recovery. The second unique property is exceptional microthrowing power; the bath will actually build brightness during plating. The deposit is essentially featureless with exceptionally fine crystal structure.

Industrial Gold Plating

The printed circuit industry of the late 1950s led to the rediscovery of the stability of potassium gold cyanide on the acid side (below a pH of 7). This was first hinted at in a Ruolz French patent of addition of 1840-45. The stability was described in the English edition of *Cyanogen Compounds* by H.E. Williams in the 1890s. Finally, the Lukens patent of 1938 made use of low-pH gold cyanide plating to ensure good adhesion on stainless steel. Lukens referred to this bath, made up with sodium gold cyanide, sodium cyanide, and hydrochloric acid as *acid gold plating.*

The alkaline gold plating solutions in use in the early 1950s caused lifting of printed circuit resists, especially the wax-based resists introduced in an attempt to speed board preparation. The pH of the gold solutions was progressively lowered

to minimize this effect. In one case, an accident resulted in too low a drop in the pH. It was not noticed at first because the bath continued to plate and there was no lifting of the resist. However, a drop in cathode current efficiency and a decrease in the thickness of the gold deposit alerted the operator. On investigation it was found that the pH had fallen to 4.0.

Separately, it was discovered by Duva that at a pH of 3.5 to 5, it was possible to add small amounts of cobalt, nickel, iron, and other metals to harden the gold deposit and cause it to plate bright. The purity of the deposit was still over 98% gold, but the hardness could be as high as 230 HK. Later, it was also noticed that the crystal structure of the surface could be plated to yield a (111) crystal plane, which greatly increased the wear resistance of the contact surface. Depending on the added metal or metals, the chemical form of the addition, and the pH of the electrolyte, deposits of various hardnesses and other characteristics could be made (Table 4).

Table 4 Acid gold industrial plating baths

Component or parameter	**Bright, hard acid**	**Weak acid**
Regular baths		
Gold as potassium gold cyanide g/L (oz/gal)	4-16 (0.5-2)	4-8 (0.5-1)
Potassium citrate, citric acid, g/L (oz/gal)	180 (24)	. . .
Mono- and dipotassium phosphate, g/L (oz/gal)	. . .	180 (24)
Brightener	[a]	. . .
pH	3.5-5.0	5.5-7.0
Temperature, °C (°F)	20-50 (68-122)	65-74 (150-165)
Current density, A/dm^2 (A/ft^2)	1-10 (9-90)	0.1-0.5 (1-5)
Current efficiency, %	30-40	85-100
High-speed baths		
Gold as potassium gold cyanide, g/L (oz/gal)	4-24 (0.5-3)	8-32 (1-4)
Citrates, g/L (oz/gal)	90 (12)	. . .
Phosphates/citrates, g/L (oz/gal)	. . .	90 (12)
Brighteners	[a]	[a]
Temperature, °C (°F)	49-60 (120-140)	71-82 (160-180)

Current density[b], A/dm^2 (A/ft^2)	10-200 (93-1860)	5-50 (46-460)
Current efficiency, %	40-50	50-60

(a) As required.

(b) Values given are typical; they depend on agitation and the individual machine.

At the same time that the above developments took place, the semiconductor industry developed a need for high-purity golds at increased thicknesses. This led to a series of formulations by Ehrheart that plated gold from mild acid solutions. Raising the pH resulted in better covering power and higher current efficiency. At first the hardness and brightness of the acid golds was lost, but it was found that by modifying the neutral electrolytes, these properties could be partially restored (Table 4). So many different solutions were developed that a standard was needed. The most recent MIL-G-45204C (1984) and ASTM B 488-86, the military specification defines the purity, hardness, and thickness of the deposit. Purity is described as:

- Type I: 99.7% gold min
- Type II: 99.0% gold min
- Type III: 99.9% gold min

Hardness is specified as:

- A, 90 HK max
- B, 91-129 HK max
- C, 130-200 HK max
- D, 201 + HK

Thickness is specified as:

- Class 00, 0.5 μm (20 μin.)
- Class 0, 0.75 μm (30 μin.)
- Class 1, 1.25 μm (50 μin.)
- Class 2, 2.5 μm (100 μin.)
- Class 3, 5.0 μm (200 μin.)
- Class 4, 7.5 μm (300 μin.)
- Class 5, 12.5 μm (500 μin.)
- Class 6, 37.5 μm (1500 μin.)

Type I purity cannot have hardness D, and Type II purity cannot have hardness A. Type III purity can only be hardness A.

Strike Plating. Gold is a noble metal and deposits at a very low applied potential. These characteristics can cause nonadherence of the gold deposit if the substrate is either passive or not perfectly clean. Poor adhesion can be prevented by using a gold strike bath. A *strike* is generally a solution with very low metal concentration that is operated at high voltage and high current density for a very short period of time. For rack plating, the strike plating time is less than 1 min at a current density of 1 to 3 A/dm^2 (9 to 28 A/ft^2). A gold strike generally is not needed when plating from an acid gold solution unless the gold concentration is greater than 8 g/L or the substrate is passive.

Noncyanide Gold Plating Solutions. Sulfite gold industrial baths are used for their unique physical properties in addition to the desirable property of being noncyanide. As discussed above, sulfite golds have exceptional microthrowing power, which makes them the only gold formulations that build brightness. Furthermore, they have the best infrared reflectivity of any gold plating solution. The following table shows the composition and operating parameters of sulfite gold industrial baths:

Component or parameter	Value
Gold as sodium gold sulfite, g/L (oz/gal)	4-16 (0.5-2)
Sodium sulfite and sulfate, g/L (oz/gal)	90 (12)
pH	8.5-10.0
Temperature, °C (°F)	50-60 (122-140)
Brightener	As required
Current density, A/dm^2 (A/ft^2)	0.1-0.4 (1-4)
Current efficiency, %	100

Electroplating Calculations. Factors to use with gold electroplating calculations are:

- The price of gold, as given in newspapers and on the radio, is expressed in dollars per troy ounce (1 troy ounce = 31.1 g).
- A deposit of gold that is 1 μm thick = 19.58 g/m^2 (1.82 g/ft^2).
- At 100% cathode current efficiency, 7.35 g of gold can be electrodeposited in 1 ampere-hour, or 0.123 g in 1 ampere-minute.
- At 100% cathode current efficiency, 160.5 ampere-minutes are required for a gold deposit that is 1 μm thick and covers 1 m^2.

Time, temperature, and amperage can be accurately measured and controlled in gold electroplating. The largest errors that can affect gold calculations are the inaccuracies in the current density and the current efficiency. Current density is determined by calculating the area measurement, which is not always an easy task. Outside surface areas may be correctly calculated, but inside surfaces and holes, such as solder cups, must be calculated and then their effective plating area must be estimated.

Current efficiency is determined by current density, metal concentration, electrolyte concentration, and impurity content. The impurities that change the current efficiency are the metallic impurities, the organic impurities from masking materials and resists, and airborne dust. Current efficiency can be measured with a weighed coupon plated in the laboratory using a sample of the solution.

In practice, a good way to measure the efficiency of a solution is to estimate the required amperage and time based on theory, increase the amount by, say, 10%, and then plate a load under these conditions. The thickness of the gold on the

plated work can be measured by microsection, x-ray diffraction, beta-ray backscatter, or other means. The thickness actually measured should be used to correct the estimated efficiency and to modify the plating conditions. It is best to measure the thickness periodically, because the cathode current efficiency of a gold bath will change not only with the variability of all the chemical constituents but also with the age of the bath. Periodic monitoring of the thickness ensures consistent quality control.

Dragout

Minimizing the dragout of gold solutions is of both economic and environmental concern. It is an economic advantage to decrease the cost of gold loss, and it is an environmental advantage to reduce the amount of processing needed to purify the waste stream before discharge.

Many factors affect dragout:

- The thickness of the gold plated
- The shape of the part to be plated
- The number of holes or other solution-trapping structures
- The speed of removing the plated part from the plating tank
- Provisions for air jets or wiper blades to return the drippings to the plating tank

In some cases the dragout is from 30 to 50% of the gold actually deposited. Typically, however, it is 10 to 20%. It is far better to limit the dragout than to expend effort in processing the cyanide and recovering the gold from the dragout.

Minimizing the dragout can be done with simple procedures such as training the operator to remove the rack slowly and to "nudge" or shake the withdrawn rack over the gold tank so droplets return to the tank. Barrels should be allowed to drip over the gold tank and should be rotated one-half turn or more before being dipped into the dragout recovery tank. Continuous plating machines should have an air knife or a synthetic sponge to remove excess gold solution.

All gold-plated work should be rinsed in a stagnant gold recovery tank that is treated frequently to recover the dragged-out gold. The gold can be recovered by passing the dragout solution through an appropriate ion exchange resin, or it may be recovered by plating out, in which the dragout is circulated and continuously electroplated on a carbon or wire-mesh cathode. The gold-plated cathode should periodically be sent to a refiner.

Platinum-Group Metals Plating

Ch.J. Raub, Forschungsinstitut für Edelmetalle und Metallchemie

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Introduction

THE SIX PLATINUM-GROUP METALS (PGMs), listed in order of their atomic numbers, are ruthenium, rhodium, palladium, osmium, iridium, and platinum. The PGMs are among the scarcest of metallic elements, and thus their cost is high. Their most exceptional trait in the metallic form is their excellent corrosion resistance. The electroplating of PGMs from aqueous electrolytes for engineering applications is limited principally to palladium and, to a much lesser extent, to platinum, rhodium, and thin layers of ruthenium. There are practically no electrolytes on the market for the deposition of osmium or iridium. While solution formulations have been published for these last two metals, they have not proven themselves in practical use for any significant applications, and thus will be discussed only briefly in this article.

Detailed information about the general availability, properties, and applications of PGMs is provided in *Properties and Selection: Nonferrous Alloys and Special-Purpose Materials,* Volume 2 of *ASM Handbook.* Good overview coverage of plating of these metals is available in Ref 1, 2, and 3.

Acknowledgement

The section on anode materials was prepared by Ronald J. Morrissey, Technic, Inc.

References

1. F.H. Reid, Platinum Metal Plating-A Process and Application Survey, *Trans. Inst. Met. Finish.,* Vol 48, 1970, p 112-123
2. F.H. Reid, Electrodeposition of Platinum-Group Metals, *Met. Rev.,* Vol 8, 1963, p 167-211
3. Ch.J. Raub, Electrodeposition of Platinum-Group Metals, *GMELIN Handbook of Inorganic Chemistry,* Platinum Supplement, Vol A1, 1982

Ruthenium Plating

Ruthenium in the solid form is hard and brittle; furthermore, it oxidizes rather easily. These factors limit its use, even as its low price relative to the other PGMs provides impetus for its application. Despite extensive research work on electroplating of ruthenium, it has obtained a small market share in only two areas: for decorative applications such as eyeglass frames and for layers on electrical contacts used in sealed atmospheres.

All ruthenium plating electrolytes are based on solutions of simple ruthenium salts or ruthenium nitrosyl derivatives. Typical examples are ruthenium sulfate, ruthenium phosphate, ruthenium sulfamate, or ruthenium chloride (Ref 4). These electrolytes are all essentially based on those described in Ref 5 and 6. They work in a wide range of current densities from 1 to 10 A/dm^2 (9 to 93 A/ft^2) at temperatures between 50 and 90 °C (120 and 195 °F), and at current efficiencies of 50 to 90%. Compositions and operating conditions for two ruthenium plating solutions are given in Table 1.

Table 1 Ruthenium electroplating solutions

Constituent or condition	Amount or value
General-purpose solution	
Ruthenium (as sulfamate or nitrosyl sulfamate), g/L (oz/gal)	5.3 (0.7)
Sulfamic acid, g/L (oz/gal)	8 (1.1)
Anodes	Platinum
Temperature, °C (°F)	
Sulfamate solution	27-60 (80-140)
Nitrosyl sulfamate solution	21-88 (70-190)
Current density, A/dm^2 (A/ft^2)	1-3 (10-30)
Current efficiency, %	20
Time to plate thickness of 0.003 mm (0.0001 in.)	30-40 min at 2 A/dm^2 (20 A/ft^2)
Flash-plating solution for decorative deposits	

Ruthenium (as nitroso salt), g/L (oz/gal)	2.0 (0.3)
Sulfuric acid, g/L (oz/gal)	20 (2.7)
Current density, A/dm^2 (A/ft^2)	2-3 (20-30)
Temperature, °C (°F)	50-80 (120-180)

Note: Both solutions require a flash-plated undercoat of gold or palladium. Source: Ref 7

The preparation of the electrolyte constituents is rather critical. Deposits are hard and highly stressed, making it difficult to obtain crack-free layers at higher thicknesses. For electrical contact applications, a layer of gold flash plated on top of the ruthenium is recommended to ensure excellent wear and good contact resistant on a long-term basis (Ref 8, and 9). Smooth and bright deposits can be obtained from cyanide melts (Ref 10, 11). Microhardness of such layers is between 600 and 900 HK.

References cited in this section

4. F.H. Reid and J.C. Blake, *Trans. Inst. Met. Finish.,* Vol 38, 1961, p 45-51
5. H.C. Angus, *Trans. Inst. Met. Finish.,* Vol 43, 1965, p 135-142
6. T.A. Palumbo, *Plat. Surf. Finish.,* Vol 66, 1979, p 42-44
7. A.M. Weisberg, Ruthenium Plating, *Met. Finish.,* Vol 90 (No. 1A), 1992, p 257
8. R.G. Baker and T.A. Palumbo, *Plat. Surf. Finish.,* Vol 69, 1982, p 66-68
9. A.F. Bogenschütz, J.L. Jostan, and W. Mussinger, *Galvanotechnik,* Vol 67, 1976, p 98-105
10. R.N. Rhoda, *Plating,* Vol 49, 1962, p 69-71
11. G.S. Reddy and P. Taimsalu, *Trans. Inst. Met. Finish.,* Vol 47, 1969, p 187-193

Rhodium Plating

Rhodium in its solid form is hard (microhardness about 800 to 1000 HV) and tough. It is nearly as tarnish resistant as platinum and palladium. However, because of its rare occurrence in PGM ores and market speculation, it is much more expensive, limiting its engineering use. Like silver, it has one of the highest reflectivities of all metals, making it ideal for use as a counterpoint to cut diamonds in jewelry and as a nontarnishing reflective coating for mirrors. Its excellent wear resistance and its superb contact resistance prompt its frequent use for rotating electrical contacts.

The electrolytes for deposition of rhodium from aqueous solutions are similar to those for ruthenium insofar as they are either based on simple rhodium salts or on special rhodium complexes (Ref 12, and 13). Because, in most cases, only layer thicknesses of 1 μm or less are specified, most commercial electrolytes have been developed to produce layers in this thickness range. The deposits have a high concentration of nonmetallic impurities (e.g., up to 1000 ppm H and/or O) (Ref 14), which causes high hardnesses and internal stresses, which easily lead to cracks. This thin and highly porous layer of rhodium, coupled with the high electrochemical nobility of the metal, limits its use as a corrosion protection layer. Therefore, an electroplated base coating must be used. Silver and silver-tin alloys (with varying concentrations of tin) have exhibited excellent field service behavior and are now applied for decorative as well as engineering purposes. Nickel is not recommended for use as a base coating. For decorative use the color (better reflectivity) is most important. It changes from electrolyte to electrolyte, many of which are commercial solutions. Deposition conditions must be carefully controlled for best results.

The complex rhodium salts of solutions cited in the literature are based on sulfate, phosphate, sulfate-phosphate, sulfate-sulfite, sulfamate, chloride, nitrate, fluoroborate, or perchlorate systems. Properties of the layers are strongly influenced by the chemistry of their salts as well as by impurities present (Ref 15). Three solutions for decorative rhodium plating are given in Table 2.

Table 2 Solutions for decorative rhodium plating

Solution type	Rhodium		Phosphoric acid (concentrate) fluid		Sulfuric acid (concentrate) fluid		Current density		Voltage, V	Temperature		Anodes
	g/L	oz/gal	mL/L	oz/gal	mL/L	oz/gal	A/dm^2	A/ft^2		°C	°F	
Phosphate	2[(a)]	0.3[(a)]	40-80	5-10	. . .	. . .	2-16	20-160	4-8	40-50	105-120	Platinum or platinum-coated[(b)]
Phosphate-sulfate	2[(c)]	0.3[(c)]	. . .	. . .	40-80	5-10	2-11	20-110	3-6	40-50	105-120	Platinum or platinum-coated[(b)]
Sulfate	1.3-2[(c)]	0.17-0.3[(c)]	. . .	. . .	40-80	5-10	2-11	20-110	3-6	40-50	105-120	Platinum or platinum-

(a) Rhodium as metal, from phosphate complex syrup.

(b) Platinum-coated products are also known as platinized titanium.

(c) Rhodium, as metal, from sulfate complex syrup

A typical, widely used production bath is based on rhodium sulfate (Ref 15). With use of proper additives, especially sulfur-containing compounds, crack-free layers may be obtained in thicknesses of about 10 μm and microhardnesses of 800 to 1000 HV (Ref 15). The deposition temperature of such baths is about 50 °C (120 °F), the current density is between 1 and 10 A/dm^2 (9 to 93 A/ft^2), and current efficiency is approximately 80%. Insoluble anodes are normally used.

For electronic applications where undercoatings are undesirable, special low-stress compositions have been developed. One electrolyte contains selenic acid and another contains magnesium sulfamate (Table 3). Deposit thickness obtained from these solutions range from 25 to 200 μm (1 to 8 mils), respectively. The low-stress sulfamate solution is used for barrel plating of rhodium on small electronic parts. Operating conditions for various plating thicknesses using this solution are given in Table 4.

Table 3 Solutions for electroplating low-stress rhodium deposits for engineering applications

Solution	Selenic acid process	Magnesium sulfamate process
Rhodium (sulfate complex)	10 g/L (1.3 oz/gal)	2-10 g/L (0.3-1.3 oz/gal)
Sulfuric acid (concentrated)	15-200 mL/L (2-26 fluid oz/gal)	5-50 mL/L (0.7-7 fluid oz/gal)
Selenic acid	0.1-1.0 g/L (0.01-0.1 oz/gal)	. . .

Magnesium sulfamate	. . .	10-100 g/L (1.3-13 oz/gal)
Magnesium sulfate	. . .	0-50 g/L (0-7 oz/gal)
Current density	1-2 A/dm^2 (10-20 A/ft^2)	0.4-2 A/dm^2 (4-22 A/ft^2)
Temperature	50-75 °C (120-165 °F)	20-50 °C (68-120 °F)

Table 4 Plating parameters for producing low-stress deposits from a rhodium sulfamate solution

Required thickness		**Thickness of plate**		**Apparent current density**[(a)]		**Calculated current density**[(a)]		**Plating time**
µm	**mil**	**µm**	**mil**	**A/dm^2**	**A/ft^2**	**A/dm^2**	**A/ft^2**	
1	0.04	0.5-1.5	0.02-0.06	0.55	5.5	1.6-2.2	16-22	35 min
2.5	0.1	1.75-3.25	0.07-0.127	0.55	5.5	1.6-2.2	16-22	$1\frac{1}{4}$ h

(a) Calculated current density is an estimate of the amount of current being used by those parts that are making electrical contact and are not being shielded by other parts in the rotating load in the barrel. Calculated current density is considered to be about three times the apparent current density, that is, the actual current used for the load divided by the surface of that load.

Rhodium also can be electroplated from fused-salt electrolytes. This deposition process is interesting because the requirements are that the coatings must be highly ductile for high-temperature use (e.g., coatings on molybdenum for combustion engine parts or glass-making equipment). For fused-salt electrolysis, a variety of mixtures have been tested, ranging from cyanide to chloride melts (Ref 16).

Thickness class designations for engineering applications of electroplated rhodium are given in Table 5.

Table 5 Thickness classifications for rhodium plating for engineering use

Specification	**Class**	**Minimum thickness**	
		µm	**mil**
ASTM B 634-78	0.2	0.2	0.008
	0.5	0.5	0.02
	1	1	0.04

	2	2	0.08
	4	4	0.16
	5	6.25	0.25
MIL-R-46085A	1	0.05	0.002
	2	0.3	0.01
	3	0.5	0.02
	4	2.5	0.10
	5	6.4	0.25

Source: Ref 17

References cited in this section

12. G.R. Smith, C.B. Kenahan, R.L. Andrews, and D. Schlain, *Plating,* Vol 56, 1969, p 804-808
13. W.B. Harding, *Plating,* Vol 64, 1977, p 48-56
14. Ch. J. Raub, unpublished research
15. F. Simon, Degussa-Demetron, Information Sheet, and article in *GMELIN Handbook of Inorganic Chemistry,* Platinum Supplement, Vol Al, 1982
16. R.N. Rhoda, *Plating,* Vol 49, 1962, p 69-71
17. L.J. Durney, Ed., *Electroplating Engineering Handbook,* 4th ed., Van Nostrand Reinhold, 1984, p 276

Palladium Plating

Palladium has been electroplated since before the turn of the 20th century. However, it stirred little interest until the 1960s and 1970s, when the price of gold peaked, prompting a search for alternatives. Palladium plating is currently used for jewelry and electrical contacts; however, the decorative applications of palladium are limited due to the dark color of the metal. Three typical palladium plating solutions are listed in Table 6.

Table 6 Palladium electroplating solutions

Constituent or condition	Amount or value
Solution A	
Palladium (as tetraamino-palladous nitrate, g/L (oz/gal)	10-25 (1-3)[(a)]
pH	8-10

Temperature, °C (°F)	40-60 (100-140)
Current density, A/dm^2 (A/ft^2)	0.5-2.2 (5-20)[(b)]
Cathode efficiency, %	90-95
Anodes	Insoluble; palladium, platinum, or platinized titanium
Tank lining	Glass or plastic
Solution B	
Palladium (as diamino-palladous nitrite), g/L (oz/gal)	10 (1)
Ammonium sulfamate, g/L (oz/gal)	110 (15)
Ammonium hydroxide	To pH
pH	7.5-8.5
Temperature	Room
Current density, A/dm^2 (A/ft^2)	0.5-2.2 (5-20)[(b)]
Cathode efficiency, %	70
Anodes	Insoluble; platinum or platinized titanium
Tank lining	Glass or plastic
Solution C	
Palladium (as palladous chloride), g/L (oz/gal)	50 (7)
Ammonium chloride, g/L (oz/gal)	30 (4)
Hydrochloric acid	To pH
pH	0.1-0.5
Temperature, °C (°F)	40-50 (100-120)

Current density, A/dm^2 (A/ft^2)	0.5-1.1 (5-10)
Anodes	Soluble palladium
Tank lining	Rubber, plastic, or glass

Source: Ref 18

(a) Normally 10-15 g/L (1-2 oz/gal).

(b) Normally 0.5 A/dm^2 (5 A/ft^2).

Palladium alloys such as palladium-nickel, palladium-iron, and, to a lesser extent, palladium-cobalt are also electroplated. The plating solutions for palladium alloys are generally based on the same or similar complexes as the ones for palladium alone. The main application at present for these alloy electrodeposits is for electrical connectors (Ref 19, 20, 21, 22). A solution composition for depositing palladium-nickel is given in Table 7.

Table 7 Palladium-nickel electroplating solutions

Constituent or condition	**Amount or value**
Palladium as $Pd(NH_3)_2(NO_2)_2$, g/L (oz/gal)	6 (0.8)[a]
Nickel sulfamate concentrate, mL/L (fluid oz/gal)	20 (2.6)[b]
Ammonium sulfamate, g/L (oz/gal)	90 (12)
Ammonium hydroxide	To pH
pH	8-9
Temperature, °C (°F)	20-40 (70-100)
Current density, A/dm^2 (A/ft^2)	0.5-1.0 (5-9)
Anodes	Platinized

Note: Formulation is for plating an alloy of about 75 wt% Pd. A strike of gold or silver is recommended for most base metals prior to plating.

Source: Ref 23

(a) Palladium metal, 3 g/L (0.4 oz/gal).

(b) Nickel metal, 3 g/L (0.4 oz/gal).

The properties of palladium electrodeposits are generally similar to those of gold, but it has higher receptivity and hardness. Soldering, crimping, and wire wrapping present no serious problems. The sliding and wear behavior of palladium are similar to those of hard gold. Palladium coatings may be slightly less porous than gold coatings, and they resist tarnish and corrosion. On the other hand, the chemical properties of palladium are quite different from those of gold, which may explain why an effective agent for stripping palladium and palladium alloy electrodeposits has not yet been developed.

In service, palladium and palladium alloys tend to exhibit what is called a *brown powder effect,* in which a "brown polymer" catalytically forms on the contact surface upon exposure to organic compounds in the environment. This effect can be minimized by application of flash plating a layer of fine gold on top of the palladium surface. The biggest challenge when electrodepositing palladium is avoiding hydrogen embrittlement. Palladium in electrodeposition may dissolve fairly large amounts of hydrogen, and this expands the palladium lattice, especially if the so-called β-Pd/H phase is formed. However, this hydrogen diffuses out of the palladium during storage at room temperature, and the lattice contracts again. This expansion/contraction generates stresses in the deposit that cause cracks and pores. Furthermore, palladium promotes diffusion of atomic hydrogen, which may cause secondary reactions (e.g., hydrogen embrittlement of underlying steel bases or blister) if the base material does not take up the diffused hydrogen.

Electrolytes have been developed that effectively solve the problem of hydrogen embrittlement. The most economical are based on palladium chloride. In these solutions, the palladium ion is complexed by ammonia or amines. Other systems using other complexes have also been developed (Ref 19, 20, 21, 22, 24). Currently, no electrolyte for the deposition of palladium-silver or palladium-copper alloys is available. The influence of organic and inorganic impurities on palladium-nickel deposits has been studied extensively (Ref 19).

Thickness class designations for engineering applications of electroplated palladium are given in Table 8.

Table 8 Thickness classifications for palladium plating for engineering use

Specification	Class	Minimum thickness	
		µm	mil
ASTM B 679-80	5.0	5.0	0.20
	2.5	2.5	0.10
	1.2	1.2	0.05
	0.6	0.6	0.02
	0.3	0.3	0.01
	F	0.025	0.0010

MIL-P-45209	. . .	1.3[a]	0.05[a]

Source: Ref 17

(a) Unless otherwise specified.

References cited in this section

17. L.J. Durney, Ed., *Electroplating Engineering Handbook,* 4th ed., Van Nostrand Reinhold, 1984, p 276
18. N.V. Parthasaradhy, *Practical Electroplating Handbook,* Prentice Hall, 1989, p 202-205
19. Ch.J. Raub, *Platinum Met. Rev.,* Vol 28, 1992, p 158-166
20. F.H. Reid, *Plating,* Vol 52, 1965, p 531-539
21. M. Antler, *Platinum Met. Rev.,* Vol 26, 1982, p 106-117
22. H. Grossmann, M. Huck, and G. Schaudt, *Galvanotechnik,* Vol 71, 1980, p 484-488
23. R.J. Morrissey, Palladium and Palladium-Nickel Plating, *Metal Finishing,* Vol 90 (No. 1A), 1992, p 247-248
24. German Society for Electroplating and Surface Technology, Precious Metals Working Group, Electroplating of Palladium and Palladium Alloys, *Galvanotechnik,* Vol 84, 1993, p 2247-2938

Osmium Plating

Currently, no practical applications exist for electrodeposited osmium, primarily because the metal oxidizes readily at room temperature, forming poisonous and volatile osmium tetroxide. The metal itself is hard and brittle and has few industrial uses. For a review of the existing literature on electrodeposition of osmium, see Ref 25, 26, and 27.

References cited in this section

25. J.M. Nutley, *Trans. Inst. Met. Finish.,* Vol 50, 1972, p 58-62
26. L. Greenspan, *Plating,* Vol 59, 1972, p 137-139
27. J.W. Crosby, *Trans. Inst. Met. Finish.,* Vol 54, 1976, p 75-79

Iridium Electroplating

The electroplating of iridium has up to now not found any widespread application. Essentially, no electrolytes are available that can deposit iridium from aqueous electrolytes at reasonable thicknesses and with satisfactory properties.

Known electrolytes are mostly based on the chloro-iridic acid. The bath is highly acidic and works at a temperature of about 80 °C (176 °F) and at a current density of 0.15 A/dm^2 (1.4 A/ft^2). The microhardness of deposits is 900 DPN, and their total reflectivity is about 61% that of silver. At thicknesses of more than 1 μm, the layers are cracked. The current efficiency of these processes approaches 50%. At low current densities, the plating rate is close to 1 μm/h (Ref 28, 29, 30, 31).

Iridium has been deposited from fused salts. The solution was prepared by passing alternating current between two electrodes suspended in the melt, which was a eutectic of NaCN or KCN/NaCN, with melting points of 564 and 500 °C (1050 and 930 °F), respectively (Ref 32). However, these electrolytes have not proven to be usable in commercial practice.

References cited in this section

28. F.H. Reid, *Met. Rev.,* Vol 8, 1963, p 167, 211

29. C.J. Tyrell, *Trans. Inst. Met. Finish.,* Vol 43, 1965, p 161-166

30. F.H. Reid, *Trans. Inst. Met. Finish.,* Vol 48, 1970, p 115-123

31. G.A. Conn, *Plating,* Vol 52, 1965, p 1256-1261

32. R.N. Rhoda, *Plating,* Vol 49, 1962, p 69-71

Platinum Plating

The electrodeposition of platinum from aqueous electrolytes is of limited engineering value. The metal is very expensive, and the currently available plating solutions are not capable of consistently producing ductile and pore-free deposits at thicknesses above a few microns. Today, most of the deposits produced are less than 1 μm thick and are used primarily for decorative applications.

The main challenge when electroplating platinum from aqueous electrolytes is to obtain a clean, ductile platinum coating with a minimum of nonmetallic impurities, which act as hardeners and embrittle the platinum. This is rather difficult because platinum compounds tend to hydrolyze even at rather low pH levels. Therefore, close control of plating parameters is very important.

The three most common electrolytes used today are platinum chloride, diamino-dinitroplatinum (platinum "P" salt), and alkali hydroxy platinate. The current efficiency of the highly acidic baths is close to 90%, but the electrolytes are difficult to handle. Two platinum plating solutions are listed in Table 9.

Table 9 Platinum electroplating solutions

Constituent or condition	**Amount or value**
Solution A	
Platinum (as sulfatodinitrito-platinous acid), g/L (oz/gal)	5 (0.7)
Sulfuric acid	To pH
pH	1.5-2.0
Temperature, °C (°F)	Room to 40 (100)
Current density, A/dm^2 (A/ft^2)	5-20 (5-20)
Anode	Platinum or platinized titanium
Cathode efficiency	10-20%
Solution B	
Platinum (as diaminodinitrito salt), g/L (oz/gal)	10 (1.3)
Ammonium nitrate or phosphate, g/L (oz/gal)	100 (13.4)

Sodium nitrite, g/L (oz/gal)	10 (1.3)
Ammonium hydroxide (28% solution), mL/L (fluid oz/gal)	50 (6.4)
Temperature, °C (°F)	90-100 (190-210)
Current density, A/dm^2 (A/ft^2)	3-10 (30-100)[(a)]
Anode	Platinum (insoluble)
Tank lining	Glass or plastic
Cathode efficiency	Low[(b)]

Source: Ref 18

(a) Normally 4 A/dm^2 (40 A/ft^2).

(b) 10% at 6 A/dm^2 (60 A/ft^2).

A commercial process gaining more and more importance for engineering applications in the chemical, electronics, and glass industries is the electrodeposition of platinum from salt melts, because the process forms highly dense and ductile platinum layers. The platinum compound can be formed by electrolytic dissolution with alternating current in a NaCN/KCN fused-salt mixture, melting at 500 °C (930 °F). For deposition, a cyanide/cyanate mixture operating at about 450 °C (840 °F) is recommended.

For decorative platinum deposits, the use of a flash-plated base coat is recommended. Suitable layers include palladium-iron, silver, and copper-tin systems. Detailed information on platinum electroplating is available in Ref 33, 34, 35, 36, 37, and 38.

References cited in this section

18. N.V. Parthasaradhy, *Practical Electroplating Handbook,* Prentice Hall, 1989, p 202-205

33. F.H. Reid, *Trans. Inst. Met. Finish.,* Vol 48, 1970, p 115-123

34. F.H. Reid, *Met. Rev.,* Vol 8, 1963, p 167-211

35. K. Wundt, *Oberfl. Surf.,* Vol 25, 1984, p 207-212

36. R.N. Rhoda, *Plating,* Vol 49, 1962, p 69-71

37. H.H. Beyer and F. Simon, *Metall.,* Vol 34, 1980, p 1016-1018

38. C. Hood, *Plat. Met. Rev.,* Vol 20, 1976, p 48-52

Anodes for PGM Plating

In most aqueous or oxygen-bearing environments, the platinum-group metals are coated with a very thin layer of the appropriate metal oxide. This film is referred to as a *passive layer,* and it serves to prevent the underlying metal from corroding. Thus, anodes fabricated from PGMs are insoluble (inert) in most environments. The anode processes are mainly

$$2H_2O \rightarrow O_2 + 4H^+ + 4E^-$$

in acid solutions, or

$$4OH^- \rightarrow O_2 + 2H_2O + 4E^-$$

in alkaline solutions.

There are exceptions to this rule. The platinum metals are soluble in hot halogen acids (HF, HCl, HBr) and will dissolve anodically under these conditions. Similarly, oxidizing ligands such as nitrate and nitrite tend to dissolve PGMs, particularly in the presence of halogen acids. Plating solutions based on such systems are highly corrosive, and it is usually necessary to protect the work to be plated by prestriking with gold. Platinum-group metal anodes are also soluble in molten cyanide systems, from which PGMs can be deposited to very heavy thicknesses. Molten cyanide systems operate under an argon atmosphere at temperatures of about 600 °C (1100 °F), and for these reasons are not widely used. They are useful for heavy deposition because the high temperature provides some degree of stress-relief annealing during the plating operation.

Because anodes fabricated from PGMs are inert in most aqueous environments, they are useful not only for the electrodeposition of PGMs but also for plating of other metals, such as gold. Platinum is the metal of choice for such applications and is available in the form of wire mesh, or plated onto anodizable metals such as titanium, or clad onto passive-prone metals such as niobium or tantalum. In the plated and clad configurations, the required mechanical strength is provided by the substrate, and the actual amount of platinum used is quite small.

Reference 39 is a good general resource of information about anode selection and general plating practices.

Reference cited in this section

39. F.A. Lowenheim, Ed., *Modern Electroplating,* 3rd ed., Wiley, 1974

Copper Alloy Plating

Henry Strow, Oxyphen Products

Introduction

COPPER ALLOYS are widely used as electroplated coatings, and they can be used with practically any substrate material that is suitable for electroplating. While alloys such as copper-gold and copper-gold-nickel are commonly electroplated, these are usually considered as part of gold plating technology. The most frequently electroplated copper alloys are brass (principally alloys of copper and zinc) and bronze (principally alloys of copper and tin). Brass and bronze are both available in a wide variety of useful compositions that range in content practically from 100% Cu to 100% Zn or Sn.

The history of brass and bronze plating dates back at least as far as the 1840s. Early work that was commercially exploited occurred in Russia, France, and England. All of the early copper alloy plating solutions were cyanide based and used batteries for power. Progress was slow, with much of the work being of an academic nature. A major advance was made in 1938 when patents on a high-speed copper plating process by DuPont were extended to a high-speed process for plating of both yellow and white brass (alloys containing about 70 to 80% Cu). The solution was cyanide based with a relatively high hydroxide content.

Brass Plating

Decorative Applications. The largest use of brass plating is for decorative applications. Copper-zinc alloys that contain more than 60% Cu have distinct colors, depending on the composition. The 60Cu-40Zn alloys are pale yellow, sometimes with a brown cast. Alloys with compositions from 70Cu-30Zn to 80Cu-20Zn are yellow, with only slight color

variations over this range. The 85Cu-15Zn alloys are darker and resemble gold. The 90Cu-10Zn alloys are darker still, with a reddish, bronze-like cast. With proper control of plating parameters, the variation of the alloy composition of brass plate can be kept within 1%, and consistency in color can be achieved. Plated alloys have the same color as wrought alloys of the same composition and surface treatment. Brass darkens with age due to the formation of copper oxide on the surface, so the appearance of old samples will not match that of newly plated items.

Yellow brass plate (normally a 75Cu-25Zn alloy) is frequently flash plated over bright nickel plating to maintain its bright appearance; the surface is subsequently lacquered to preserve the finish. (*Flash plating* is the electrodeposition of a thin layer of material; plating times are usually under 1 min.) This type of flash plating is accomplished in both rack plating and barrel plating operations. Heavy brass plate can be buffed to a bright finish or oxidized to a dark finish; dark finishes can be *relieved* (selectively buffed) for an antique appearance. Brass plated items can also be burnished in tumbling barrels to give a uniform bright finish. Cosmetic cases are frequently plated with an 85Cu-15Zn alloy to impart a golden appearance; the alloy can be applied as a flash plate or as a heavier plate that is subsequently burnished. Builders hardware plated with a 90Cu-10Zn alloy called *architectural bronze* uses these same techniques.

Engineering applications for brass plating are also important. Brass plate on sheet steel and wire performs a lubricating function in deep drawing and wire drawing operations. Brass plating is used to promote adhesion of rubber bonded to steel. For example, the wire in steel-belted radial tires is plated with a brass alloy containing between 63 and 70% Cu (to secure the best adhesion, it is important that composition limits of the alloy be kept within 1%). After plating, the wire is drawn from 1.2 mm (0.049 in.) to approximately 0.15 mm (0.006 in.) without a break in the coating. The wire bonds to rubber so that blistering of the tires does not occur. Brass is also plated on sheet steel from which parts are stamped.

Equipment. Brass plating can be done in all the standard plating equipment, including barrel, rack, and continuous wire and strip machines. Steel is a suitable material for tanks, coils, and filters. However, rubber- or plastic-lined tanks with stainless or titanium coils are preferred because the iron in the steel can form ferrocyanides that precipitate as zinc ferrocyanide, resulting in the formation of a gray-colored sludge.

Surface Preparation. Brass can be plated on most metallic surfaces (e.g., zinc castings, steel, nickel, and aluminum) after only standard preplating procedures. Direct brass plating of zinc castings requires the use of relatively heavy coatings to prevent diffusion of the brass into the zinc and a resulting loss of color; an intermediate layer of plate is often used for this purpose. One method of brass plating uses this diffusion interaction to produce brass by plating separate layers of copper and zinc of appropriate thickness and then heating the plate to create the alloy by diffusion.

Plate thickness can be varied as required from very thin flash deposits for decorative purposes to deposits over 0.02 mm (0.001 in.) thick. The heavier plates are needed to withstand buffing, bright dipping antiquing, and other post-treatments that require heavier plate to maintain coverage.

Solution Composition and Operating Conditions. The majority of currently used brass plating solution are based on cyanide complexes. No other material brings the deposition potential of copper and zinc so close together. Solutions using a pyrophosphate base have been used commercially with limited success. Brass solutions using polyhydroxy aliphatic chemicals have also been used commercially with limited success. Formulas for low-pH brass plating solutions are given in Table 1.

Table 1 Low-pH brass plating conditions

Constituent or condition	Standard brass solution	High-copper brass solution
Makeup		
Sodium cyanide, g/L (oz/gal)	50 (6.7)	75 (10.0)
Copper cyanide, g/L (oz/gal)	35 (4.7)	45 (6.0)

Zinc cyanide, g/L (oz/gal)	10 (1.3)	7.5 (1.0)
Sodium carbonate, g/L (oz/gal)	10 (1.3)	10 (1.3)
Sodium bicarbonate, g/L (oz/gal)	7.5 (1.0)	7.5 (1.0)
Ammonia (aqua), %	0.5	0.1
Analysis		
"Total" sodium cyanide, g/L (oz/gal)	22 (2.9)	33 (4.4)
Copper (as metal), g/L (oz/gal)	23 (3.1)	22 (2.9)
Zinc (as metal), g/L (oz/gal)	6 (0.8)	4.2 (0.6)
pH	9.8-10.2	9.8-10.5
Operating conditions		
Temperature, °C (°F)	24-35 (75-95)	27-45 (80-113)
Current density, A/dm^2 (A/ft^2)	≤ 3 (≤ 28)	≤ 2.5 (≤ 23)
Sodium cyanide to zinc		
Ratio	3.5:1	7.0:1
Range	3-5:1	6-9:1

The formulas for standard brass plating solution can be varied to suit various uses while maintaining the ratios of components. The solution listed in Table 1 is well suited for barrel plating, where high efficiency is needed and good conductivity enables the use of maximum current. (Barrel plating is carried out at a voltage of 6 to 14 V.) Where flash plating is used, the solution should be operated with the cyanide constituents at approximately half the amounts shown in Table 1. This reduced cyanide concentration allows the use of a wider range of current densities and results in excellent covering power. The plating efficiency at the reduced cyanide concentration is lower, but this is not a significant factor in flash plating. For rack plating, the optimum cyanide concentration is about two-thirds of that shown in Table 1; this level provides improved efficiency (compared to flash plating) while still allowing use of a wide range of current densities.

Formulas for high-alkalinity brass plating solutions are given in Table 2. The solutions listed in Table 2 may be varied to meet specific applications. The functions of the solution constituents are somewhat different than in the low-pH solutions. In the high-alkalinity solutions, the hydroxide and cyanide can work together so that a higher hydroxide content increases the zinc content of the deposit; thus, the ratio of cyanide to zinc is not applicable. The high-alkalinity solutions have high efficiencies and can be used at high current densities; the use of additives is needed to secure uniform color at low current densities. Thus they are difficult to use in barrel plating operations.

Table 2 High-alkalinity brass plating solutions

Constituent or condition	Original (potassium)	High-speed strip plating	Modern
Makeup			
Sodium cyanide, g/L (oz/gal)	. . .	120 (16.1)	125 (16.8)
Potassium cyanide, g/L (oz/gal)	125 (16.8)	. . .	. . .
Copper cyanide, g/L (oz/gal)	44 (5.9)	100 (13.4)	75 (10.1)
Zinc cyanide, g/L (oz/gal)	17.3 (2.3)	. . .	5 (0.7)
Sodium hydroxide, g/L (oz/gal)	. . .	11 (1.5)	45 (6.0)
Potassium hydroxide, g/L (oz/gal)	30 (4.0)	. . .	. . .
Analysis			
Copper (as metal), g/L (oz/gal)	31 (4.2)	70 (9.4)	50 (6.7)
Zinc (as metal), g/L (oz/gal)	9.6 (1.3)	7 (0.9)	3 (0.4)
"Total" cyanide, g/L (oz/gal)	80 (10.7)	50 (6.7)	53 (7.1)
Sodium hydroxide, g/L (oz/gal)	. . .	11 (1.5)	45 (6.0)
Potassium hydroxide, g/L (oz/gal)	30 (4.0)	. . .	. . .
Operating conditions			
Temperature, °C (°F)	45 (113)	80 (176)	70 (158)
Current density, A/dm^2 (A/ft^2)	1-4 (9-37)	3-16 (28-149)	1-8 (9-74)

The copper cyanide content of the plating solution serves as a source of copper for the plating deposit, but also is a major factor in plating efficiency. Cyanide is necessary to form the complexes that enable the copper and zinc to plate together to form brass. The ratio of cyanide to zinc in a conventional brass solution is the major determinant of the resulting composition of the plated alloy. The zinc can form a complex with either cyanide or hydroxide, depending on the hydroxide content of the solution. Cyanide is also necessary for solubility of the anodes. While zinc is usually added as cyanide, a very pure grade of zinc oxide can also be used.

The carbonate content of a brass solution is usually regarded as an impurity. It is formed by breakdown of the cyanide. Small amounts (15-20 g/L) are necessary in low-pH solutions to buffer the solution. Without carbonate, the solution is unstable and will give inconsistent plating. Hydroxide acts as a stabilizer in the solutions in which it is present, and thus carbonate is not essential in these solutions. The carbonate in the low-pH solutions exists as an equilibrium between carbonate and bicarbonate, making the use of both necessary to secure the proper pH. Carbonates in sodium baths can be frozen out; potassium baths can be treated with barium cyanide or barium hydroxide to precipitate the carbonate. It should be noted, however, that the use of barium cyanide or barium hydroxide creates insoluble sludges that are poisonous and cannot be destroyed, so that a hazardous waste is created. The use of calcium salts is recommended.

Hydroxide is used in the high-speed solutions to complex the zinc and increase efficiency. Increasing the hydroxide content increases the zinc content in the plated alloy.

Ammonia is a very important constituent in the low-pH brass plating solutions. Ammonia serves as a brightener and improves the appearance of plating accomplished at both high and low current densities. Ammonia is formed during plating by the decomposition of cyanide and is usually stable at temperatures up to 30 °C (86 °F). Higher temperatures (and the high hydroxide content of high-speed solutions) drive off ammonia faster than it is formed, making regular additions necessary to maintain color. Amines may be used to secure the benefit of ammonia at higher temperatures. An excess of ammonia causes the alloy to become richer in zinc; large excesses may result in white plate. Additions of ammonia do not change the pH level of the solution.

The temperature of the plating solution should be controlled to give constant alloy composition. A rise in temperature increases the copper content of the plate and also increases the plating efficiency.

Impurities in the solution affect the quality of the plating. Soluble oils and soaps will cause a brown smutty plate; they can be removed by carbon filtration. Tin is not usually troublesome but can cause dullness and white plate in recesses. Treatment is by dummy plating. Iron is not troublesome because it forms ferrocyanides, which precipitate out of the solution (but, as noted above, may result in the formation of sludge). Lead is by far the most troublesome impurity. As little as 10 ppm Pb will result in red recesses in the plate, especially in barrel-plated parts. Higher amounts of lead will cause dullness, black areas, and blistering. The source of lead is usually the anodes, although lead pipe and other lead-containing objects in the solution can cause contamination.

Anodes for brass plating may be forged, cast, extruded, or rolled, and differences in performance are minimal. Balls or nuggets (chopped rod) are frequently used with steel or titanium baskets; these furnish a uniform high current area, which is especially good for barrel plating where a relatively high current is used. Brass anodes should be used at low current densities because high current densities will cause polarization. The anodes should be of high purity and contain less than 0.02% Pb and less than 0.1% Fe or other metals. The optimum composition of yellow brass anodes is 70% Cu and 30% Zn. Use of anodes with higher copper contents will necessitate frequent additions of zinc to the solution. Deposition of brass with higher copper content requires the use of 85Cu-15Zn or 90Cu-10Zn anodes; the composition of the anodes should approximate that of the alloy being plated. Anodes of the composition types mentioned above are readily available. Steel anodes can be used in place of some of the brass anodes in order to lower the metal concentration in the solution.

Solution Analysis. Analysis and close control of the plating solution are essential for maintaining control of the alloy composition and color of the plated deposit. Analysis of copper and zinc content can be done by several methods, ranging from simple titrations to x-ray fluorescence. The results of these methods are generally accurate and reproducible.

Analysis of cyanide content is not so simple. Many methods analyze the "free" cyanide content, which is applicable to copper cyanide solutions but of dubious value when zinc is present, as in brass plating solutions. A simple and reproducible method is that used to determine the total cyanide content in zinc cyanide plating solutions: The cyanide is titrated with silver nitrate using a small amount of hydroxide in the sample being analyzed. This makes all of the cyanide in the brass solution available except that which is combined with the copper. A meaningful number is the ratio of this "total" cyanide to the zinc content of the solution. Another method for analyzing cyanide content involves distilling the cyanide from an acidified sample. This method is used to determine the cyanide content of waste solutions. Its results include cyanide present in the solution as ferrocyanide, so this method may indicate relatively high cyanide contents.

The pH level can be determined by meters, pH papers, or colorimetric comparison with suitable indicators. Hydroxide content can be determined by titration with acid using a high pH indicator. Carbonate content is easily determined by standard methods involving precipitation of the carbonate, separation, and titration.

Ammonia content can be determined by using a specific ion electrode, but is more commonly determined by using a plating cell and checking the effects of ammonia additions. For the standard Hull cell, a total current of 1 A for 10 min. can be used. The plating cell panel will also indicate the effect of impurities and additions determined by analysis. For high-speed solutions, a current of 2 A for 10 min. is recommended. Effects at various current densities can also be determined by reading the panels. For flash plating, a Hull cell preplated with bright nickel and a total current of 1A for 1 min is preferred.

Bronze Plating

Applications of bronze plating are varied. Alloys containing from 10 to 15% Sn are attractive and are used for decorative wares. These alloys have gold color that is browner than true gold; equivalent copper-zinc alloys are pinker in color.

Bronze plating is used on builders hardware, locks, and hinges to provide an attractive appearance and excellent corrosion resistance. Bronze-plated steel or cast iron bushings replace solid bronze bushings for many uses. Bronze plating is used where improved lubricity and wear resistance against steel are desired. Its good corrosion resistance makes it desirable as an undercoat on steel for bright nickel and chromium plate. Speculum alloys (45Sn-65Cu) are similar in appearance to silver and are used almost entirely for decorative purposes.

Solution Composition and Operating Conditions. Copper-tin alloys are plated from a simple system containing copper as a cyanide complex and tin as a stannate complex. A typical formula is given in Table 3. Because there are no interrelated complexes in the bronze plating solution, the alloy composition is controlled by the relative amounts of copper and tin in the solution (i.e., raising the tin content of the solution produces a higher tin content in the bronze plate). Alloys with very high tin contents, such as speculum, can be produced by simply increasing the tin content of the solution. Additives can be used to produce a bright plate. These additives usually contain lead, which acts as a brightener in bronze plating solutions.

Table 3 Composition and operating conditions for a typical bronze plating solution

Composition of plated deposit, 88Cu-12Sn

Constituent or condition	Amount
Makeup	
Potassium cyanide, g/L (oz/gal)	64 (8.6)
Copper cyanide, g/L (oz/gal)	29 (3.9)
Potassium stannate, g/L (oz/gal)	35 (4.7)
Potassium hydroxide, g/L (oz/gal)	10 (1.3)
Rochelle salt, g/L (oz/gal)	4.5 (6.0)
Analysis	
"Free cyanide," g/L (oz/gal)	22 (2.9)
Copper (as metal), g/L (oz/gal)	20 (2.7)

Tin (as metal), g/L (oz/gal)	14 (1.9)
Hydroxide, g/L (oz/gal)	10 (1.3)
Operating conditions	
Temperature, °C (°F)	65 (149)

The temperature of the solution is an important plating variable. Temperatures below 40 °C (105 °F) generally produce poor deposits that are almost always higher in copper content. Higher temperatures create higher efficiencies and allow the use of a wide range of current densities. Normal temperatures are from 60 to 80 °C (140 to 175 °F). Barrel plating solutions usually use lower temperatures.

Equipment requirements for bronze plating are similar to those for brass plating; however, the tanks should be built to withstand the higher temperatures that are generally used for bronze plating.

Anodes. The choice of anodes for bronze plating is complicated by a number of factors. The tin in bronze plating solutions is present as stannate, and when bronze alloy anodes are used, the tin dissolves as stannite; thus bronze anodes are not suitable for use. Dual anodes of copper and tin, where each type of anode has a separate current source, have been used. To eliminate the need for separate current sources, it is customary to use oxygen-free copper anodes and to add stannate tin as stannic oxide, potassium stannate, or a slurry of stannate oxide to replace the tin being plated. The presence of stannite is indicated by a dark color in the solution. The stannite is oxidized to stannate by the use of hydrogen peroxide, which must be added slowly and with constant stirring to prevent reaction with cyanide. Other impurities are not of major concern in bronze plating solutions.

Waste Water Treatment

The treatment of waste water from brass and bronze plating operations is relatively simple. Normal procedures for eliminating cyanide (i.e., treating the waste water with chlorine and adjusting pH to precipitate the metals) are all that is required. The metallic limits and allowance for chemicals in the final discharge are fixed by federal, state, and local regulations. Waste water treatment systems are usually designed by engineers who are conversant with local regulations and can make sure the equipment meets the necessary requirements.

Tin Alloy Plating

Reginald K. Asher, Sr., Motorola Semiconductor Product Sector

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Introduction

ELECTRODEPOSITION of tin alloys is used to protect steel against corrosion or wear, to impart resistance to etching, and to facilitate soldering. Four types of tin alloys are available in commercial processes.

Tin-lead is the most commonly used of these processes because of its simplicity and low cost. It is especially popular in the electronics industry because of its excellent solderability, resistance to tin whisker growth, and resistance to tin pest (formation of a gray powder on the surface, also called *tin disease*). These properties make it a valuable coating for integrated-circuit leads, surface-mount (small outline transistor) components, and circuit board connections.

Tin-bismuth processes have been developed in recent years as a substitute for tin-lead. Bismuth as an alloying agent prevents the whiskering and tin pest that can occur in tin coatings.

Tin-nickel is used for corrosion-resistant coatings, especially in seawater environments. It has an attractive chromelike appearance and high lubricity when plated over bright nickel.

Tin-zinc provides outstanding corrosion protection, comparable to cadmium, and is a possible replacement for cadmium at a lower cost.

Acknowledgement

Portions of this article were adapted from Nicholas J. Spilotis, Tin-Lead Plating, *Metals Handbook,* 9th Edition, Volume 5, ASM, 1982, p 276-278.

Tin-Lead Plating

Tin-lead plating is a relatively simple process because the standard electrode potentials of tin and lead differ by only 10 mV. Tin-lead alloys have been deposited from electrolytes such as sulfonates, fluosilicates, pyrophosphates, chlorides, fluoborates, and, infrequently, phenosulfonates or benzenesulfonates. Of these, fluoborate and sulfonates (methane sulfonic acid, or MSA, also known as nonfluoborates, or NF) are available commercially. Tin-lead plating has traditionally been done with fluoborate solutions, but MSA solutions have become popular in the electronics industry because they are less corrosive to plating equipment, more uniform in deposition, easier to control, and more acceptable environmentally.

Fluoborate and methane sulfonate solutions plate tin from the stannous valance state. The term *stannous valence state* refers to the valence of tin in solution. In the case of fluoborate and MSA solutions, the tin is in the +2 valence state as Sn^{+2}. Tin will plate only from the +2 state in acid solution. Alkaline stannate solutions plate tin from the +4 valence state. In fluoborate and MSA solutions, the stannous tin requires only two electrons to reduce it to metal:

$$Sn^{+2} + 2e \rightarrow Sn^{0} \text{ (metal)} \quad \textbf{(Eq 1)}$$

Stannous fluoborate, along with lead fluoborate, fluoboric acid, and an addition agent, comprises the plating solution. The ingredients of the nonfluoborate MSA solution are stannous methane sulfonate with lead methane sulfonate, MSA, grain refiners (wetting agents), antioxidants, and fungicides. These components, as well as various addition agents, are available in commercial quantities. The solution operates at 100% cathode and anode efficiency.

Uses of Tin-Lead. Electrodeposition of tin-lead alloys was first patented in 1920, when these alloys were used to protect the interiors of torpedo air flasks against corrosion. When air was pumped into a flask under pressure, moisture in the air condensed and corroded the flask, weakening it. Lead coatings had been used to protect the interior against corrosion, but tin-lead alloy was found to be more corrosion resistant.

Today, tin-lead deposits are used as corrosion-resistant protective coatings for steel. The deposits usually contain 4 to 15% Sn, but the composition varies with the application. Automotive crankshaft bearings are plated with tin-lead or tin-lead-copper alloys containing 7 to 10% Sn, whereas an alloy containing 55 to 65% Sn is plated onto printed circuit boards. Tin-lead plating on circuit boards acts as an etch-resistant coating and facilitates soldering of board components after they have been inserted into the board. Copper alloys and alloy 42 (42Ni-58Fe) substrates are ordinarily plated with 80% Sn/20% Pb ± 10% MSA solutions in the manufacture of electronic components such as integrated circuits and surface mounts for postsoldering requirements. The shelf life, storage, and thickness of this composition have been proven by some Taguchi fractional multivariable experiments.

MSA Plating Solutions for Tin-Lead

In the electronics industry, MSA solutions are replacing fluoborate solutions for tin-lead plating of contacts on integrated circuits, surface-mount devices, radio-frequency components, and similar devices. The tin-lead MSA solution is well-established worldwide for rack, vibratory bowl, barrel, reel-to-reel, and especially high-speed cut-strip plating. Rack plating of components is being replaced where possible by semiautomated cut-strip lines.

Advantages. The MSA process is preferred over fluoborate solution for several reasons. First, it produces a better-quality, more uniform finish. For a typical specification of a coating thickness of 7 to 20 μm (300 to 800 μin.) with a composition of 80% Sn + 20% Pb ± 10%, it can maintain 6-sigma reliability (fewer than 3.4 rejects per million). MSA solutions are faster and have higher throwing power than fluoborate solutions, and they are able to produce a finer grain size. A recently developed, patented process is able to produce a semibright solderable finish. Because of low levels of occluded codeposited organic substances (<500 ppm C), coatings are suitable for soldering as-plated or after standard

thermal excursions. Coatings produced from MSA solutions have excellent storage life and pass the bake and steam age solderability requirements of MIL-883, Method 2003.7. They also pass MIL-38510 requirements for surface finish on electronic components.

Second, the MSA process is environmentally more acceptable. MSA is less corrosive than fluoborate solutions, and because there is no boron or fluorine in the solution, it is more acceptable for wastewater treatment and water reuse. The electrolyte is safer to handle, and the MSA activator (10 to 20 vol%) can be recycled. The latter consideration offsets the higher initial cost and higher operating cost of MSA.

Third, the MSA process is easily automated. Cut strips of electronic components are loaded into high-speed plating equipment by magazine or cassette for easy handling. Deposition rates are two to five times higher than for fluoborate solutions, ranging from 5.4 to 21.5 A/dm^2 (50 to 200 A/ft^2). Table 1 lists deposition rates for a high-speed solution. There are high-speed fluoborate baths operating at from 500 to 1000 A/ft^2.

Table 1 Time required to plate 2.54 μm (100 μin) of 80Sn-from high-speed methane sulfonic acid (MSA) solution

Total metal content		Time required at indicated current density, min				
g/L	oz/gal	10.8 A/dm^2 (100 A/ft^2)	13.5 A/dm^2 (125 A/ft^2)	16.1 A/dm^2 (150 A/ft^2)	18.8 A/dm^2 (175 A/ft^2)	21.5 A/dm^2 (200 A/ft^2)
20	2.7	0.78	0.72	0.65	0.59	0.56
30	4.0	0.70	0.64	0.56	0.52	0.47
40	5.3	0.62	0.63	0.44	0.40	0.37
50	6.7	0.55	0.47	0.40	0.36	0.33
60	8.0	0.54	0.46	0.38	0.34	0.30
70	9.3	0.53	0.46	0.37	0.33	0.28
80	10.7	0.52	0.45	0.36	0.32	0.27
90	12.0	0.51	0.43	0.35	0.31	0.26
100	13.4	0.50	0.42	0.34	0.29	0.25

Source: Ref 1

Experimental modified MSA tin-lead plating solutions are being evaluated for semiautomatic plating of leaded-glass sealed integrated-circuit packages, with excellent results.

A minimum of 2% Pb in a tin deposit is reported to prevent whiskering, eliminating the need for reflow as required by MIL-38510 for integrated-circuit devices. The electrolyte will accommodate any tin-lead composition.

Automation. Commercially available automated process lines for electronic devices are loaded manually or from a magazine or cassette. The process operations include deflashing, deoxidation, activation, tin-lead plating, neutralization (if necessary), final rinse, hot deionized water rinse, hot air dry, and automatic reloading into the magazine or cassette. Rinses are pressure spray, with air knives to remove the maximum water for recovery and reuse.

At the time of this writing, equipment for electronic components is limited to strips 23 cm (9 in.) long and 6.4 cm (2.5 in.) wide. A contact rail 3 mm (0.12 in.) wide for light strips and 5 mm (0.20 in.) wide for heavy strips is necessary for gripping the top edge of the strip.

Substrates. The MSA process is generally used for electronic solderable leads on integrated circuits, surface-mount devices, radio-frequency components, and similar devices. The materials used are typically copper or alloy 42 (42Ni-58Fe). Silicon and zirconium copper alloys require special, proprietary preparations for plating.

Properties of the Coated Surface. The deposit usually has a smooth matte finish. Some newly developed solutions give a semibright finish with dense deposits and excellent solderability.

Health and Safety Considerations. Local exhaust is required for fumes from the electrolyte. This is generally provided in the commercial equipment. Chemical goggles, a face shield, rubber gloves, and an acid-resistant apron should be worn when handling the electrolyte. Ordinarily, exhaust fans eliminate the problem of lead fumes in the air (Ref 2), and there should be no problem with meeting Occupational Safety and Health Administration requirements OSHA Standard 1910.1025.

Parameters. Any desired tin-lead alloy composition can be plated from an MSA solution. The composition of the deposit depends on the amount of stannous tin and lead in the solution, the type and amount of addition agent, the current density, and the tin-lead content of the anodes (usually 85Sn-15Pb for high-speed plating). Solution temperature and degree of agitation affect composition, especially in high-speed solutions.

Multivariable fractional factorial experiments have shown that the 80Sn-20Pb (80/20) coating has a slightly higher solderability quality than 90/10 or 60/40 compositions, and much better than rack 100% Sn.

Solution Components. Concentrated solutions of stannous and lead nonfluoborates, MSA, and additives are available commercially, so alloy plating solutions are made by mixing and diluting concentrates. Additives are wetting agents, antioxidants, and fungicides.

80Sn-20Pb high-speed MSA solution (Ref 3) is used for high-speed automated plating of leads for electronic components, including dual-inline-pin and surface-mount integrated circuits, radio-frequency components, and similar devices where highly consistent coating thickness, surface finish, and solderability are required, along with high production rates. The solution composition is:

- Stannous tin: 52±7 g/L (7.0±1.0 oz/gal)
- Lead: 13.0±1.9 g/L (1.73±0.25 oz/gal)
- Free MSA: 255±15 g/L (34.0±2.0 oz/gal)
- Mixed nonionic surfactant: 5 to 10 g/L
- Antioxidant: 0.5 to 1.5 g/L

The operating conditions are:

- Temperature: 21±2.8 °C (70±5 °F)
- Current density: 10.8±5.4 A/dm^2 (100±50 A/ft^2) with less than 1% current ripple on the plating rectifiers
- Agitation: very rapid, mechanical pump and hydraulic pressure
- Anodes: 85Sn-15Pb
- Filtration: continuous through polypropylene or acrylic filter cartridges

80Sn-20Pb MSA solution (Ref 4) is used for barrel plating of electronic components and applications requiring higher throwing power than the high-speed solution. The solution composition is:

- Stannous tin: 14±2 g/L (1.9±0.3 oz/gal)
- Lead: 2.0 to 4.0 g/L (0.27 to 0.54 oz/gal), 3.4 g/L (0.45 oz/gal) optimum
- Free MSA: 165±32 g/L (22.0±4.3 oz/gal)
- Proprietary additive: 5 to 10%

The operating conditions are:

- Temperature: 21±2.8 °C (70±5 °F)
- Current density: 0.32 to 0.64 A/dm^2 (3 to 6 A/ft^2)
- Agitation: mechanical (sparger)
- Anodes: 80Sn-20Pb
- Filtration: continuous through polypropylene or acrylic filter cartridges

Table 2 is a troubleshooting guide to MSA plating solutions.

Table 2 Troubleshooting guide for tin alloy plating with methane sulfonic acid (MSA) solutions

Problem	**Possible cause**	**Solution**
Burn (dark, rough deposit) at high current density	Low metal content	Analyze metal content and adjust if necessary.
	Current density too high	Lower rectifier settings.
	Temperature of plating solution too high	Check and adjust to 19-21 °C (66-70 °F).
	Lack of solution circulation	Check to be sure all circulating pumps are operating.
	Excessive copper in plating solution	Analyze and remove contamination by dummy plating.
	Additive low	Analyze and adjust.
Dark, nonuniform deposit at low density	Low acid content of the plating solution	Analyze and adjust.
	Plating current density too low	Check and adjust current setting.
	Poor cleaning or inadequate activation	Check parts going out of descale/activator. Adjust to proper operating conditions if necessary.
Poor throwing power or plating distribution	Metal content too high	Analyze and adjust.

distribution	Plating current density too low	Check and adjust current setting.
Pitting	Organic contamination	Check for carbon and treat if necessary.
	Oil or grease in solution	Check and dump if positive.
	Poor cleaning	Check/analyze descale and activation for proper operating conditions.
	Insufficient solution agitation	Check circulating pump.
Rough deposits	Particles (anode sludge, dirt) in solution	Check filter for proper operating condition. Replace cartridge.
	Excessive current setting	Check and adjust.
	Insufficient solution agitation	Check circulation.
Alloy composition in deposit out of specification	Incorrect bath composition	Analysis and adjust
Poor solderability	Low thickness	Check and adjust.
	Organic contamination in the bath	Analyze for carbon and treat if necessary.
	Copper contamination in the bath	Check and do low-current dummy plating if necessary.
	Incorrect alloy composition	Check and adjust.
	Insufficient/poor cleaning of base metal	Check parts going out of descale. Check descale and activator for proper operating conditions.
Excessive foaming	Air being drawn into filter	Check for line leaks.
	Imbalance of system circulation	Set discharge line flow. Close down on drain back valves.
	Excessive additive concentration	Analyze and dilute if necessary.
	Air blow offset too high	Reduce air wipe flows.

Poor adhesion	Poor pretreatment	Adjust to proper operating range. Makeup new when necessary.
	Poor rinsing	Check and adjust rinse flow.
	Excessive additive	Analyze and adjust.
Staining or discoloration	Air blower nozzle offset	Check and reset.
	Poor/insufficient rinse	Check and adjust flows.
	Air wipe blocked or offset	Check and reset.
	Insufficient additive	Analyze and adjust.

References cited in this section

1. Techni-Solder NF Acid process information sheet, Technic, Inc., Cranston, RI
2. Techni-Solder NF Acid material safety data sheet, Technic, Inc., Cranston, RI, 1991
3. Techni-Solder NF 80/20 Alloy High Speed Matte product data sheet, Technic, Inc., Cranston, RI
4. Techni-Solder NF 1957 product data sheet, Technic, Inc., Cranston, RI

Fluoborate Plating Solutions for Tin-Lead

Any desired tin-lead alloy composition can be plated from a fluoborate solution. The composition of the deposit depends on the amount of stannous tin and lead in the solution, the type and amount of addition agent, the current density, and the tin-lead content of the anodes. Bath temperature and degree of agitation also affect the composition, especially in high-speed solutions.

Solution Components. Concentrated solutions of stannous and lead fluoborates and fluoboric acid are available commercially, so alloy plating solutions are made by mixing and diluting concentrates. Some compositions of concentrates are given in Table 3. The fluoborates of tin and lead contain free or excess fluoboric and boric acids for stability, and fluoboric acid contains free boric acid for the same reason.

Table 3 Composition of fluoborate alloy plating solution concentrates

Constituent	Amount		
	wt%	g/L	oz/gal
Lead fluoborate			
Lead fluoborate, $Pb(BF_4)_2$	51.0	893	119
Lead, Pb[(a)]	27.7	485	65

Fluoboric acid, free HBF_4	0.6	10.5	1.4
Boric acid, free H_3BO_3	1.0	18	2.4
Stannous (tin) fluoborate			
Stannous fluoborate, $Sn(BF_4)_2$	51.0	816	109.0
Tin, $Sn^{-2(a)}$	20.7	331	44.3
Fluoboric acid, free HBF_4	1.8	29	3.9
Boric acid, free H_3BO_3	1.0	16	2.1
Fluoboric acid			
Fluoboric acid, HBF_4	49	671	89.9
Boric acid, free H_3BO_3	0.6	8.3	1.1
Hydrofluoric acid, free HF	None	. . .	. . .

(a) Equivalent

The reason that excess boric and fluoboric acids provide stability in the fluoborate concentrates can best be shown by the reactions described below, with lead fluoborate used as an example, although the same is true for all other fluoborate concentrates. In the absence of boric acid, the metal fluoride will form. To stabilize the lead fluoborate, the following reaction takes place:

$$4PbF_2 + 2H_3BO_3 \rightarrow Pb(BF_4)_2 + 3Pb(OH)_2 \quad \textbf{(Eq 2)}$$

The reaction is incomplete unless fluoboric acid is added to produce the result:

$$3Pb(OH)_2 + 6HBF_4 \rightarrow 3Pb(BF_4)_2 + 3H_2O \quad \textbf{(Eq 3)}$$

The overall reaction is then:

$$4PbF_2 + 2H_3BO_3 + 6HBF_4 \rightarrow 4Pb(BF_4)_2 + 6H_2O \quad \textbf{(Eq 4)}$$

Commercially, fluoboric acid is made by reacting hydrofluoric acid with boric acid:

$$4HF + H_3BO_3 \rightarrow HBF_4 + 3H_2O \quad \textbf{(Eq 5)}$$

When excess boric acid is added beyond the amount required to react stoichiometrically with the hydrofluoric acid present, the reaction is driven far to the right, thus stabilizing the fluoboric acid and preventing the formation of fluorides.

A tin-lead plating solution deficient in free boric acid can precipitate insoluble lead fluoride. To guard against this possibility, anode bags filled with boric acid should be hung in corners of the plating tank and immersed in solution. Bags should be refilled when the boric acid has dissolved.

Addition agents are important for the production of dense, fine-grain deposits and the improvement of throwing power in a tin-lead solution operation. Many organic addition agents have been used in tin-lead solutions, including bone glue, gelatin, peptone, aldehyde condensation products, glycols, sulfonated organic acids, beta-naphthol, hydroquinone, and resorcinol. Peptone is the addition agent most frequently used because of its commercial availability as a stabilized solution specifically prepared for tin-lead plating solutions.

Solution Compositions and Operating Conditions. Listed below are the tin-lead fluoboric bath compositions that are used most frequently.

7Sn-93Pb solution is used for bearings and corrosion protection of steel. The solution composition is:

- Stannous tin: 6.0 g/L (0.80 oz/gal)
- Lead: 88.0 g/L (11.8 oz/gal)
- Fluoboric acid: 100 g/L (13.4 oz/gal) min
- Boric acid: 25 g/L (3.4 oz/gal)
- Peptone, dry basis: 5 g/L (0.67 oz/gal)

The operating conditions are:

- Temperature: 18 to 38 °C (65 to 100 °F)
- Current density: 3.2 A/dm^2 (30 A/ft^2)
- Agitation: mild, mechanical
- Anodes: 7Sn-93Pb

60Sn-40Pb solution is used for printed circuit boards, barrel plating of small parts, and applications requiring high throwing power. The solution composition is:

- Stannous tin: 15 g/L (2 oz/gal)
- Lead: 10 g/L (1.3 oz/gal)
- Fluoboric acid: 400 g/L (53.4 oz/gal)
- Boric acid: 25 g/L (3.4 oz/gal)
- Peptone, dry basis: 5 g/L (0.7 oz/gal)

The operating conditions are:

- Temperature: 18 to 38 °C (65 to 100 °F)
- Current density: 2.1 A/dm^2 (20 A/ft^2)
- Agitation: mild, mechanical
- Anodes: 60Sn-40Pb

60Sn-40Pb high-speed solution is used for high-speed wire and strip plating, or for general plating where throwing power is not of prime importance. The solution composition is:

- Stannous tin: 52 g/L (7.0 oz/gal)
- Lead: 30 g/L (4.0 oz/gal)
- Fluoboric acid: 100 g/L (13.4 oz/gal) min
- Boric acid: 25 g/L (3.4 oz/gal)
- Peptone, dry basis: 5 g/L (0.7 oz/gal)

The operating conditions are:

- Temperature: 18 to 38 °C (65 to 100 °F)
- Current density: 3.2 A/dm^2 (30 A/ft^2)
- Agitation: mild, mechanical
- Anodes: 60Sn-40Pb

When this solution is used to deposit 60Sn-40Pb on wire or strip, current densities in excess of 32 A/dm^2 (300 A/ft^2) can be used if the wire or strip is moved continuously through the plating solution at a relatively high speed.

$HBF_4$60Sn-40Pb solution (Ref 5) provides high throwing power. The solution composition is:

- Fluoboric acid 48%: 350 mL/L
- Tin fluoborate 50%: 46.2 mL/L
- Lead fluoborate 50%: 25.2 mL/L
- Proprietary additive: 20 mL/L
- Boric acid: 26 g/L
- Tin-lead salt No. 1: 2 g/L

The optimum operating conditions are:

- Temperature: 21 °C (70 °F)
- Current density: 2.5 A/dm^2 (25 $A/ft^{2)}$
- Agitation: mechanical, slow to moderate
- Filtration: continuous through polypropylene or Dynel

Table 4 is a troubleshooting guide for this solution.

Table 4 Troubleshooting guide for $HBF_4$60Sn/40Pb high-throw bath

Problem	Possible cause	Remedy
Treeing	Low addition agent	Replenish.
Edge feathers	Too high a current density	Lower current density.
Grainy deposit	Organic contamination	Replenish addition agent. As a last resort, carbon treat.
Burning	Too high a current density	Lower amperage.

	Too low a metal content	Add stannous fluoborate or lead fluoborate.
	Low acid content	Add fluoboric acid.
Wrong alloy composition	Incorrect bath composition	Adjust bath composition.
	Wrong current density	Plate at 2.5-3 A/dm^2(25-30 A/ft^2).
	Insufficient addition agent	Replenish.
	Improper agitation	Use cathode rod agitation.
Poor throwing power	High pH	Add fluoboric acid.
	Too high an anode-to-cathode ratio	Remove some anodes.
	Low agitation agent	Replenish.
Precipitate in bath, roughness	Chloride or sulfate drag-in	Improve rinsing.
	Torn anode bags	Replace anode bags.
	Oxidation of tin from excessive agitation	Look for air leak in filter, if used.
Poor reflow	Insufficient deposit. Minimum should be 0.00025 in.	Do not reflow unless thickness is above minimum.
	Wrong alloy	Check reason for wrong alloy as described above.
	Organic contamination	Carbon treat.
	Metallic contamination	Dummy the bath.
	Copper substrate not active or clean	Check cleaning cycle.

Compositions of anodes and solutions for deposits up to 50% Sn are listed in Table 5. The composition of the anode should be the same as that desired in the deposit. If deposits do not have the desired composition, anode composition should be maintained as indicated and adjustments should be made to the solution formula.

Table 5 Composition of anode and fluoborate solution for deposits up to 50% Sn

Plated 3.2 A/dm^2(30 A/ft^2); compositions of all baths contains a minimum of 100 g/L (13.3 oz/gal) of free HBF_4, 25 g/L. (3.3 oz/gal) of free H_3BO_3, and 5.0 g/L (0.7 oz/gal) of peptone

Composition of deposit and anode, %		Composition of bath			
		Stannous tin		Lead	
Tin	Lead	g/L	oz/gal	g/L	oz/gal
5	95	4	0.5	85	11.3
7	93	6	0.8	88	11.8
10	90	8.5	1.1	90	12.0
15	85	13	1.7	80	10.7
25	75	22	2.9	65	8.7
40	60	35	4.8	44	5.8
50	50	45	6.0	35	4.7

Table 5 is based on an operating density of 3.2 A/dm^2 (30 A/ft^2). Higher or lower current densities may result in deposition of alloys of compositions differing from those given in the table. It is then necessary to make compensating corrections in solution composition. Deposition rates of tin-lead coatings can be controlled by current density. Table 6 shows that as the current density of a fluoborate solution is increased, the rate of 60Sn-40Pb deposition also increases.

Table 6 Rate of 60Sn-40Pb deposition from the fluoborate solution

100% cathode efficiency

Current density		Time in bath, min, at thickness of:			
A/dm^2	A/ft^2	25µm (0.0001 in.)	7.5µm (0.0003 in.)	12.5µm (0.0005 in.)	25µm (0.001 in.)
1.0	10	4.5	13.5	22.5	45
1.5	15	3.0	9.0	15.0	30
2.0	20	2.3	6.8	11.3	22.5
2.5	25	1.8	5.4	9.0	18
3.0	30	1.5	4.5	7.5	15

Temperature. Tin-lead fluoborate solutions operate efficiently in a temperature range of 18 to 38 °C (65 to 100 °F). Upper temperatures slightly increase tin in deposits, and lower temperatures can decrease tin.

Current densities below the specified amount for a particular solution formula can decrease the tin content of deposits. Higher current densities can increase tin content.

Agitation is an important factor in tin-lead plating. Optimum conditions exist when mild agitation is used. Use of a still bath results in nonuniform deposits because of local exhaustion of the solution at the cathode surface. Vigorous agitation may increase the stannic tin content of a solution, resulting in a decrease of tin in deposits. Cathode rod agitation or circulation through an outside pump provides suitable agitation for a tin-lead plating solution. Air agitation should not be used because it can oxidize stannous tin.

Boric acid is added to maintain solution stability. Approximately 25 g/L (3.4 oz/gal) of boric acid has been found desirable, but its concentration is not critical. An anode bag filled with boric acid may be hung in a corner of the tank to maintain the required concentration. Excess boric acid prevents fluoride precipitates, which can deplete lead from the solution. This is based on the following formula:

$4HF + H_3BO_3$ € $HBF_4 + 3H_2O$ **(Eq 6)**

where $HBF_4$is the resultant fluoboric acid. The reaction is reversible if the stoicheiometric amount of boric acid (H_3BO_3)is used to react with the hydrofluoric acid (HF) present. As the amount of boric acid in the above reaction is increased, the reaction is driven far to the right so that the reaction becomes irreversible and no free hydrofluoric acid is regenerated. This is important because if free hydrofluoric acid were present, then insoluble fluorides, especially lead fluoride, would precipitate. Thus, all fluoborate concentrates and plating baths contain free boric acid. Although 25 g/L of boric acid is optimum (close to its solubility), any amount of free boric acid is acceptable to prevent the formation of fluorides.

Free fluoboric acid is maintained in the solution to provide the requisite acidity and to raise conductivity. In conjunction with peptone, it can prevent "treeing" and give a fine-grain deposit. Free fluoboric acid can be added in amounts ranging between 100 to 500 g/L (13.4 to 67 oz/gal), depending on the solution formula used.

Peptone is added to the plating bath to promote formation of fine-grain adherent deposits and prevent treeing. Peptone solution is available commercially, and proper amounts can be measured and poured directly into the plating bath. The bath can then be used immediately, after it is gently stirred to ensure complete mixing of peptone. During the operation of the plating bath, a loss of peptone can result because of dragout, chemical breakdown, and codeposition with the metal. As peptone is depleted, it must be replenished. Replenishment amounts should be determined by experience. As a guide, 1 L (2.1 pints) of peptone solution per 380 L (100 gal) of plating bath can be used per week. A Hull cell operated at 1 A for 10 min can be used to control the peptone content of a plating solution.

Tin-lead fluoborate solutions containing peptone should be filtered through activated carbon at least four times per year to ensure removal of organic breakdown products and avoid buildup of peptone from indiscriminate additions. The plating bath should be treated with about 4.5 kg. (10 lb) of activated carbon per 380 L (100 gal) of bath until, after filtration, the solution is water white. The bath should not be heated during carbon treatment, because stannous will be oxidized to stannic tin. Fresh peptone is added after carbon treatment. Because there is no simple analytical method for determining peptone concentration in this solution, carbon treatment and replenishment of peptone every 3 or 4 months ensures proper amounts of peptone in a solution.

Proprietary synthetic wetting agents can be purchased for grain refinement, as a substitute for peptone. Because these components are synthetic, they are less susceptible to algae and bacterial growth.

Metallic impurities are removed by low-current-density electrolysis, but in a tin-lead bath, low current density favors deposition of lead, which may unbalance the solution. Metallic impurities can be removed by dummying a bath at a current density of 0.2 A/dm^2 (2 A/ft^2) for at least 8 h. The solution should then be analyzed and brought up to specification with stannous or lead fluoborate. Iron, nickel, and other metals above hydrogen in the electromotive series are not removed by dummying, although copper is easily removed.

Filtration. A tin-lead fluoborate plating solution should be filtered constantly, to keep the bath clear. If constant filtration is not used, a bath can turn cloudy because of sulfates entering the solution and precipitating as lead sulfate.

Stannic salts can also precipitate out of the solution. Anode sludge or breakdown products from peptone solutions can contribute to a cloudy appearance as well. Polypropylene filter spools or cartridges can be used as filters, but they must first be leached in hot water (65 °C, or 150 °F) to remove organic agents used in their manufacture. The end of the return hose from the filter must be submerged in the bath to prevent aeration of the bath.

Anodes. Tin-lead alloy anodes of at least 99.9% purity must be used. The most objectionable anode impurities are arsenic, silver, bismuth, antimony, copper, iron, sulfur, nickel, and zinc. Extruded anodes are preferred over cast anodes, because cast anodes have a larger grain size and suffer from intergranular corrosion, which causes large pits or depressions to form on the anode surface. The finer grain size of extruded anodes provides uniform and efficient corrosion during plating. Tin-lead anodes should be left in an idle tin-lead fluoborate bath because they exercise a reducing effect on tin in solution, thus helping to maintain the bath in a stannous valence state. Tin-lead anodes should be bagged with acrylic or polypropylene cloth to contain any anode sludge that may form. Anode sludge suspended in solution can cause rough deposits.

Materials of construction for tin-lead plating equipment include:

- Steel lined with rubber or polypropylene or made entirely of polypropylene, used for tanks and pumps
- Monel metal, used for anode hooks
- Polypropylene, used for anode bags and filter spools
- Pure paper pulp (alpha cellulose), used for filter aid

The following materials should not be used in contact with fluoborate solutions: glass; quartz or other silicated materials; nylon; neoprene; or titanium. Equipment in contact with fluoborates should have the recommendation of the manufacturer for use in a fluoborate solution.

Lead disposal for fluoborate and MSA solutions is most commonly accomplished by diverting the lead-containing rinse water (or dilute concentrate) to a pH-controlled holding tank, filtering the solution, and then running it through an ion exchanger. The fluoborate rinse will have to be regenerated with MSA before going to a holding tank and then to electrowinning. The MSA rinse can go directly to electrowinning, where the lead is plated out on a reusable cathode. The water can then be carbon treated, ion exchanged, and reused for certain rinses.

Reference cited in this section

5. Techni HBF_4 60/40 High Throw PC product data sheet, Technic, Inc., Cranston, RI

Other Tin Plating

Tin-Bismuth Plating. A small amount of bismuth or antimony added to tin helps to eliminate whiskering and tin pest in tin coatings that are subjected to temperatures below 13.2 °C (55.8 °F). MIL-QQS-571 recommends 0.27% Sb to prevent tin pest. Several processes for tin-bismuth plating have been patented (Ref 6, 7, 8) and commercialized. Experimental processes using inert anodes, such as platinized titanium, have been used to produce printed circuit board prototypes with tin-bismuth coatings on parts. An MSA solution similar to that used for tin-lead plating has been developed, and solutions are being developed for commercial sales by chemical suppliers. Tin methane sulfonate and bismuth methane sulfonate are used in the solution. Plating is done at room temperature with mild agitation.

Tin-Zinc Plating. In most environments, tin-zinc alloys approach the corrosion resistance and solderability of cadmium. Because cadmium can release toxic fumes when heated, and because it is a strategic element and therefore relatively expensive and subject to availability concerns, tin-zinc coatings are often used as substitutes. Compositions ranging from 10Sn-90Zn to 85Sn-15Zn have been used. Electrolytes are made from a mixture of potassium stannate, zinc cyanide, potassium cyanide, and potassium hydroxide. The amount of potassium cyanide determined by analysis is higher than that added to the bath initially, because the analysis also detects the cyanide in zinc cyanide.

80Sn-20Zn solution is the most commonly used. The solution compositions are:

Still tank

- Stannous tin: 38 to 53 g/L (5.1 to 7.1 oz/gal)
- Zinc: 4.5 to 7.5 g/L (0.60 to 1.0 oz/gal)
- Potassium cyanide: 38 to 53 g/L (5.1 to 7.1 oz/gal)
- Free potassium hydroxide: 4.9 to 8.3 g/L (0.65 to 1.1 oz/gal)

Barrel

- Stannous tin: 32 to 40 g/L (4.3 to 5.3 oz/gal)
- Zinc: 6.8 to 10 g/L (0.91 to 1.3 oz/gal)
- Potassium cyanide: 41 to 60 g/L (5.5 to 8.0 oz/gal)
- Free potassium hydroxide: 8.3 to 11.3 g/L (1.1 to 1.51 oz/gal)

The operating conditions are:

- Temperature: 65 ± 2 °C (149 ± 4 °F)
- Anode current density: 1.5 to 2.5 A/dm^2 (14 to 23 A/ft^2)
- Cathode current density: 0.1 to 0.9 A/dm^2 (1 to 8 A/ft^2)
- Agitation: none for still tanks, or barrel agitation
- Anodes: 80Sn-20Zn
- Equipment: mild steel

Anodes must be filmed. (An oxide film is deposited on the anode by plating it at a high current density.) Unfilmed anodes cause formation of stannite (Cu_2FeSnS_4), which inhibits plating.

Temperature. Temperatures in the high end of the range increase the tin content and cause the cyanide to break down. Low temperatures decrease cathode efficiency and lower the percentage of tin.

Current densities at the low end of the range result in tin-rich deposits.

Electrolyte Concentrations. The proportions of zinc and tin in the deposit vary with the amounts in the solution. Higher concentrations of zinc in solution result in higher levels in the deposit, and likewise with tin. Higher levels of free potassium hydroxide increase the percentage of zinc in the deposit. Small changes in free cyanide content have little effect, because the solution contains more cyanide than is necessary. Excessively low levels of cyanide decrease tin content (Ref 9).

Tin-Nickel Plating. The intermetallic compound 65Sn-35Ni can be plated from several commercial electrolyte solutions. The finish has high lubricity and a bright, chromelike appearance with excellent corrosion resistance, especially in seawater environments. It is used more often for general industrial applications than for electronic components, because it is more difficult to solder than other tin-alloy coatings. The solution composition is:

- Nickel chloride: 250 g/L (33 oz/gal)
- Stannous chloride: 50 g/L (6.7 oz/gal)
- Ammonium chloride: 50 g/L (6.7 oz/gal)
- Starter (makeup and additives containing surfactants and grain refiners): 20% by volume

The operating conditions are:

- Temperature: 60 to 70 °C (140 to 160 °F), 66 °C (151 °F) optimum
- Current density: 0.1 to 3.2 A/dm^2 (1 to 30 A/ft^2), 1.6 A/dm^2 (15 A/ft^2) optimum

- Agitation: cathode rod, solution, or barrel. Still racks may be used at low current densities.
- Anodes: high-purity nickel in polypropylene bags
- Filtration: continuous through polypropylene or chlorinated polyvinyl chloride (CPVC) above 60 °C (140 °F)

Preparation. Metallic substrates should be cleaned. A common acid cleaning procedure is a 10 to 20% HCl bath immediately before plating. Steel substrates should be plated with an alkaline copper or acid nickel strike coating.

Equipment. All equipment in contact with the plating solution should be nonmetallic. Tanks and filters should be polypropylene or CPVC. Heaters should be fluorocarbon coated.

Handling Precautions. Gloves, protective clothing, and goggles should be worn when handling electrolyte solution or its components.

Environmental Considerations. Electrolyte solutions and their components should be treated according to procedures for fluoride- and cyanide-containing wastes. They should not be mixed with metal-bearing waste streams, because they contain metal chelators (Ref 10, 11).

Table 7 is a troubleshooting guide to tin-nickel plating solutions.

Table 7 Troubleshooting guide for tin-nickel plating solutions

Problem	**Possible cause**	**Remedy**
Powdery gray deposit	Current density too high	Use a lower current density.
	Nickel content too low	Analyze nickel content, add nickel chloride if necessary.
Dull or black deposit	Tin content too low	Analyze tin content, add stannous chloride if necessary (starter concentrate must be added at the same time as stannous chloride).
Brittle or milky deposit	Low replenisher	Add replenisher.
	Metallic contamination	Remove metal by electrolyzing solution.
Dark or black deposits in low-current-density plating areas	Copper contamination	Eliminate source of contamination, remove copper by electrolyzing.
Dark deposit with standard current density or burn with high current density	Organic contamination	Filter solution through activated carbon. Never add hydrogen peroxide, potassium permanganate, or other oxidizing agents.
Incorrect alloy composition	Incorrect solution composition	Analyze tin and nickel contents of bath and adjust.
Nickel content increases during operation	Excess anode area	Decrease anode area.

Source: Ref 10

References cited in this section

6. T.I. Murphy and B.R. Reynolds, "Low Temperature Tin-Bismuth Electroplating System," International Patent Application PCT/US92/08485, April 1993
7. H.P. Wilson, "Bismuth Composition, Method of Electroplating a Tin Bismuth Alloy and Electroplating Bath Therefor," U.S. Patent 4,331,518, May 1982
8. H.P. Wilson, "Electrodeposited Eutectic Tin-Bismuth Alloy on a Conductive Substrate," U.S. Patent 5,039,576, Aug 1991
9. F.A. Lowenheim, Ed., *Modern Electroplating,* 3rd ed., Wiley, 1974, p 531-533
10. Nicostan product data sheet, LeaRonal, Freeport, NY
11. Techni Tin-Nickel product data sheet, Technic, Inc., Cranston, RI

Zinc Alloy Plating

Nabil Zaki, Frederick Gumm Chemical Company, Inc.

Introduction

ZINC ALLOY PLATING has found significant use since about 1980 in Japan and Europe, and more recently in the United States. The driving force behind the development of this technology was the quest for higher-performance coatings, especially in the automotive industry. Another driver was the urgent need to find an adequate replacement for cadmium plating; cadmium is highly toxic and has been banned in many industrial countries.

The use of zinc alloys provides several advantages. Electrochemically, alloys have different corrosion potentials from their alloying elements. Alloys of zinc, for example, can be designed to maintain anodic protection to steel, but remain less electrochemically active than pure zinc. Thus, a zinc alloy coating can still be sacrificial to steel components, but corrodes much more slowly than zinc when exposed to a corrosive environment.

Several zinc alloy processes are currently in commercial use. The choice of a particular process depends on the end-product requirements and conditions of use. Available alloys are zinc-iron, zinc-cobalt, zinc-nickel, and tin-zinc. As in unalloyed zinc plating, chromate conversion coating post-treatments are used to improve the overall corrosion resistance of the alloy, and especially to retard the bulky "white rusting" characteristic of unalloyed zinc. Specialty chromating processes designed to work with these alloys are used for this purpose. See the article "Zinc Plating" in this Volume for more information.

Zinc-Iron Plating

Zinc-iron plating produces alloys containing 15 to 25% Fe as-plated. Advantages of this alloy are good weldability and ductility. It is electroplated on steel coil and strip for auto bodies. Strip for the manufacture of automotive components is also plated in baths that produce 1% Fe in the alloy deposit; a special feature of this alloy is its suitability for deep black chromating.

The corrosion resistance of zinc-iron is generally lower than that of the other zinc alloys, especially after exposure to high temperatures such as those encountered by under-the-hood automotive components. A typical zinc-iron solution composition used in strip line plating is:

Constituent	Content	
	g/L	oz/gal
Ferric sulfate	200-300	27-40
Zinc sulfate	200-300	27-40
Sodium sulfate	20-40	2.7-5.3
Sodium acetate	10-30	1.3-4
Organic additive	1-5	0.1-0.66

Zinc-Cobalt Plating

Zinc-cobalt coatings contain 0.6 to 2% Co. Zinc-cobalt alloys find extensive use for relatively inexpensive components in applications that require improved abrasion resistance and corrosion protection. Typically, an 8 μm film with 1% cobalt will last up to 500 h in a neutral salt spray test before red rust if the proper chromate is applied. Some reduction in corrosion resistance is experienced after exposure to high temperature, but not as much as with zinc-iron alloys. A unique attribute of zinc-cobalt is its corrosion resistance to sulfur dioxide in accelerated corrosion tests. This suggests that these coatings may be suitable for use in sulfur-containing corrosive environments.

There are two types of zinc-cobalt plating baths; acid and alkaline. Alkaline baths are preferred for tubes and other configurations with internal unplated areas. Exposure to acidic electrolyte reduces the corrosion resistance of such parts. Available chromates include clear, yellow, iridescent and black.

Typical zinc-cobalt bath compositions and process parameters are given in Table 1.

Table 1 Compositions and process parameters for zinc-cobalt plating solutions

Constituent or parameter	Amount or value
Acid baths	
Zinc chloride, g/L (oz/gal)	80-90 (10-12)
Potassium chloride, g/L (oz/gal)	150-200 (20-27)
Ammonium chloride[(a)], g/L (oz/gal)	50-70 (7-9)
Boric acid[(a)], g/L (oz/gal)	20-30 (3-4)
Cobalt chloride, g/L (oz/gal)	1-20 (0.1-2.7)

Organic additive, g/L (oz/gal)	5-20 (0.66-2.7)
pH	5.0-6.0
Temperature, °C (°F)	20-40 (70-100)
Anodes	Zinc
Alkaline baths	
Zinc oxide, g/L (oz/gal)	10-20 (1.3-2.7)
Sodium hydroxide, g/L (oz/gal)	80-150 (10-20)
Cobalt salt complex, g/L (oz/gal)	1.0-2.0 (0.1-0.3)
Organic additive, g/L (oz/gal)	5-10 (0.66-1.3)
Temperature, °C (°F)	25-40 (77-100)
Anodes	Zinc

(a) Used only in some compositions

Zinc-Nickel Plating

Zinc-nickel alloys produce the highest corrosion resistance of electroplated zinc alloys. These alloys contain from 5 to 15% Ni. Corrosion resistance improves with nickel content up to 15 to 18%. Beyond this range the alloy becomes more noble than steel and loses its sacrificial protection property. An alloy containing 10 to 13 wt% Ni is electroplated on steel strip and coil as an alternative to zinc-iron or electrogalvanizing. An advantage of this composition is the formability of the steel after coiling. For components, chromatizing is required; however, best results are achieved on alloys containing 5 to 10% Ni. For alloys in this range of nickel content, corrosion resistance to neutral salt spray reaches 1000 h or more before red rust. An advantage of zinc-nickel alloys is their retention of 60 to 80% of their corrosion resistance after forming and after heat treatment of plated components. This attribute makes these alloys suitable for automotive applications such as fasteners, brake and fuel lines, and other under-the-hood components.

Zinc-nickel alloys plated from alkaline baths have shown potential as substitutes for cadmium coatings in aircraft and military applications. Available chromates are clear, iridescent, bronze, and black. Typical zinc-nickel bath compositions and process parameters are given in Table 2. Alkaline formulations are preferred for their ease of operation and because they provide more uniform alloy composition and better overall corrosion resistance, especially on tubing and on internal configurations of parts.

Table 2 Compositions and process parameters for zinc-nickel plating solutions

Constituent or parameter	Amount or value

Acid baths	
Zinc chloride, g/L (oz/gal)	120-130 (16-17)
Nickel chloride, g/L (oz/gal)	110-130 (15-17)
Potassium chloride, g/L (oz/gal)	200-250 (27-33)
Ammonium chloride[(a)], g/L (oz/gal)	100-200 (13-27)
Organic additives, g/L (oz/gal)[(a)]	5-10 (0.66-1.3)
pH	5-6
Anodes	Zinc and nickel connected to two separate rectifiers
Alkaline baths	
Sodium hydroxide, g/L (oz/gal)	100-130 (13-17)
Zinc, g/L (oz/gal)	6-15 (0.8-2.0)
Nickel, g/L (oz/gal)	0.5-1.5 (0.07-0.20)
Organic additives, g/L (oz/gal)	2-5 (0.25-0.66)
Anodes	Zinc and steel, one rectifier
Temperature, °C (°F)	20-35 (70-95)

(a) Used only in some compositions

Tin-Zinc Plating

Tin-zinc alloys contain 70 to 90% Sn and 10 to 30% Zn. Cyanide, acid, and neutral commercial baths are available. Tin-zinc baths are expensive to operate because they require the use of special cast tin-zinc anodes. Tin-zinc alloys exhibit excellent solderability, ductility, and corrosion resistance.

Chromate posttreatments are limited to yellow or clear. The tin-zinc deposit is semibright as-plated and is used primarily as a functional coating. Tin-zinc is finding increasing application in the automotive and electronic industries and as a substitute for cadmium plating.

Additional information about tin-zinc coatings is contained in the article "Tin Alloy Plating" in this Volume.

Corrosion Protection

Corrosion rates for zinc alloy coatings as demonstrated by the neutral salt spray test are:

Coating[a]	Hours to red rust
Zinc	200-250
Zinc-iron (1% Fe)	350
Zinc-cobalt (0.8% Co)	500
Zinc-nickel (8% Ni)	1000
Tin-zinc (70% Sn)	1000

(a) Coating thickness, 8 μm; iridescent yellow chromate post-treatment

Nickel Alloy Plating

S. Alec Watson, Nickel Development Institute

Introduction

NICKEL ALLOYS electroplated for engineering applications include nickel-iron, nickel-cobalt, nickel-manganese, and zinc-nickel. Zinc-nickel plating is covered elsewhere in this Volume; see the article "Zinc Alloy Plating." Iron is a cheap metal, and solutions for plating nickel-iron alloys were developed mainly in order to reduce the cost of the metal used to form a layer of given thickness, but they were also developed for special magnetic purposes. Cobalt and manganese are used to increase the hardness and strength of nickel plating. Additionally, nickel-manganese alloys have improved resistance to sulfur embrittlement when heated. Alloy layers 20 to 30 μm thick of nickel with about 15% Mo exhibit higher hardness and resistance to corrosion than pure nickel but at the expense of a reduction in ductility to around 1% (Ref 1). Coatings of nickel-tungsten show very high resistance to corrosion, but they are believed not to be true alloys (Ref 2) and have not been used in practice. This article will discuss the alloys nickel-iron, nickel-cobalt, and nickel-manganese that are of practical interest, plus a few paragraphs on nickel-chromium binary and ternary alloys.

References

1. E. Chassaing, K. Vu Quang, M.E. Baumgärtner, M. Funk, and Ch.J. Raub, High Temperature Ni-Mo Electrodeposited Alloys--Structure and Properties, *Plating and Surface Finishing,* Vol 77 (No. 8), Aug 1990, p 60-65
2. G. Raucher, V. Rogoll, M.E. Baumgärtner, and Ch.J. Raub, Investigation of the Dissolution Behaviour of Electrodeposited Ni-W Layers in Concentrated Hydrogen Chloride Solution, *Transactions of the Institute of Metal Finishing,* Vol 71 (Part 3), Aug 1993, p 95-98

Nickel-Iron

Bright nickel-iron plating was strongly promoted as a substitute for bright nickel plating in the period from 1970 to the early 1980s when the relative price of nickel was high (Ref 3, 4, 5, 6).

Advantages. The main advantage of the alloy is the significant saving in the cost of metal, because up to 35% of the nickel is replaced by iron. An additional advantage is that iron entering the plating solution through chemical dissolution of steel substrates, which is highly detrimental in straight nickel plating solutions, is readily dissolved and subsequently plated out. This feature is particularly relevant during plating onto tubular steel parts. Ductility is usually higher for the alloy coatings than for bright nickel, which may be advantageous if the plated parts are subject to deformation.

Disadvantages. The organic addition agents are more expensive than those needed for bright nickel, substantially negating the saving on metal. The addition agent system is also more complex so that electrolyte control is more difficult. At equal thickness, nickel-iron plating is less resistant to corrosion than nickel, and the higher the iron content, the lower its resistance. The corrosion product is rust-colored, and there is no international standard for the alloy coatings.

Process Description. Preferred solutions for plating bright nickel-iron are slightly more dilute than nickel plating solutions in order to obtain a high-iron alloy without using a high iron concentration in the solution. A typical solution is given in Table 1 (Ref 4). Addition agents include stabilizers for the ferrous iron, organic brighteners, leveling agents, and wetting agents. Total iron includes ferrous and ferric ions, and it is important to control the ratio, with ferric usually below 20%. Solution temperature is typically 54 to 60 °C (130 to 140 °F), and solution pH must be kept low at 2.8 to 3.6. The solution is preferably used with air agitation rather than cathode-rod movement, because higher plating rates can be used, a higher iron content can be obtained in the deposits, and iron content can be altered at will by increasing or reducing the rate of air bubbling.

Table 1 Typical nickel-iron solution composition

Constituent	Amount, g/L (oz/gal)
Ni^{+2}	56 (7.46)
Iron (total)	4 (0.53)
$NiSO_4 \cdot 6H_2O$	150 (20.00)
$NiCl_2 \cdot 6H_2O$	90 (12.00)
$FeSO_4 \cdot 7H_2O$	20 (2.67)
H_3BO_3	45 (6.00)
Stabilizer[(a)]	15 (2.00)

(a) Concentration will vary between 10-25 g/L (1.3-3.3 oz/gal), depending on the type of stabilizer used.

Properties of the alloy deposits that are of interest include ductility, deposit hardness, internal stress, and magnetic properties.

Ductility depends on iron content, brightener concentration, solution temperature, and pH.

Deposit hardness varies with iron content. With iron content increasing from zero to about 10%, microhardness rises from 490 to 560 HK, then falls to around 510 HK with 49% Fe for coatings plated at standard conditions of 4 A/dm^2 (40 A/ft^2), 60 °C (140 °F), pH 3.5, and air agitation. Changes in solution pH and brightener concentration also influence deposit hardness, enabling values exceeding 700 HV to be achieved.

Internal stress is tensile, in contrast to that of most bright nickel deposits. It is influenced by iron content and, more sharply, by solution pH. Increasing iron content from 10.8 to 27.6% raises stress from 93 to 154 MN/m^2 (13,500 to 22,400 psi). Increasing pH from 2.8 to 4.5 raises stress from 17.5 to 230 MN/m^2 (2500 to 33,600 psi) (Ref 4).

Magnetic properties of nickel-iron are not important in the application of bright decorative coatings. Similar alloys are, however, deposited for magnetic applications from solutions not containing brightening additions (Ref 7). The alloys with 18 to 25% Fe are soft magnetic materials with low coercive force, low remanence, and high maximum permeabilities (Ref 8). They can be used as coatings or as electroformed parts (i.e., freestanding electrodeposited shapes detached from the substrate after being deposited).

References cited in this section

3. R.J. Clauss, R.A. Tremmell, and R.W. Klein, Decorative Nickel-Iron Alloy Electrodeposits: Present Status and Future Possibilities, *Transactions of the Institute of Metal Finishing,* Vol 53 (No. 1), Spring Conference 1975, p 22-27
4. R.A. Tremmell, Decorative Nickel-Iron Coatings: An Acceptable and Economic Alternative to Bright Nickel--No. I, *Plating and Surface Finishing,* Vol 68, Jan 1981, p 22-26
5. R.A. Tremmell, Decorative Nickel-Iron Coatings: An Acceptable and Economic Alternative to Bright Nickel-No. II, *Plating and Surface Finishing,* Vol 68, Feb 1981, p 30-33
6. J.S. Hadley and J. O'Grady, Corrosion Studies on Nickel-Iron Electrodeposits, *Transactions of the Institute of Metal Finishing,* Vol 59 (No. 3), Autumn 1981, p 89-92
7. P.J. Boden, D.E. Eastham, and M.E. Henstock, Recent Developments in the Electrodeposition of Permalloy Films, *Transactions of the Institute of Metal Finishing,* Vol 50 (No. 3), Summer 1972, p 117-118
8. H.H. Law, C.A. Holden, C.A. Mattoe, J. Sapjeta, Y. Degani, and T.H. Tiefel, Prototype Manufacture of Miniature Nickel/Iron Alloy Magnetic Sleeves for Optical Switching, *Plating and Surface Finishing,* Vol 79 (No. 8), Aug 1992, p 50-54

Nickel-Cobalt

Some of the earliest solutions for bright nickel plating contained cobalt, formate, and formaldehyde additions, but with the development of modern bright nickel solutions based on organic addition agents only, the cobalt-containing solutions have fallen into disuse. Today, the cobalt additions are used when it is necessary to increase the hardness and strength of nickel plating, especially in electroforming applications.

Advantages. Compared with nickel itself, nickel-cobalt alloys are harder and stronger. In contrast to nickel hardened with conventional organic addition agents such as naphthalene 1:3:6 trisulfonic acid, nickel-cobalt alloys can be heated to high temperatures without embrittlement by sulfur incorporated from addition agents.

Disadvantages. Compared with nickel alone, the need to maintain the level of cobalt ions in solution introduces an additional maintenance requirement. Also, deposit internal stress is moved in the tensile direction, and there is a practical limit to the level of cobalt that can be used. Hence the maximum hardness of about 400 HV is less than the 600 HV that can be attained using conventional organic additives.

Process Description. Most of the published data about nickel-cobalt plating were determined using the 600 g/L nickel sulfamate solution of the Ni-Speed process (Ref 9, 10, 11). The initial charge of cobalt is added to the base solution as cobalt sulfamate. Replenishment during operation of the solution is usually made by metered additions of cobalt sulfamate. It can, however, be achieved by dividing the anodic current between a nickel anode and a cobalt anode, so that the percentage of total current passing to the cobalt is the same as the percentage of cobalt required in the alloy deposited at the cathode. Good control of solution cobalt content by analysis is needed.

Processing Variables and Properties of the Alloy from 600 g/L Nickel Sulfamate Solution. With solution composition and pH standardized, the cobalt content and the properties of the alloys depend on solution temperature and deposition current density. The properties are modified by subsequent heat treatment (Ref 12, 13, 14) and by simultaneous use of sulfur-free organic addition agents (Ref 15). The main results of various studies were drawn together in 1989 (Ref 16).

Alloy Hardness. The relationship between cobalt content and deposit hardness is shown in Fig. 1. The broken curve shows microhardness versus cobalt content in the deposits formed at 5.4 A/dm^2 (50 A/ft^2), and the solid curve shows microhardness versus cobalt content in the solution. A peak hardness of about 520 HV is attained with 6 g/L Co in the solution, which gives an alloy containing about 34% Co. At peak hardness, internal tensile stress is too high for electroforming applications, although the alloy can be used as a coating on a solid substrate. For electroforming purposes, the limit of tolerable deposit stress is reached with alloys containing about 15% Co that have hardnesses around 350 to 400 HV.

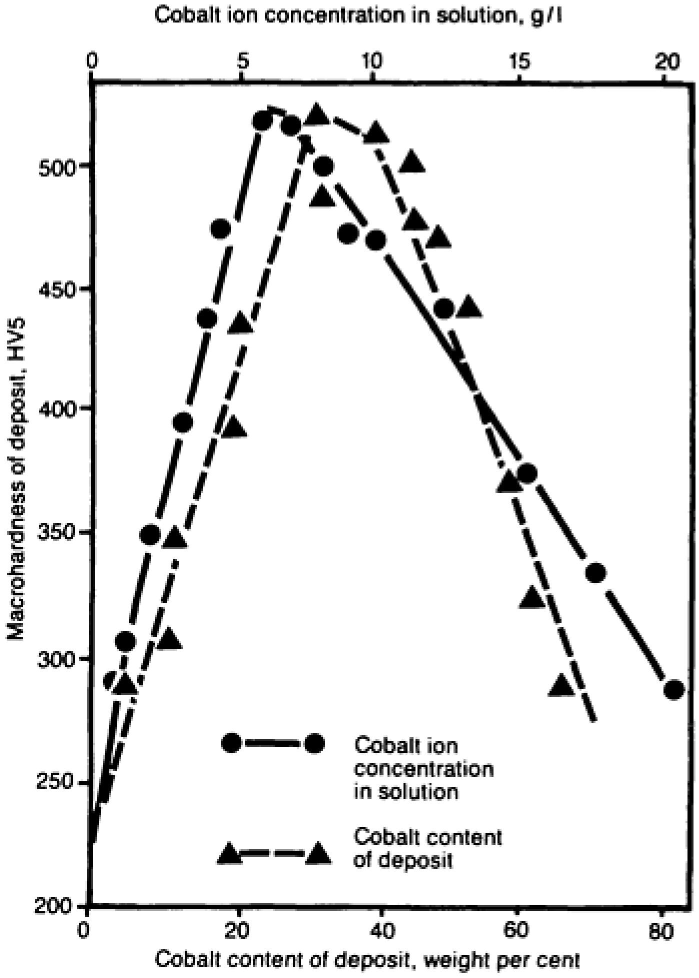

Fig. 1 Relationship between deposit hardness and cobalt concentration in the sulfamate solution and in the deposit

Alloy hardness depends on both the cobalt content of the solution and the deposition current density. Figure 2 shows hardness plotted against current density for different concentrations of cobalt in a solution operated at 60 °C(140 °F), pH 4.0. Deposit stress also depends on deposition current density, and moving left to right along any one of the curves, deposit stress changes from compressive through zero to tensile. The superimposed dotted line is a zero-stress contour linking the combinations of cobalt ion concentration and current density for zero-stress alloys. The corresponding value of deposit hardness can be read from the graph for each combination. The overall relationship is that the higher the cobalt ion concentration, the lower the current density that can be used for zero-stress alloys, but the higher the hardness of the alloy.

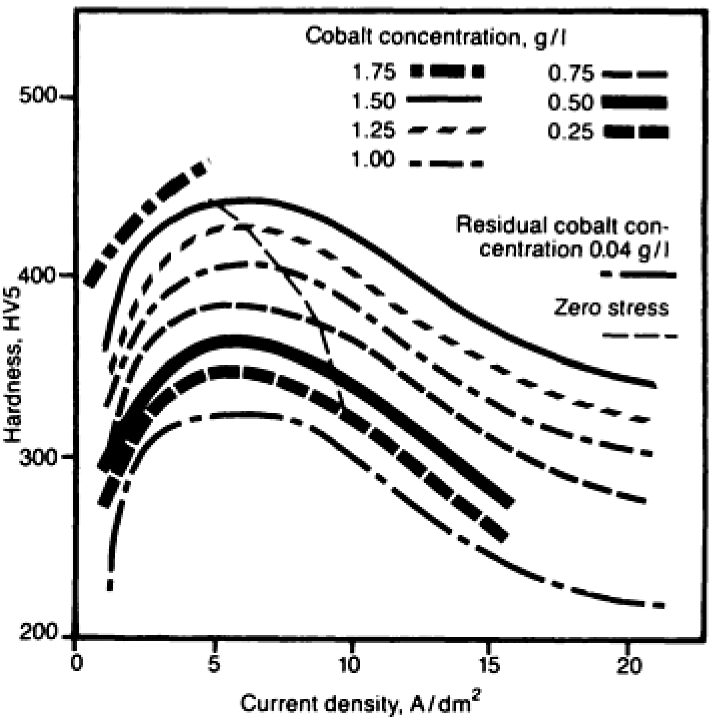

Fig. 2 Relationship between current density and alloy deposit hardness for various cobalt concentrations in solution with superimposed zero stress contour

Effect of Heat. Heating at temperatures up to 300 °C (570 °F) has little effect on the mechanical properties of the alloys. At higher temperatures deposit hardness falls, but nickel-cobalt alloys still retain greater hardness than that of nickel deposits similarly heat treated (Fig. 3).

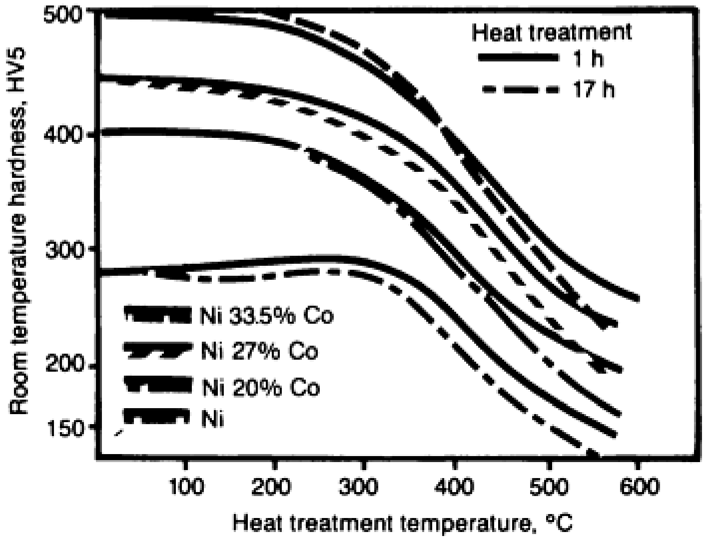

Fig. 3 Room-temperature hardness of electroformed nickel and nickel-cobalt alloys after heating

Tensile strength, 1034 MN/m^2 (150,000 psi) for a 15% Co alloy and 745 MN/m^2 (108,000 psi) for a 10% Co alloy (Ref 14), falls progressively as heat-treatment temperature is increased above 300 °C (570 °F) (Fig. 4). The effect is similar with proof stress, 677 MN/m^2 (98,000 psi) for an as-deposited 15% Co alloy and 531 MN/m^2 (77,000 psi) for a 10% Co alloy (Ref 14).

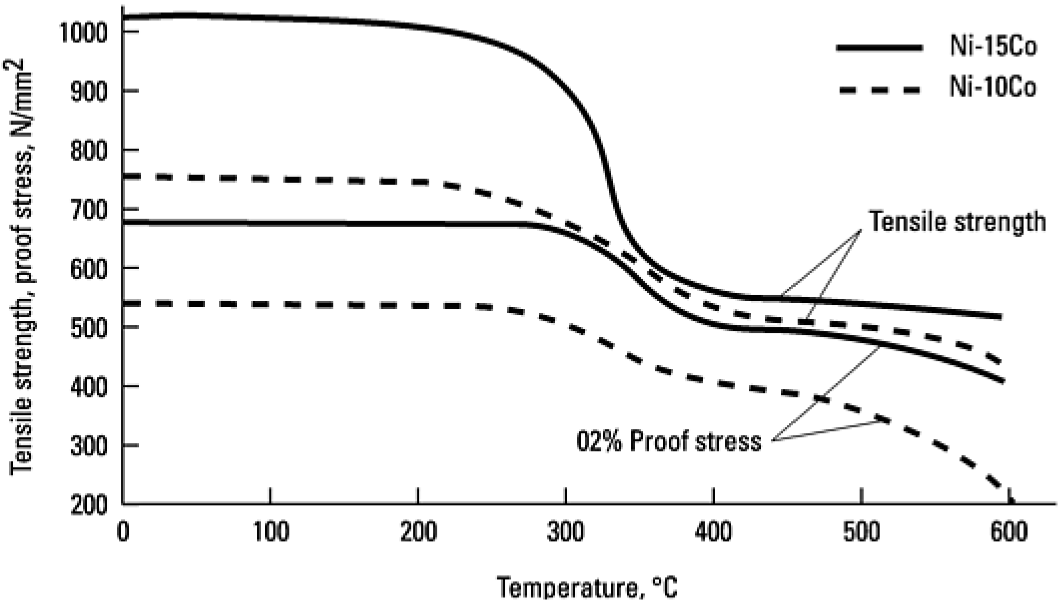

Fig. 4 Effect of heat treatment on the mechanical properties of Ni-10Co and Ni-15Co alloys

Deposit ductility increases on heating above about 300 °C (570 °F), from a value of 5% elongation as-deposited to about 40% after heating at 600 °C (1100 °F) for both 10% and 15% Co alloys (Fig. 5).

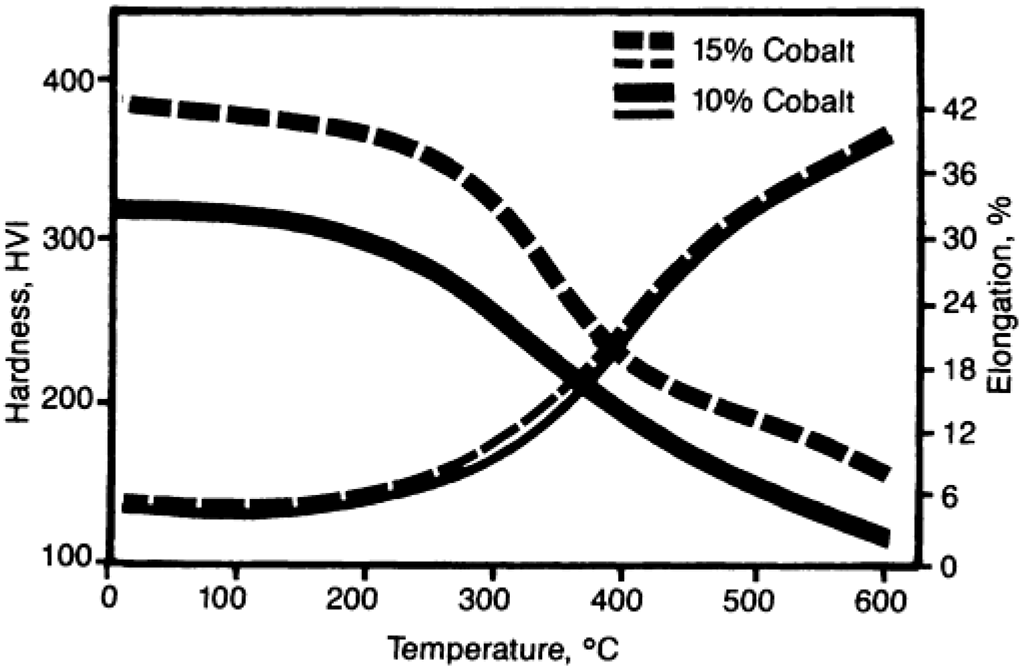

Fig. 5 Hardness and elongation of Ni-10Co and Ni-15Co alloys after heating to various temperatures

Properties of Alloys from Other Nickel Solutions. The above data apply to alloys from a 600 g/L nickel sulfamate solution. A Ni-14Co alloy deposited from a 450 g/L solution without chloride or organic additions, operated at 52 °C (126 °F), pH 4.0, and cathodic current density 2.5 A/dm^2 (23 A/ft^2) has a hardness of 350 to 400 HV, ductility less than 5%, and internal tensile stress of 50 to 60 MN/m^2 (7000 to 9000 psi) (Ref 17).

Measurements of the effects of heat treatment at 204 °C (400 °F) on alloys containing 53 to 55% Co indicate a small increase in yield strength, from 1062 MN/m^2 (154,000 psi) to 1124 MN/m^2 (163,000 psi), and a substantial increase in elongation, from 10 to 16% (Ref 18). Heat treatment at 260 °C (500 °F) or more reduces yield strength, as with alloys from the 600 g/L nickel sulfamate solution. Prior heat treatment of the 53 to 55% Co alloys at 204 °C (500 °F), 371 °C (700 °F), or 427 °C (800 °F) improves subsequent mechanical properties measured at a test temperature of 260 °C (500 °F). Thus pretreatment for 4 h at 427 °C (800 °F) increases yield strength from 372 to 448 MN/m^2 (54,000 to 65,000 psi) and elongation from 28 to 32%.

Alloys deposited from a sulfosalicylate-based solution exhibit a maximum hardness value above 700 HV (Ref 19). To date, this solution has not been used industrially.

References cited in this section

9. R.J. Kendrick, High Speed Nickel Plating from Sulphamate Solutions, *Transactions of the Institute of Metal Finishing,* Vol 41 (Advance Copy, International Conference), 1964; also Inco Publication 2782
10. R.J. Kendrick and S.A. Watson, Plating with Nickel Sulphamate, *Electrochimica Metallorum,* Symposium on Sulfamic Acid and Its Electrometallurgical Applications (Milan), 25-27 May 1966; also Inco Publication 4055
11. "The Ni-Speed Electrodeposition Process: Operating Conditions," Inco Publication 2902a
12. K.C. Belt, J.A. Crossley, and S.A. Watson, Nickel-Cobalt Alloy Deposits from a Concentrated Sulphamate Electrolyte, *Transactions of the Institute of Metal Finishing,* Vol 48 (No. 4), Autumn 1970, p 132-139
13. W.R. Wearmouth and K.C. Belt, The Mechanical Properties and Electroforming Applications of Nickel-Cobalt Electrodeposits, *Transactions of the Institute of Metal Finishing,* Vol 52 (No. 3), Summer 1974, p 114-118
14. W.R. Wearmouth, Application of New Developments in Electroforming Technology in the Toolmaking Industry, *Plastics and Rubber: Processing,* Vol 2 (No. 4), Dec 1977, p 131-138
15. W.R. Wearmouth and R.C.E. Bishop, Hard Smooth Stress-Free Electroformed Nickel for Video Discs, *Transactions of the Institute of Metal Finishing,* Vol 62 (No. 3), Autumn 1984, p 104
16. S.A. Watson, Additions to Sulphamate Nickel Solutions, Nickel Development Institute Technical Series, Publication 10053, 1989, p 1-7
17. W. Metzger and L. Läser, Electrolytic Manufacture of Line Gratings, *Galvanotechnik,* Vol 77 (No. 12), Dec 1986, p 2985-2986
18. R.J. Walter, Tensile Properties of Electrodeposited Nickel-Cobalt, *Plating and Surface Finishing,* Vol 73 (No. 10), Oct 1986, p 48-53
19. J. Vitec, J. Neuman, and P. Nejedly, Some Properties of Nickel-Cobalt Alloys Electrodeposited from Sulphosalicylate Solutions, *Transactions of the Institute of Metal Finishing,* Vol 69 (No. 3), Aug 1991, p 86-89

Nickel-Manganese

Embrittlement of nickel by incorporated sulfur when heated above 200 °C (390 °F) can arise by formation of brittle grain boundary films. In electrodeposits, the sulfur incorporation can result from the use of organic addition agents put into the solution in order to control internal stress in the plating. In these circumstances, manganese ions can be added to the solution so as to allow deposition of a nickel-manganese alloy resistant to sulfur embrittlement.

Manganese ions are also added in the absence of sulfur-bearing addition agents in the solution in order to produce nickel-manganese alloys that are stronger than plain nickel. There are both actual and potential applications of nickel-manganese alloy deposition in electroforming.

Advantages. The ability to neutralize the harmful effect of sulfur is not shared by iron or cobalt. Harder, stronger nickel alloys can be attained with manganese than with cobalt.

Disadvantages. Manganese does not codeposit as readily as iron or cobalt with nickel, and so nickel-manganese alloys contain much less manganese for a given concentration in solution of the second metal. Nickel-manganese alloys containing a useful amount of manganese tend to have high tensile internal stress and to be brittle.

Process Variables and Properties of the Alloys from Solutions with Stress Reducer. The percentage of manganese in the alloy at a fixed level of manganese in solution rises as deposition current density is increased, whether the solution is Watts-type, conventional sulfamate, or 600 g/L nickel sulfamate Ni-Speed (Ref 20). Manganese content rises from 0.02 to 0.03% at 4.3 A/dm^2 (40 A/ft^2) to 0.17 to 0.22% at 12.9 A/dm^2 (120 A/ft^2). These data were obtained in a solution that contained 15 g/L Mn and 0.25 g/L soluble saccharin to control deposit stress. Although sulfur uptake in the deposit also rises with increasing current density, by a half in the Watts and Ni-Speed solutions, the ratio of manganese content to sulfur content rises much more, from 1.1 to 6.2. Measurements of deposit ductility after heat treatment at various temperatures show that a higher ratio is required to avoid embrittlement for higher temperatures: 1.1 for 200 °C (390 °F) and 5.1 for 500 °C (930 °F) (Ref 20).

Alloy Hardness. As-deposited hardness of alloys plated with 15 g/L Mn and 0.25 g/L saccharin rises with an increase in percentage manganese in the alloy, from 287 HV at 0.02% Mn to 420 HV at 0.27% Mn when the base solution is Watts, and from 338 HV at 0.04% Mn to 445 HV at 0.23% Mn when the base solution is conventional sulfamate (Ref 21). Heat treatment for 22 h at 200 °C (390 °F) increases room-temperature hardness about 10% for all alloys with 0.1% Mn or more. Similar periods of heat treatment at 300 °C (570 °F) drastically reduce hardness to about 170 HV for all alloys irrespective of manganese content. Further increase in temperature to 400 °C (750 °F) or 500 °C (930 °F) has little further effect.

Internal stress in deposits from the 15 g/L Mn plus 0.25 g/L saccharin system is compressive for alloys deposited at up to 10.8 A/dm^2 (100 A/ft^2), whether the base solution is Watts, conventional sulfamate, or 600 g/L nickel sulfamate. Values lie in the range of 43 to 62 MN/m^2 (6200 to 9000 psi) for Watts, 62 to 91 MN/m^2 (9000 to 13,200 psi) for 600 g/L nickel sulfamate, and 94 to 100 MN/m^2 (13,600 to 14,500 psi) for conventional sulfamate (Ref 20). At the highest current density, 12.9 A/dm^2 (120 A/ft^2), the Watts deposit remains in its compressive range while the conventional and 600 g/L nickel sulfamate deposits show small tensile stress values, respectively 17 MN/m^2 (2500 psi) and 36 MN/m^2 (5200 psi). These low-stress deposits produced at 12.9 A/dm^2 (120 A/ft^2), with hardness values 420 to 443 HV, are harder than any low-stress alloys produced with the nickel-cobalt system.

Properties of Alloys from Solutions without Stress Reducer. Alloys deposited from straight nickel plating solutions with only manganese additions can have tensile strengths exceeding 1000 MN/m^2 (145,000 psi) and yield strengths up to 800 to 950 MN/m^2 (116,000 to 138,000 psi) (Ref 22). However, ductility is low when more than a small percentage of manganese is alloyed with the nickel, deposit internal stress is tensile, and the alloys may crack during formation. Nonetheless, such alloys have been used as rigid electroforms (Ref 23). Heat treatment of the alloys increases ductility and relieves stress, the values depending on heat-treatment temperature and manganese content, and deposit properties can be further modified using pulse plating during deposition of the alloys (Ref 22).

References cited in this section

20. W.R. Wearmouth and K.C. Belt, Electroforming with Heat-Resistant Sulfur-Hardened Nickel, *Plating and Surface Finishing,* Vol 66, Oct 1979, p 53-57
21. W.R. Wearmouth, Nickel Alloy Electrodeposits for Non-Decorative Applications, *Transactions of the Institute of Metal Finishing,* Vol 60 (No. 2), Summer 1982, p 68-73
22. G.A. Malone, New Developments in Electroformed Nickel-Based Structural Alloys, *Plating and Surface Finishing,* Vol 74 (No. 1), Jan 1987, p 50-56
23. G.A. Malone, Multi-Stage Electroforming of High Energy Chemical and Excimer Laser Components, *Plating and Surface Finishing,* Vol 75 (No. 7), July 1988, p 58-62

Nickel-Chromium

There are many references in the published literature to the deposition of nickel-chromium and iron-nickel-chromium alloys from simple salt solutions, but these solutions have not achieved commercial application except for a proprietary process used for depositing thin decorative coatings (Ref 24).

Alloys of nickel with 22% Cr can be prepared by codepositing chromium carbide particles with nickel followed by heat treatment for 24 h at 1000 °C (1800 °F) in hydrogen. Hardness of the alloy after the heat treatment is 223 HV, compared with 55 HV for similarly treated plain nickel (Ref 21, 25).

Alloys containing 19% Co or 20% Fe in addition to chromium are produced by codepositing chromium carbide from nickel-cobalt or nickel-iron base solutions and heat treating (Ref 21).

Heat treatment in hydrogen gives almost complete decarburization with the nickel-cobalt-chromium alloy, and hardness after heat treatment is 215 HV. Approximately 0.8% C remains in the nickel-iron-chromium alloy, however, which might account for its higher hardness, 332 HV.

References cited in this section

21. W.R. Wearmouth, Nickel Alloy Electrodeposits for Non-Decorative Applications, *Transactions of the Institute of Metal Finishing,* Vol 60 (No. 2), Summer 1982, p 68-73
24. M. Law, Electrodeposition of a Ternary Alloy of Chromium, *Finishing,* Vol 8 (No. 7), July 1984, p 30-31
25. A.C. Hart and W.R. Wearmouth, U.K. Patent 1,476,099, 10 June 1977

Environmental, Health, and Safety Considerations

For practical purposes, the environmental, health, and safety considerations for these nickel-base alloys and their production are the same as those for nickel and nickel plating.

Environmental Considerations. Nickel is a naturally occurring constituent of our day-to-day environment. The soil worldwide contains 5 to 500 ppm Ni, with an average of 100 ppm. Food is grown and consumed in areas with higher levels still, without leading to any health problems for the inhabitants (e.g., 661 ppm in Hawaii) (Ref 26). Nickel has been determined to be an essential trace element for plant life, and some plants that accumulate nickel are regularly eaten by people with no harmful effects. Nickel is also present naturally in the atmosphere, rivers, seas, and oceans. Nonetheless, the desire to maintain the natural environment as it is has led to the establishment of maximum permitted levels for the discharge of nickel and other metals by industry. In nickel plating, the levels are attained by measures to reduce spray emission, process solution dragout, and effluent treatment. Details of all necessary techniques are available from suppliers to the metal finishing industry.

Health and Safety Considerations. Some 1.2% of men and 10 to 15% of women are sensitized to nickel and, when exposed to prolonged skin contact with nickel metal, certain nickel alloys, or nickel-containing solutions, may develop dermatitis at the point of contact. The occurrence of nickel contact dermatitis was first observed as a result of exposure to nickel-containing solutions in electrorefining of nickel. Today most electroplaters are aware of "nickel itch" but have never seen a case of it. The reason is that, despite increasing use of nickel-containing products, industry has adopted work practices that prevent occurrence of contact dermatitis. Today, nickel contact dermatitis occurs most frequently as a result of domestic exposures from close and persistent contact of the skin with nickel-plated articles or with certain nickel alloys. Accordingly, legislation in Europe will control the use of nickel metal, nickel alloys, and nickel-containing materials that come in contact with the skin. The main problem is with those articles that come into direct and prolonged contact, such as earrings, necklaces, bracelets, watch cases and straps, buttons, and rivets. It is important to note that nickel alloys that do not react with sweat do not cause dermatitis. Transient contact with nickel or nickel alloys is not damaging because there is insufficient time for reaction with sweat to form the soluble products that can penetrate the skin (Ref 27).

In nickel plating, plant design, exhaust ventilation, and methods of operation should be such as to avoid any risk of skin contact with the solutions. Protective clothing should be inspected regularly for leaks and tears. Where protective gloves are necessary it is recommended that cotton inner gloves be worn to reduce perspiration. The outer gloves should be rinsed off before removal to prevent process solution transfer to the hands or the inside of the gloves on removal (Ref 28).

A few cases of asthma, claimed to be nickel-induced, have reportedly arisen from aerosols of soluble nickel salts. The content of nickel in the atmosphere should be kept below the occupational exposure limit.

There is evidence that inhalation of some nickel compounds (nickel oxide, nickel subsulfide) occurring in the atmosphere associated with certain nickel refining operations may cause respiratory cancers in humans. There is no good evidence

that occupational exposure to metallic nickel or nickel oxide, sulfate, or chloride during plating or polishing is associated with increased mortality due to cancer (Ref 29).

References cited in this section

26. B.K. Davison, BKD Consulting, personal communication, 1994
27. "Nickel and Nickel Alloy Articles That Come into Contact with the Skin," Nickel Development Institute Status Report, Toronto, Sept 1992
28. "Nickel: Meeting the Control Limits for Nickel and Its Inorganic Compounds," Health and Safety Bulletin 1, The Metal Finishing Association, Birmingham, England, June 1991
29. The Toxicity of Nickel and Its Inorganic Compounds, Toxicity Review 19, Her Majesty's Stationery Office, London, 1987

Chromium Alloy Plating

Eric W. Brooman, Concurrent Technologies Corporation

Introduction

CHROMIUM ALLOYS, which are relatively difficult to deposit, yield alloy coatings with properties that range from completely satisfactory to marginally acceptable, depending on the end use. The idea of depositing a thin, stainless steel type of coating has been receiving renewed interest since the 1970s. Stainless steel coatings would conserve strategic metals, facilitate the manufacturing process, and lower cost if they could be applied to strip or sheet, or to a component that has been fabricated to the required size and shape. This would also mean that a component could be made from a material that is more easily worked than stainless steel.

For both chromium and stainless steel types of alloys, the most important properties to develop in a coating are corrosion resistance, abrasion and wear resistance, hardness, surface texture, and luster. Thickness requirements can range from a few microns up to a few hundred microns. Thicker coatings are rarely specified, primarily because the relatively poor throwing power of the plating solution gives an uneven surface coverage. Further, the low plating efficiencies can lead to high internal stresses from hydrogen uptake. The resulting microcracking has a detrimental effect on coating properties.

It is difficult to deposit chromium from aqueous solutions because of its low hydrogen overvoltage. As a result, cathodic coulombic efficiency typically ranges from 10 to 20% for commercial processes. In order to deposit chromium-containing alloys, it is usually necessary to implement the approaches summarized below and described more fully in Ref 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11:

- Complexing agents are needed to bring the deposition potentials of the alloying metals (e.g., nickel and iron) closer together.
- The plating solution should contain a greater proportion of chromium salts, relative to the alloy addition, in order to obtain significant amounts of chromium in the deposits.
- Care must be taken to deposit metallic coatings rather than hydrated, chromium-containing salts, especially if chloride-base solutions are used.
- Close control of temperature, agitation, current density, and pH is necessary with most of the reported solution chemistries, in order to obtain reproducible alloy compositions and properties, as well as reasonable plating rates.
- Trivalent chromium-base solution chemistries provide better prospects for depositing satisfactory alloy coatings from aqueous solutions. An additional benefit is that waste-treatment requirements are less stringent than they are for hexavalent chromium-base solutions.
- The chromium concentration in the alloy should be limited in order to avoid microcracking.
- Aqueous solutions with a low pH value (between 1 and 3) seem to produce better deposits than solutions with pH values outside this range.
- Nonaqueous solutions, especially those based on molten salts, can provide useful alloy deposits.

However, these tend to be relatively thick.

- Thin deposits offer the best prospect for providing lustrous finishes.
- Post-plating heat treatments can sometimes improve the mechanical properties and corrosion resistance of the deposits.

References to chromium alloy plating date back to the mid-1950s, when corrosion- and wear-resistant coatings were first developed for the inside of gun barrels used in military applications, and patents date back to circa 1970. This article will emphasize just the work performed since the 1980s. Those chromium alloys that contain nickel or iron or both are discussed first, because of their importance. Other alloying elements that have been deposited with chromium are discussed as a group, in less detail.

The variables and techniques available to apply coatings based on chromium and other alloys are extensive (Table 1). Because of space limitations, many of these variables or options are mentioned only briefly, where appropriate, and the discussion of deposit properties is similarly limited.

Table 1 Technology options for the deposition of chromium-base alloys

Type of bath
Aqueous
Acid
Alkaline
Nonaqueous
Organic
Molten salt
Applied current
None (electroless)
Conventional direct current
Pulsed direct current
Periodic reversed direct current
High-speed direct current
High-speed pulsed direct current
Composition
Alloy
Mixture
Amorphous
Structure
Homogeneous
Multilayer
Composite

Dispersed
Post treatments Heat treatment Diffusion Laser glazing

References

1. V.M. Dokras, Codeposition of Nickel and Chromium, *Symp. Electroplat. Met. Finish.,* Vol 5, 1952, p 134-139
2. C. Levy, Electrodeposition of Chromium Alloys, *Met. Finish.,* Vol 57 (No. 8), 1962, p 59-62
3. A. Brenner, Electrodeposition of Chromium Alloys, in *Electrodeposition of Alloys,* Vol II, Academic Press, Inc., 1963
4. M. Sarojamma and T.L. Rama Char, Electrodeposition of Stainless Steel, *Electroplat. Met. Finish.,* Vol 23 (No. 10), 1970, p 13-20
5. R. Sivakumar and T.L. Rama Char, Electrodeposition of Ternary Alloys: 1964-1969 Developments, *Electroplat. Met. Finish.,* Vol 24 (No. 1), 1971, p 14-27
6. M. Bonnemay and J. Royon, "Electrolytic Deposition of Chromium Alloys: Factors of Electrolysis," Bulletin of the Information Center for Hard Chromium, June-July 1973, p 12-22
7. H. Benninghoff, Functional Electroplating: Properties of Electrodeposited Metal and Alloy Coating, II--Chromium, Chromium-Iron-Nickel Alloys, Copper Plus Nickel Plus Chromium Systems, Nickel Plus Chromium Systems, Dispersion Systems, *Metalloberfläche,* Vol 33 (No. 9), 1979, p 361-371
8. S.C. Srivastava, Electrodeposition of Ternary Alloys: Developments in 1972-1978, *Surf. Technol.,* Vol 10, 1980, p 237-257
9. M.A. Shulgar and L.D. Tok, New Electrolytes for Chromium and Chromium Alloy Plating, *Zh. Vses. Khim, Ova. im D.I. Mendeleeva,* Vol 33 (No. 3), 1988, p 297-305
10. V.V. Bondar et al., Electrodeposition of Amorphous Chromium and Alloys Based on It, *Itogi Nauki Tekh., Ser.-Electrokhhim.,* Vol 33, 1990, p 37-49
11. "Electroplating of Chromium (Latest Citations from the Compendex Database)," NTIS Accession No. PB93-873412/XAB, NERAC, Inc., June 1993

Chromium-Iron, Chromium-Nickel, and Chromium-Iron-Nickel Alloys

Chromium-Iron Alloys. In contrast to nickel-iron alloys, which have been investigated to replace materials based on iron-nickel alloys in magnetic applications, relatively little work has been done on the chromium-iron analog. No well-defined, large-volume manufacturing application exists for the latter.

Chromium-iron alloys have been deposited from sulfate solutions. Early work in India favored a mixed sulfate-citrate solution (Ref 12), but more recent work used sulfates (Ref 13). Deposits were obtained at low pH levels, near-ambient temperatures, and low current densities (~10 A/dm^2, or 100 A/ft^2). In Japan, the emphasis has been on using modified, commercial trivalent chromium solutions (Ref 14, 15). One patent specifically calls for the presence of divalent chromium ion (Ref 16). The divalent chromium solution also operates at a pH less than 2.0, but at higher temperatures (30 to 80 °C, or 80 to 175 °F) and higher current densities (10 to 80 A/dm^2, or 100 to 800 A/ft^2). In the United States, some work has been performed with a mixed trivalent/hexavalent solution (Ref 17, 18, 19). These efforts focused on using organic additives, such as alcohol, to improve deposit properties. However, solution chemistry and plating efficiencies

changed with time, and the deposits tended to be lamellar (banded). Different bands contained different amounts of chromium (up to 90 wt%). The addition of barium carbonate was said to give crack-free coatings.

If suitable additives are used, then chromium can be deposited as an amorphous coating with excellent properties (Ref 19). Recently, it has been shown that amorphous coatings containing chromium, iron, and other minor elements (such as phosphorus and carbon) also can be electrodeposited. Corrosion-resistant amorphous alloys have been obtained from an acid-citrate-base solution containing sodium hypophosphite (Ref 20). Unfortunately, deposits from this solution with greater than 10 wt% Cr are rough and porous. Also, a semipermeable membrane is needed to prevent oxidation of trivalent chromium at the anode.

Other investigators have reported on the use of a chromic acid/formic acid solution containing ferrous chloride and sulfuric acid (Ref 21), or a sulfate-base solution containing organic additives such as sodium citrate and several organic acids (Ref 22). Deposition conditions were similar to those described above for chromium-iron alloys plated from trivalent chromium-type solutions. The sulfate-base solution type also required the use of a semipermeable membrane.

Chromium-Nickel Alloys. The early work on the deposition of chromium-nickel alloys from aqueous and nonaqueous (organic) plating solutions is summarized in Ref 23. Most of the solutions referenced gave poor deposits, and plating efficiencis were low. Deposit quality decreased as plating time increased and as the solution aged. As a result, banded deposits were often obtained, and each band had a slightly different composition. Subsequent work in the United States and Europe gave similar results.

For example, a patented process (Ref 24) calls for using a solution comprising chromous (trivalent) chloride, nickelous chloride, formic acid, boric acid, and sodium nitrate. The solution is operated at 20 to 60 °C (70 to 140 °F), and the chromium content in the deposit is a function of current density and the duty cycle of the pulsed current used. Low duty cycles and high current densities (>70 A/dm^2, or 700 A/ft^2) yield the highest chromium contents (about 60 to 70 wt%). The layered alloy structures are more corrosion resistant in acidic and chloride environments than sulfamate nickel, hard chromium deposits, or conventional stainless steels.

Continued interest has been shown in dimethylformamide-base solutions containing between 10 and 50% water (Ref 25, 26). Water content, temperature, and current density exert a strong influence on deposit quality and composition with such solutions. At low temperatures (7 to 15 °C, or 45 to 60 °F) and high current densities, chromium-rich alloys can be obtained. At higher temperatures (20 to 35 °C, or 70 to 95 °F), nickel-rich deposits are produced. Thicker deposits were cracked and layered in those solutions that contained chromic (hexavalent) chloride, nickelous chloride, ammonium chloride and boric acid, with vanadyl sulfate in some cases. Agitation helps to minimize the banding effect (Ref 26).

Two problems to avoid when plating chromium-nickel alloys are localized pH changes at the cathode surface, which can lead to the precipitation of a hydrated chromium compound, and excessive amounts of divalent chromium in trivalent chromium solutions (Ref 27). Divalent chromium is a strong reducing agent and can precipitate nickel as metal, leading to dark, powdery deposits. In some sulfate-base solutions, commercial nickel-chromium alloy anodes are not satisfactory (Ref 28) because they passivate, or dissolve, to produce hexavalent chromium, which interferes with the alloy deposition process. A plating cell that can alleviate this problem incorporates an ion-exchange membrane (Ref 29). If chloride ions are present in the solution, the problem with passivation can be overcome (Ref 28).

A Japanese patent (Ref 30) claims that satisfactory alloy deposits can be obtained from an organic (imide base) electrolyte containing boric acid and nickel and chromium sulfates. Bright deposits are said to be obtained at a pH equal to 2.5, a temperature of 50 °C (120 °F), and a current density of about 25 A/dm^2 (250 A/ft^2). A nickel-chromium alloy anode can be used.

Amorphous chromium-nickel deposits, which are similar to chromium-iron coatings, also can be obtained, either by electroless (Ref 31, 32) or electrolytic (Ref 33, 34) techniques. These amorphous coatings contain either phosphorus or boron as a minor alloying element, and they provide excellent corrosion resistance if they do not contain any microdiscontinuities, such as pores and cracks.

Chromium-Nickel-Iron Alloys. Although electrodeposited stainless steel type alloys have been deposited, they have had limited commercial success. These coatings did not exhibit comparable corrosion resistance, unless a significant thickness of nickel was first deposited. Although lustrous coatings can be obtained, they tend to be darker in color than the "blue-white" color traditionally associated with decorative chromium or polished stainless steel.

Several patents exist for depositing chromium-nickel-iron alloys (Ref 35, 36, 37), but only one process has been made available commercially. It is known as the "Oztelloy" process, originally promoted in the United Kingdom in the early 1980s (Ref 38). The coating consists of two layers. The first layer is a thick deposit of nickel, and the second layer is an alloy of 55Cr-10Ni-35Fe (wt%). To obtain good corrosion resistance, at least 8 wt% Ni is necessary. The solution is a complexed chloride-base electrolyte operating at a pH of 2.4, a temperature of 25 °C (77 °F), and a current density ranging from 12 to 22 A/dm^2 (120 to 220 A/ft^2). Carbon rods are used as anodes. The deposition rate is slow for the alloy layer (~0.2 to 0.3 μm/min, or 8 to 12 μin./min), and chlorine gas is evolved at the anode. Therefore, proper ventilation above the plating tank is required. Other investigators (Ref 39, 40) have attempted to use complexed, mixed chloride solutions to deposit ternary alloys, but with less success.

Ternary chromium-nickel-iron alloys have been obtained by some Japanese researchers (Ref 41), who used a mixed sulfamate electrolyte with an excess of the iron salt and a high concentration of the chromium salt. The solution also contained potassium citrate and potassium fluoride. It was operated at temperatures ranging from 30 to 50 °C (85 to 120 °F) and a current density ranging from 1.0 to 2.5 A/dm^2 (10 to 25 A/ft^2). The cathode efficiency ranged from 20 to 40%, and bright, fine-grained, homogeneous deposits were said to have been obtained. Fine-grained, semibright to fully bright deposits also have been obtained from a mixed sulfate solution containing boric acid and glycine (Ref 42). However, in chloride solutions, the corrosion resistance of those deposits was not as good as that of comparable conventional stainless steels.

In an effort to obtain homogeneous, crack-free deposits, techniques based on high-speed interrupted current (Ref 43) and periodically reversed current (Ref 44) have been tried, but their success also has been limited. Both pulsed current approaches used a trivalent chromium solution as the base electrolyte, with various additives. With the periodically reversed current approach, low-carbon steel anodes and a semipermeable membrane were used. The pulse frequency was 10 to 15 Hz, and the current density was approximately 20 A/dm^2 (200 A/ft^2). In the former approach, a semipermeable membrane was not necessary because a flowing electrolyte was used. Ternary iron-chromium-nickel alloys (stainless steels) were used as anodes. Deposits with low internal stress were obtained, but only thick coatings provided good corrosion resistance. Heat treating the highly stressed coatings obtained with the periodically reversed current technique did not improve their properties.

In the United States, a novel approach to producing chromium-nickel-iron coatings has been developed specifically for applications that require thick coatings or electroforms (Ref 45). The technique consists of codepositing chromium particles from a nickel-iron sulfate-base alloy plating solution. Subsequent heat treatment of the deposit at 1100 °C (2010 °F) for 8 h in a vacuum or under an inert gas yields a homogeneous, ternary, stainless steel type alloy coating. When depositing the coating, care must be exercised to prevent oxidation of the ferrous ions in the solution. When ferric ions are present, they prevent the occlusion of the chromium particles. The deposited coatings can be polished to provide a lustrous finish.

Other Chromium-Base Alloys. Attempts to deposit chromium-cobalt alloys have been made using fluoborate and dimethylformamide/water solutions (Ref 46). Like many chromium alloys that were plated from similar solutions, it was difficult to sustain a reasonable rate of deposition. Consequently, only thin films (with controlled composition) could be obtained.

Chromium-molybdenum alloy coatings have been used on automobile wheels (Ref 47). The plating solution for this alloy consisted of sulfuric acid, chromous oxide, ammonium molybdate, and sodium hexafluosilicate. It was operated at a temperature of 48 °C (120 °F) and a current density of 25 A/dm^2 (250 A/ft^2).

The literature (Ref 48, 49) also contains a number of references to the deposition of chromium-zinc coatings, with zinc being the major alloying element. Russian workers have used an acidic glycine-base solution, both with and without the application of a pulsed current. Some Japanese steel companies have developed techniques for depositing a chromium-zinc alloy on steel sheets to improve either the subsequent bonding of a (modified) polyethylene film (Ref 50, 51) or the corrosion resistance of the alloy (Ref 52, 53). A chloride-base solution has been used to deposit a ternary zinc-nickel-chromium alloy for similar applications (Ref 54).

Other alloying elements that have been deposited with chromium include gold, molybdenum, rhenium, selenium, tellurium, titanium, vanadium, and zirconium.

The bath compositions and operating parameters for depositing binary and ternary chromium-base alloys are summarized in Table 2. A discussion of the properties of some of these and other electrodeposited alloys is provided in Ref 55.

Table 2 Summary of bath compositions and plating parameters for deposition of selected chromium-base alloys

Alloy	Bath composition	pH	Operating temperature		Current density		Anode	Comments	Ref
			°C	°F	A/dm^2	A/ft^2			
Chromium-iron	250 g/L CrO_3; 72.2 g/L $CrCl_3$; 62.6 g/l $FeCl_2$; 1 ml/L H_2SO_4; 20 ml/L CH_3OH	. . .	40	105	25	250	Lead	Current efficiency 55% (max), decreased as bath aged; shiny deposits	18
Chromium-iron	250 g/L CrO_3; 72.2-143 g/L $FeCl_2$; 1 ml/L H_2SO_4; 20 ml/L CH_3OH	. . .	40	105	11-35	110-350	Lead	Composition and current efficiency changed as bath aged; shiny deposits	18
Chromium-iron	100 g/L CrO_3; 5 g/L H_2SO_4; 60 g/L $FeCl_2$; 20 ml/L (85%) HCOOH	. . .	50	120	40	400	Lead-5% antimony	Amorphous deposits, gray, slightly bright deposits; 6% current efficiency	21
Chromium-iron	167 g/L $Cr_2(SO_4)_3$; 40 g/L $Fe(NH_4)(SO_4)_2$; 80 g/L $(NH_4)_2SO_4$; 10 g/L NaH_2PO_2; 20 g/L K_2SO_4	1-2	30	85	20-90	200-900	Platinum	Nafion membrane used lowered chromium content in deposit; current efficiency ~10% (max), deposits contained phosphorus and were amorphous	22
Chromium-nickel	100 g/L CrO_3; 250 g/L nickel fluoborate; plus CH_3COOH	. . .	20	70	50	500	. . .	Alloys contained 9-10% Cr	23
Chromium-nickel	300 g/L $CrCl_3$; 100 g/L $NiCl_2$	. . .	20	70	20	200	. . .	Alloy contained 9% Cr; cathode efficiency 25%	23
Chromium-nickel	400 g/L $CrCl_3$; 100 g/L nickel fluoborate; plus CH_3OH	. . .	20	70	50-100	500-1000	. . .	Alloys contained 15-30% Cr	23
Chromium-nickel	100 g/L $CrCl_3$; 30-40 g/L $NiCl_2$; 30-40 H_3BO_3; 80 g/L sodium citrate; 35-40 g/L HCOOH; plus other organic additives	~3.5	35	95	10-100	100-1000	. . .	Pulsed current; alloys contained 1-60% Cr; hydrogen bromide optional additive	23
Chromium-nickel	270 g/L $CrCl_3$; 100 g/L $NiCl_2$; 30 g/L NH_4Cl; 10 g/L boric acid; 1 g/L vanadium chloride	2.4	7-20	45-70	1	10	. . .	Electrolyte was dimethylformamide with 10% water; higher temperatures decreased chromium content	25
Chromium-nickel	0.8M $CrCl_3$; 0.2M $NiCl_2$; 0.5M NH_4Cl; 0.5M NaCl;	. . .	25	75	4	40	Graphite	Electrolyte was dimethylformamide with 25% water; composition changed	27

	0.15M H_3BO_3							as bath aged	
Chromium-nickel	0.5M $Cr_2(SO_4)_3$; 0.5M $NiCl_3$; 1M lactic acid; 1.4M NaCl	. . .	60	140	20-50	200-500	Nichrome	Nichrome not satisfactory if chloride not present	28
Chromium-nickel-iron	0.15-0.3M chromium sulfamate; ~0.01M nickel sulfamate; 0.4-0.8 iron sulfamate; 0.25-0.5 potassium citrate; plus potassium fluoride	2-4	30-50	85-120	1-25	10-250	. . .	Current efficiency 24-40%; excellent brightness	41
Chromium-nickel-iron	36.4 g/L $Cr_2(SO_4)_3$; 1.47 g/L $NiSO_4$; 2.7 g/L $FeSO_4$; 147 g/L sodium citrate; 50 g/L H_3BO_3; plus sodium and potassium sulfates, sodium disulfite	. . .	25	75	5-20	50-200	Steel	Semipermeable membrane and pulsed current used	44
Chromium-nickel-iron	0.8M $CrCl_3$; 0.2M $NiCl_2$; 0.03M $FeCl_2$; 0.5M NH_4Cl; 0.5M NaCl; 0.15M H_3BO_3	~2	25	75	4	40	Graphite, steel	Electrolyte was dimethylformamide with 50% water; semibright to bright deposits	39
Chromium-nickel-iron	0.2M $KCr(SO_4)_2$; 0.45M $NiSO_4$; 0.35M $FeSO_4$; 0.5M H_3BO_3; 1M glycine	2	20-30	70-85	15-20	150-200	Platinum	Glass frit separator, current efficiency 50-55%; bright deposits	42

References cited in this section

12. P. Elsie et al., Iron-Chromium Alloy Deposition, *Met. Finish.,* Vol 68 (No. 11), 1970, p 52-55, 63
13. R. Murti et al., Electrodeposition of Iron-Chromium Alloy from Sulfate Solutions, *J. Electrochem. Soc. India,* Vol 38 (No. 1), 1989, p 6-10
14. T. Yoshida et al., Electrochemical Behavior of Electrodeposited Iron-Chromium Alloys, *Asahi Garasu Kogyo Gijutsu Shoreikai Kenkyu Hokaku,* Vol 17, 1970, p 195-209
15. T. Hayashi and A. Ishihama, Electrodeposition of Chromium-Iron Alloys from Trivalent Chromium Baths, *Plat. Surf. Finish.,* Vol 66 (No. 9), 1979, p 36-40
16. H. Kagechika et al., "Chromium Alloy Bath," U.S. Patent 4,673,471, June 1987
17. A.M. Kasaaian and J. Dash, "Effects of Chromium Electroplating Solution Composition on Properties of the Deposits," paper presented at Sur/Fin '85 (Detroit, MI), AESF Society, July 15-18, 1985
18. A.M. Kasaaian and J. Dash, "Chromium-Iron Alloy Plating Using Hexavalent and Trivalent Chromium Ion Solutions," U.S. Patent Application, May 1986
19. S. Hoshino et al., The Electrodeposition and Properties of Amorphous Chromium Film Prepared from Chromium Acid Solutions, *J. Electrochem. Soc.,* Vol 133 (No. 4), 1986, p 681-685
20. P.K. Ng, "Iron-Chromium-Phosphorus Bath," U.S. Patent 4,758,314, July 1988
21. R.Y. Tsai and S.T. Wu, Amorphous Chromium Electroplating with Iron as an Alloying Agent, *J. Electrochem. Soc.,* Vol 137 (No. 9), 1990, p 2803-2806
22. J.C. Kang and S.B. Lalvani, Electrodeposition and Characterization of Amorphous Fe-Cr-P-C Alloys, *J.*

Appl. Electrochem., Vol 22, 1992, p 797-794

23. C.H. Chisholm, Electrodeposition of Nickel-Chromium Alloys from Solvent Based Electrolytes--I: Review, Abstract No. 238, *Extended Abstr.,* Vol 83 (No. 2), 1983, p 374-375
24. D.S. Lashmore, "Process and Bath for Electroplating Nickel-Chromium Alloys," U.S. Patent 4,461,680, July 1984
25. C.H. Chisholm and M.R. El-Sharif, Deposition of Chromium-Nickel Alloys from Dimethylformamide/Water Electrolytes, *Plat. Surf. Finish.,* Vol 72 (No. 8), 1985, p 58-61
26. C.H. Chisholm and M.R. El-Sharif, Chromium-Nickel Codeposits from Dimethylformamide Baths Containing 10 Percent Water, *Plat. Surf. Finish.,* Vol 72, 1985, p 82-84
27. A. Watson et al., "The Role of Chromium II and VI in the Electrodeposition of Chromium-Nickel Alloys from Trivalent Chromium-Amide Electrolytes," paper presented at Annual Tech. Conf. (Bournemouth, UK), IMF, April 15-19, 1986
28. I.A. Polunina and A.J. Falicheva, Nichrome Soluble Anode for Electrodeposition of Nickel-Chromium Alloys, *Z. Metallov.,* Vol 24 (No. 2), 1988, p 258-261
29. H. Ariga, Chromium Alloy Plating by Ion Exchange Membrane, *Jpn. Kokai Tokkyo Koho,* No. 86/00594, 1986
30. M. Kamata and A. Shigeo, Electroplating of Nickel-Chromium Alloys Using Chromic Complexes, *Jpn. Kokai Tokkyo Koho,* No. 86/113,788, 1986
31. I. Nakayama et al., A Study of Electroless Nickel-Chromium Alloy Plating Baths, *Hyomen Gijutsu,* Vol 43 (No. 9), 1992, p 835-838
32. C.E. Cedarleaf, Solution for Electroless Chromium Alloy Plating, U.S. Patent 4,028,116, June 1977
33. J. Gruberger et al., A Sulfate Solution for Deposition of Nickel-Chromium-Phosphorus Alloys, *Surface Coat. Technol.,* Vol 53 (No. 3), 1992, p 203-213
34. K.L. Lin and J.K. Ho, Electrodeposited Nickel-Chromium and Nickel-Chromium-Phosphorus Alloys, *J. Electrochem. Soc.,* Vol 39 (No. 5), 1992, p 1305-1310
35. B.A. Shenoi et al., "Electrodeposition of Iron-Chromium-Nickel Alloy," Indian Patent 114,867, 1970
36. E. Terada, Improvement of Stainless Steel Plating Method, *Jpn. Kokai Tokkyo Koho,* No. 55-148,794, 1980
37. G.R. Schaer, "High Rate Chromium Alloy Plating, " World Patent 82103095, September 1982
38. L. Free, "Electrodeposition of a Stainless Steel Finish," paper presented at Annual Tech. Conf. (Bournemouth, UK), IMF, April 15-19, 1986
39. C.H. Chisholm and M.R. El-Sharif, Sustained Electrodeposition of Chromium-Nickel-Iron Ternary Alloys by Control of Transient Trivalent Chromium Levels, *Proc. Sur./Fin. '87* (Chicago, IL), AESF Society, July 13-16, 1987
40. M. Yasuda et al., Electroplating of Iron-Chromium-Nickel Alloys from the Chloride-Glycine Baths, *Kinzuku Hyomen Gijutsu,* Vol 39, 1988, p 19
41. T. Ishiguro and H. Ochiai, Studies on the Electrodeposition of Iron-Chromium-Nickel Alloys from Sulfamate Solution - Part I, *Puretingu to Kotingu,* Vol 6 (No. 2), 1986, p 79-90
42. M. Matsuoko et al., Electrodeposition of Iron-Chromium-Nickel Alloys, *Plat. Surf. Finish.,* Vol 74 (No. 10), 1987, p 56-60
43. M.F. El-Shazly et al., "The Development of Electrodeposited Stainless Steel Type Alloys," Final Report of Multiclient Research Project, Battelle National Laboratory, December 30, 1986
44. J. Krüger and J.P. Nepper, Galvanic Deposition of Iron-Chromium-Nickel Alloy Using Modulated Current, *Metalloberfläche,* Vol 40, 1986, p 107-111
45. G.R. Smith and J.E. Allison, Jr., "Alloy Coating Method," U.S. Patent 4,601,795, July 22, 1986
46. C.U. Chisholm, Cobalt-Chromium Coatings by Electrodeposition: Review and Initial Experimental Studies, *Electrod. Surf. Treat.,* Vol 3 (No. 5-6), 1975, p 321-333
47. L. Herbansky, Czechoslovakia Patent 214,553, 1985
48. N.B. Berezin et al., Role of Complex Formation During the Cathodic Deposition of Zinc-Chromium

Electroplates from Acidic Glycine-Containing Baths, *Zashch. Met.,* Vol 28 (No. 6), 1992, p 961-966

49. N.B. Berezin et al., Electrodeposition of Zinc-Chromium Alloy with a Pulsed Current, *Zashch. Met.,* Vol 29 (No. 1), 1993, p 99-105
50. M. Matsumoto et al., Manufacturing of Corrosion-Resistant Steel Laminates, *Jpn. Kokai Tokkyo Koho,* No. 92/357439, 1992
51. M. Kimoto et al., Electroplating of Zinc-Chromium Alloy on Steel Sheet, *Jpn. Kokai Tokkyo Koho,* No. 93/09779, 1993
52. T. Komori et al., Manufacture of Steel Sheet Electroplated with Zinc-Chromium Alloy, *Jpn. Kokai Tokkyo Koho,* No. 92/36495, 1992
53. H. Sakai et al., Manufacture of Steel Sheet Electroplated with Zinc-Chromium Alloy, *Jpn. Kokai Tokkyo Koho,* No. 91/120393, 1991
54. C. Kato et al., Alloy Electroplated Steel Sheet with High Corrosion Resistance, and its Manufacture, *Jpn. Kokai Tokkyo Koho,* No. 90/031394, 1990
55. W.H. Safranek, *The Properties of Electrodeposited Metals and Alloys,* 2nd ed., The AESF Society, 1986

Multiple-Layer Alloy Plating

Daniel T. Schwartz, University of Washington

Introduction

MULTIPLE-LAYER ALLOY PLATING is an emerging technology for engineering desirable properties into thin surface layers through the use of carefully controlled deposit microstructures. As implied by the name, multiple-layer alloy electrodeposition involves the formation of an inhomogeneous alloy consisting of lamellae of different composition, as shown schematically in Fig. 1 for a binary alloy composed of species A and B. Each lamella of species A (or species B) in the film has a nearly uniform thickness λ_A (or λ_B). The modulation wavelength ($\lambda = \lambda_A + \lambda_B$) characterizes the imposed compositional microstructure and typically takes a value anywhere from angstroms to microns in thickness. Multiple-layer thin films with spatially periodic compositional microstructures of the type shown in Fig. 1 are sometimes referred to in the literature as composition-modulated alloys (CMAs) or as superlattice alloys. A wide variety of binary and ternary alloy systems have been electroplated as multiple-layer films, including Ni/Cu, Ag/Pd, Cu/Ni-Fe, Cu/Ag, Cu/Co, Cu/Pb, Cu/Zn, Ni-P/Ni-Co-P, and Ni/Ni-P, to name a few. In many cases these alloys can be electroplated from a single electrolyte bath using either current or potential pulsing schemes. A common feature to many single-bath electroplating strategies is the use of hydrodynamic modulation that is synchronized in some manner with the pulsed plating. Multiple-layer alloys are often found to exhibit unusual (and sometimes highly desirable) mechanical, magnetic, electrical, and chemical properties, especially when the modulation wavelength λ is of the order of nanometers.

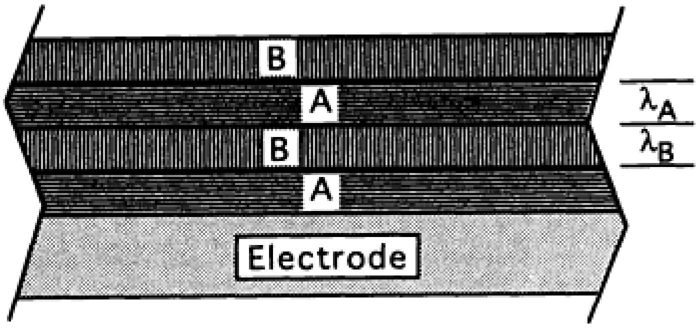

Fig. 1 Schematic representation of a multiple-layer alloy consisting of alternating lamellae of species A and species B. The thicknesses of the A and B layers are given by λ_A and λ_B, respectively. The modulation wavelength that characterizes the multiple-layer superlattice structure is $\lambda = \lambda_A + \lambda_B$. Multiple-layer alloys often exhibit a spatially periodic compositional wave throughout the film, rather than the discrete interface depicted between each lamella.

In short, multiple-layer alloy plating combines the best attributes of electroplating--high throughput, low cost, and simple equipment--with an extra degree of freedom to engineer surface film properties. The potential impact of multiple-layer plating on the performance and economics of engineered surface layers appears to be large, although most commercial applications of the technology are still being developed. This article is focused mainly on the science and engineering of multiple-layer metallic alloys with nanometer-scale modulation wavelengths, because these are the materials that have gained the most attention for surface engineering. Throughout this chapter a solidus, or virgule (/) is used to denote the two materials that are spatially modulated to form a superlattice structure, whereas a dash between elements indicates that the species is an alloy. Using this nomenclature, Fig. 1 shows an A/B alloy. If species A happens to be copper and species B is a Ni-Fe alloy, then the figure denotes a Cu/Ni-Fe multiple-layer alloy.

Applications

For the most part, applications that take advantage of the material properties of nanometer-scale multiple-layer films are still in the development stage. Within the past few years, however, a number of promising applications have emerged that seem especially well suited for multiple-layer alloy plating.

The magnetic properties of electroplated multiple-layer alloys have received a great deal of attention for applications related to magnetic recording. For example, Ref 1 shows that multiple-layer thin films of Cu/Ni-Fe ($\lambda_{Cu} \approx 10$ nm and $\lambda_{Ni-Fe} \approx 50$ nm) eliminate the classical edge-closure domains that give rise to noise in thin-film inductive heads. At the same time, the remaining magnetic properties of the multiple-layer Cu/Ni-Fe alloy are comparable to homogeneous Ni-Fe alloy properties. The combination of reduced domain noise in the multiple-layer alloy with excellent magnetic properties makes these materials extremely attractive for thin-film inductive heads with very narrow track width. It is also likely that electroplated multiple-layer alloys will soon affect the performance of magnetoresistive head technology, given the recent discovery of giant magnetoresistance in electroplated Cu/Co-Ni-Cu multiple-layer alloys with $\lambda_{Cu} <1$ nm (Ref 2).

Electroplated multiple-layer foils of Ni/Cu alloy (with $\lambda_{Cu} \approx 2$ nm and $\lambda_{Ni} \approx 18$ nm) exhibit tensile strengths that exceed homogeneous nickel or copper foil strengths by more than a factor of three (Ref 3), and steel that is coated with an electroplated Ni/Cu multiple-layer film ($\lambda_{Cu} \approx 3.8$ nm and $\lambda_{Ni} \approx 3.8$ nm) exhibits a high resistance to sliding wear (Ref 4). Because of these enhanced mechanical properties, electroplated Ni/Cu multiple-layer surface coatings are being used to extend the lifetime of printing press components that are subject to sliding-wear damage.

Other applications of electroplated multiple-layer thin films that are being explored include the use of Cu/Ag and Cu/Co alloys for high-temperature applications in rocket thrust aligners, where protective surface films are used to minimize hydrogen embrittlement.

References cited in this section

1. L.T. Romankiw and J.D. Olsen, Electroplated Laminated Cu/Ni-Fe Films from a Single Plating Bath for Inductive Recording Heads and Magnetic Shields, *Proceedings of the Symposium on Magnetic Materials, Processes, and Devices,* L.T. Romankiw and D.A. Herman, Jr., Ed., Electrochemical Society, 1990, p 339-345
2. M. Alpers, K. Attenborough, R. Hart, S.J. Lane, D.S. Lashmore, C. Younes, and W. Schwarzacher, Giant Magnetoresistance in Electrodeposited Superlattices, *Applied Physics Letters,* Vol 63, 1993, p 2144
3. S. Menezes and D.P. Anderson, Wavelength-Property Correlation in Electrodeposited Ultrastructured Cu/Ni Multilayers, *Journal of the Electrochemical Society,* Vol 137, 1990, p 440
4. A.W. Ruff and D.S. Lashmore, Effects of Layer Spacing on Wear of Ni/Cu Multilayer Alloys, *Wear,* Vol 151, 1991, p 245

Process Description and Engineering Parameters

Nanometer-wavelength multiple-layer alloys were initially fabricated in the late 1960s using vapor-phase evaporation to test theories on the thermodynamic stability and interdiffusion of layered materials. Although vacuum evaporation techniques have been used to form reproducible multiple-layer thin films, sputtering and electroplating techniques are currently the preferred fabrication methods. Multiple-layer alloys can be electroplated from a single bath that contains ions of all of the species to be deposited, or plating can take place sequentially by moving the electrode between multiple

plating baths that contain individual species of interest. From a throughput standpoint, single bath plating techniques are preferred, although not all electrolyte chemistries and species redox properties are compatible with single-bath plating.

Multiple-layer alloy plating from a single bath typically requires that the deposition of each species in the multiple-layer pair occur at potentials that differ by more than 100 mV. The more noble component of the alloy is normally plated at the mass transfer limited rate, and the less noble component is plated under kinetics limited conditions. Figure 2 is a schematic showing deposition rate versus potential for an ideal multiple-layer alloy plating bath. The more noble species A plates readily at potentials that are negative of V_A, and the less noble species B plates at potentials negative of V_B. Within the potential window between V_A and V_B, it is possible to electroplate a film that is essentially pure in the noble component A. Conversely, the less noble component B is always codeposited with the more noble species A to form a B-A alloy. Periodically switching the potential (or current) between the region where pure A deposits and the region where B-A alloy deposits results in an A/B-A multiple-layer film. The thickness of each lamella is related to the deposition charge through Faraday's law (a knowledge of the current efficiency is also needed). Figure 2 suggests that species A is codeposited with species B at the mass transfer limited rate ($R_{A.MT}$). The mole percent of species B (in the B-A alloy) is dictated largely by the potential (or current) at which deposition occurs, the strength of agitation in the cell, and the relative concentrations of reducible species A and B that are dissolved in the electrolyte. Decreasing the agitation during species B deposition serves to reduce the rate of which species A ($R_{A.MT}$) is added to the film, and increasing the concentration ratio of B to A in the electrolyte directly affects the ratio of $R_{B.MT}$ to $R_{A.MT}$. The formulation of a multiple-layer plating bath normally begins with an electrolyte that is known to work well for plating the less noble component B at high rates. A small concentration of the more noble species A ($\approx$1% of B) is then added to the bath in an effort to minimize the amount of A that codeposits with B. Using this strategy, it is possible to make an A/B alloy in which each lamella is nearly pure (>95%).

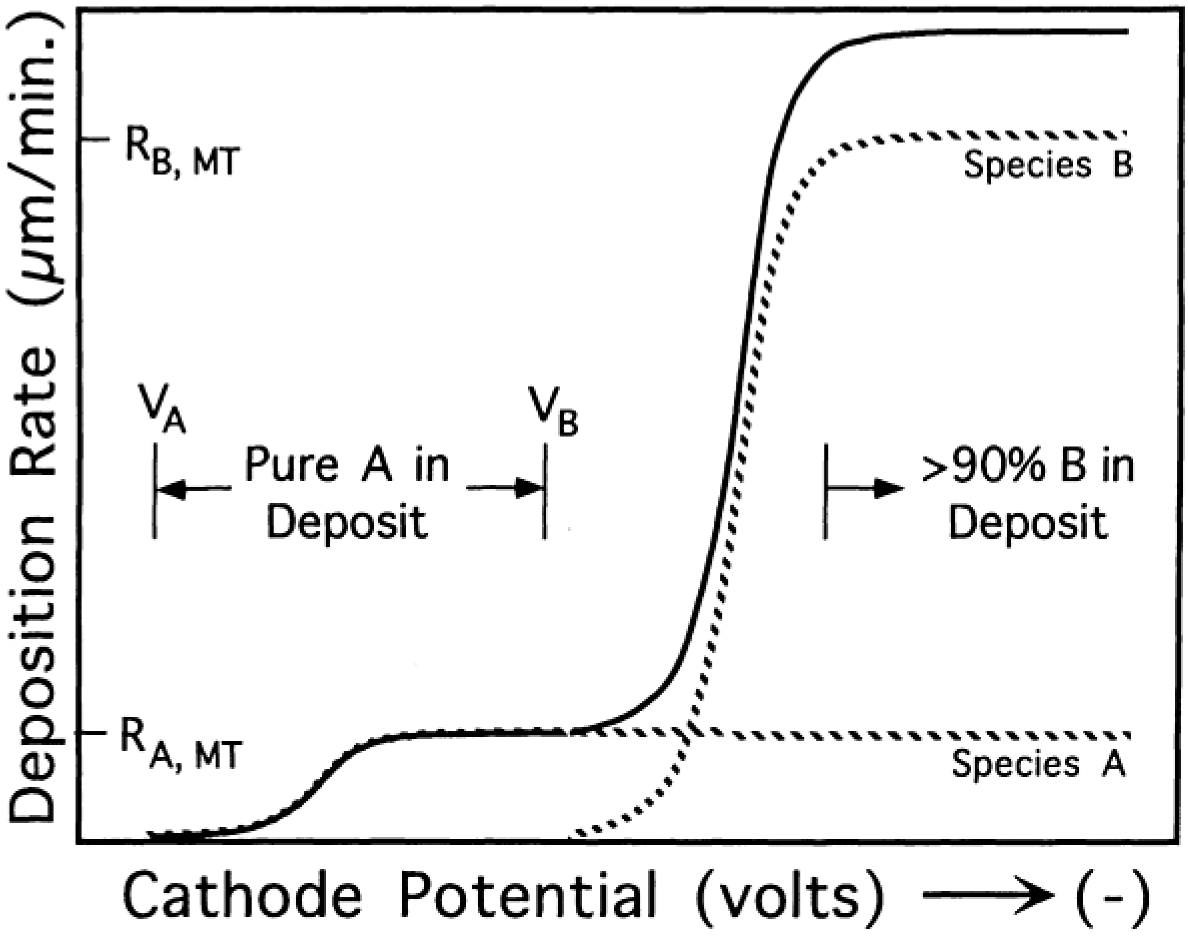

Fig. 2 Schematic of ideal deposition rate vs. applied cathodic potential characteristics for electroplating an A/B multiple-layer alloy. The dashed lines denote deposition rates for plating each individual species, and the solid line represents the total deposition rate. Note that pure A is deposited in the potential window between the reversible potential for species A (V_A) and the reversible potential for species B (V_B), whereas an impure A-B

alloy forms at potentials cathodic of V_B.

The ideal deposition conditions represented in Fig. 2 are nearly matched in reality by some alloy systems. For example, a variety of bath chemistries and deposition conditions have been found for plating Ni/Cu multiple-layer alloys, where copper is more noble than nickel by nearly 600 mV. For the case of Ni/Cu alloy plating, one often starts with a nickel-sulfate-based electrolyte (Watts nickel bath) or a nickel sulfamate bath. Small amounts of copper sulfate (50 to 1000 ppm Cu^{+2}) are then added to the bath. Table 1 shows typical sulfate and sulfamate plating baths for making Ni/Cu multiple-layer alloys. The deposition protocols for creating multiple-layer Ni/Cu alloys from these baths are nearly identical.

Table 1 Characteristic plating baths for making nanometer-scale Ni/Cu multiple-layer alloys

Plating bath	Typical bath composition	Temperature, °C
Nickel sulfate	330 g/L $NiSO_4 \cdot 6H_2O$, 45 g/L $NiCl_2 \cdot 6H_2O$, 35 g/L H_3BO_4, 0.05-0.1 g/L Cu^{+2}, 0.1 g/L coumarine, 0.1 g/L sodium dodecyl sulfate, pH ≈ 2	≈ 60
Nickel sulfamate	70-90 g/L Ni, 0.3-0.9 g/L Cu (as sulfate), 30-45 g/L boric acid, 0.15 g/L sulfamate nickel anti-pit, pH ≈ 3.5	≈ 50

Pulsed-potential plating of Ni/Cu multiple layers from either bath listed in Table 1 requires the copper lamella to be deposited at a potential near -0.4 V (referenced against a saturated calomel electrode, SCE) and each nickel lamella to be plated at a potential between -1.0 and -1.5 V versus SCE. Under these conditions, the copper deposition rate is controlled by the rate of Cu^{+2} mass transfer, and the nickel deposition rate is controlled by either electrode kinetics or by mixed mass transfer and kinetics. Copper plating proceeds with nearly 100% current efficiency, but the nickel plating has a lower current efficiency due to the simultaneous evolution of hydrogen. The electrolyte is often strongly agitated during copper plating so that higher mass transfer limited copper deposition rates are achieved. Conversely, the agitation rate is often reduced when the nickel is deposited so that the purity of the nickel layer can be increased by reducing the rate of copper codeposition. An important feature of the single-plating bath formulations described here is that the more noble species, copper, has a low deposition rate compared to nickel and therefore requires a longer duration pulse to achieve a comparable layer thickness. Reference 4 provides an example of pulsed-potential plating of Ni/Cu multiple-layer alloys from a sulfamate bath.

Pulsed-current plating is somewhat more common for making high-quality multiple-layer alloys than is pulsed-potential plating. Moreover, the best results are achieved using a triple-current-pulsing scheme that employs a brief high-current nickel deposition pulse, followed by a brief zero-current pulse and then a long-duration, low-current copper deposition pulse. The size and duration of each pulse depend on details of the electrolyte agitation, the bath formulation, and the modulation wavelength desired. The two triple-pulse-plating protocols given in Table 2 are representative of conditions that lead to coherent nanometer-wavelength Ni/Cu multiple-layer alloys (both studies used plating baths that fall in the range of the sulfamate formulations given in Table 1). The triple-pulse protocol given in Ref 3 results in a high plating rate and a high nickel alloy. The high plating rate is achieved, in part, by agitating the cell using a rotating cylinder cathode. Also contributing to the high plating rate is the formation of a high-nickel-content alloy (recall that the less noble component normally plates at high rates compared to the more noble component). The triple-pulse protocol given in Ref 5 results in lower plating rates and higher-copper-content alloys than the protocol used in Ref 3. The low overall deposition rate reported in Ref 5 is a direct result of forming a high-copper alloy using a quiescent plating bath. In the protocol given in Ref 3, the strength of agitation is modulated during each stage of current pulsing. The use and synchronization of a time-periodic agitation scheme should be carefully considered when developing a multiple-layer alloy plating protocol (Ref 6). Additional information is available in the article "Pulsed-Current Plating" in this Volume.

Table 2 Two representative triple-current-pulsing schemes for plating coherent, nanometer-scale Ni/Cu multiple-layer alloys from sulfamate electrolytes

Characteristic triple-pulse condition	Bath agitation	Growth rate (μm/h)	$\lambda Ni/\lambda Cu$	Reference

Nickel pulse: 90 mA/cm^2 for ≈ 0.7 s	60 rpm			3
"Rest" pulse: 0 mA/cm^2 for 0.25 to 1 s		≈ 7	≈ 10	
Copper pulse: 1.5 mA/cm^2 for ≈ 4 s	600 rpm			
Nickel pulse: 12-20 mA/cm^2 for ≈ 0.5 s	None			5
"Rest" pulse: 0 mA/cm^2 for ≈ 0.5 s		≈ 1	≈ 2	
Copper pulse: 0.3 mA/cm^2 for ≈ 11 s	None			

Multiple-layer alloys that are plated using two baths are not limited to species with widely separated deposition potentials, nor is it necessary to modify well-established bath chemistries. However, plating a multiple layers using two baths requires the substrate cathode to be periodically moved between the baths. If transferring the cathode between baths takes substantial time, then forming nanometer-wavelength multiple-layer alloys with appreciable total film thickness becomes prohibitively slow. Reference 7 describes the use of a novel dual-bath plating cell that provides nanometer-wavelength Ni/Ni-P multiple-layer alloys at a high deposition rate (2 to 4 μm/h). The cell employs a disk-shape cathode substrate that rotates with an angular velocity of 12 to 20 rpm. The rotating substrate is exposed to each plating bath once per revolution. After each exposure to a plating bath, the cathode is mechanically wiped free of electrolyte to avoid cross-contamination of the electrolytes. A voltage divider is used with a single power supply to control the current flowing through each bath (each bath contains a separate nickel anode). Conventional nickel and nickel phosphorous bath formulations are used in the dual-bath cell to deposit each lamella of the multiple layer. Compared to single-bath strategies, the dual-bath approach substitutes a mechanically complex plating apparatus for a much simpler electrolyte formulation.

A new two-bath electroplating strategy for making multiple-layered materials with molecular-level compositional control is described in Ref 8. The technique, called electrochemical atomic layer epitaxy (ECALE), takes advantage of the underpotential deposition (UPD) phenomenon that occurs when the first monolayer (or partial monolayer) of a surface film is formed. The energetics of the first atomic layer of a deposit is often favorable compared to bulk material deposition, thus resulting in deposition at potentials that are noble of bulk deposition. The ECALE concept has been tested for Cd/Te electrodeposition. The chemistry of each bath was manipulated to provide cathodic UPD of cadmium and anodic UPD of tellurium (at potentials that did not strip the cadmium monolayer from the surface). Low-energy electron diffraction verified the formation of ordered cadmium deposits on tellurium and ordered tellurium deposits on cadmium (Ref 8). Despite the initial verification of the ECALE concept, practical applications of the technique await further development.

References cited in this section

3. S. Menezes and D.P. Anderson, Wavelength-Property Correlation in Electrodeposited Ultrastructured Cu/Ni Multilayers, *Journal of the Electrochemical Society,* Vol 137, 1990, p 440
4. A.W. Ruff and D.S. Lashmore, Effects of Layer Spacing on Wear of Ni/Cu Multilayer Alloys, *Wear,* Vol 151, 1991, p 245
5. D.S. Lashmore and M.P. Dariel, Electrodeposited Cu/Ni Textured Superlattices, *Journal of the Electrochemical Society,* Vol 135, 1988, p 1218
6. D.T. Schwartz, P. Stroeve, and B.G. Higgings, Electrodeposition of Composition-Modulated Alloys in a Fluctuating Flow Field, *AIChE Journal,* Vol 35, 1989, p 1315
7. L.M. Goldman, B. Blanpain, and F. Spaepen, Short Wavelength Compositionally Modulated Ni/Ni-P Films Prepared by Electrodeposition, *Journal of Applied Physics,* Vol 60, 1986,p 1374

8. B.W. Gregory, D.W. Suggs, and J.L. Stickney, Conditions for the Deposition of CdTe by Electrochemical Atomic Layer Epitaxy, *Journal of the Electrochemical Society,* Vol 138, 1991, p 1279

Characterization of Multiple-Layer Alloys

One of the most common methods for characterizing nanometer-wavelength multiple-layer alloys is x-ray diffraction (XRD), which provides information about the crystalline texture and superlattice structure of a multiple-layer material. The superlattice structure of the alloy is revealed as satellite peaks located at low and high angles around the crystallographic Bragg peaks in the diffraction pattern. The dispersion angle of the satellite peaks provides the modulation wavelength of the multiple layer, and the number and amplitude of the satellite peaks provide a measure of the interfacial "sharpness" between each lamella. The wavelength of a multiple-layer alloy (λ) is quantitatively related to the first-order satellite peak locations through the relationship

$$l = \frac{l_x}{\sin(q^+) - \sin(q^-)}$$

where λ_x is the x-ray source wavelength, θ^+ is the high-angle satellite peak location, and θ^- is the low-angle satellite peak location. Transmission electron microscopy and Auger electron spectroscopy (used with sputtering) have both been employed to study nanometer-scale structure in multiple-layer alloys, but these techniques require significantly more sample preparation and handling than XRD. Moreover, the sample preparation for these techniques requires destructive treatment of the multiple-layer material.

Once the structural characteristics of a multiple-layer alloy are known, then the material properties are normally analyzed using conventional techniques. Relationships have been observed between the superlattice structure of multiple-layer alloys and their mechanical properties (e.g., tensile strength, moduli), their electrical properties (e.g., conductivity), their magnetic properties (e.g., magnetoresistance, magnetostriction, saturation magnetization), and their chemical properties (e.g., corrosion resistance).

The growing technological need for inexpensive, high-performance thin-film materials is propelling academic and industrial research efforts to understand the processing-structure-property relationships in a wider range of plated multiple-layer alloys. The degree to which plated multiple-layer films will ultimately meet the technological challenges that face surface engineers remains to be answered.

Selective (Brush) Plating

Introduction

SELECTIVE PLATING, also known as brush plating, differs from traditional tank or bath plating in that the workpiece is not immersed in a plating solution (electrolyte). Instead, the electrolyte is brought to the part and applied by a hand-held anode or stylus, which incorporates an absorbent wrapping for applying the solution to the workpiece (cathode). A direct current power pack drives the electrochemical reaction, depositing the desired metal on the substrate. In practice, movement between the anode and cathode is required for optimum results when plating, stripping, activating, and so on. A schematic of the selective plating process appears in Fig. 1.

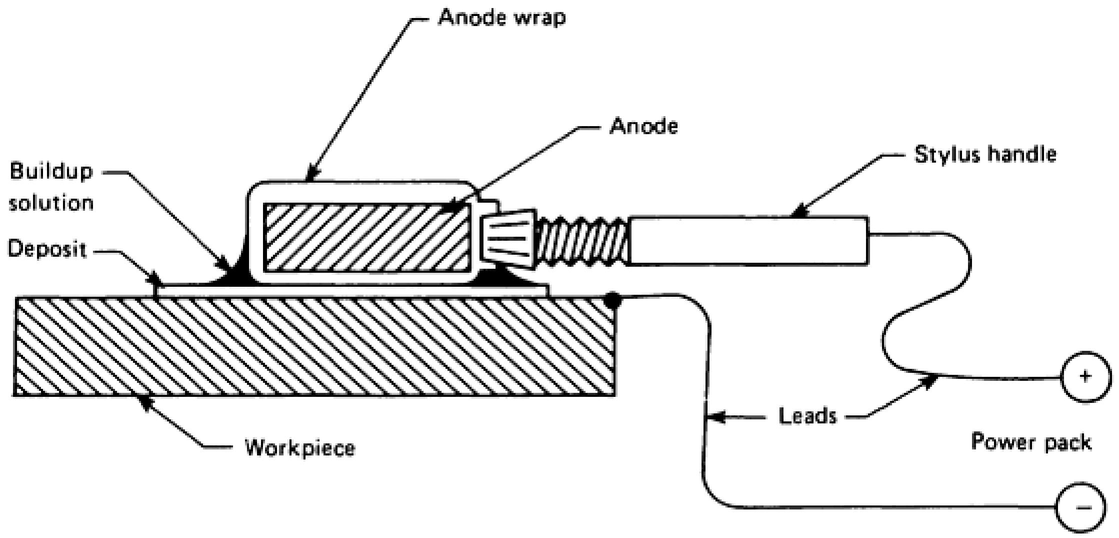

Fig. 1 Manual operation of selective plating process. Source: Ref 1

Currently, a broad range of elements and alloys can be brush plated; the majority are listed in Table 1. Even though selective plating can be done in a tank, labor-intensive masking and subsequent removal often make this option impractical.

Table 1 Energy factors for selective plating

Element or alloy	Energy factor
Cadmium	0.006
Chromium	0.200
Cobalt	0.014
Copper	0.013
Gallium	0.014
Gold	0.006
Indium	0.009
Iridium	0.069
Iron	0.025

Lead	0.006
Mercury	0.008
Nickel acid	0.047
Nickel alkaline	0.017
Nickel, black	0.025
Nickel, natural	0.025
Palladium	0.019
Platinum	0.015
Rhodium	0.030
Silver, noncyanide	0.750
Silver, pure	0.004
Babbitt	0.006
Brass	0.017
Bronze	0.017
Cobalt-nickel	0.019
Cobalt-tungsten	0.015
Nickel-cobalt	0.020
Nickel-tungsten	0.020
Tin-cadmium	0.007
Tin-indium	0.008
Tin-lead (90/10)	0.006

Tin-lead (60-40)	0.007
Tin-nickel	0.010

Note: The energy factor is the ampere-hours required to produce a deposit thickness of 0.003 mm (0.0001 in.) on a square inch of area.

Acknowledgements

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Reference

1. M. Rubinstein, *Electrochemical Metallizing,* Vinmar Press, 1987

Advantages and Limitations

The key advantage of selective plating is portability. Many systems can be moved to various locations in a production facility or be transported to the job site. Selective plating is also versatile; it permits most electroplate types to be deposited onto any conductive substrate that can be touched with an electrode. Cast iron, copper, steel, stainless steel, high-temperature nickel-base alloys, aluminum, and zinc are commonly plated by this method and exhibit good adhesion. Limited adhesion can be obtained with other materials, such as titanium, tungsten, and tantalum.

Selective plating allows higher current densities than tank plating, which translate into higher deposition rates, up to 0.010 mm/min (0.0004 in./min). In addition, inherently precise thickness control permits plate buildup or repair without the need for subsequent machining. In regard to deposit hardness, a 70 HRC trivalent chrome is available for selective plating of thick deposits, which places selective plating on a par with hexavalent tank chrome. The exceptions are the harder deposits of cobalt and gold (Table 2). Table 3 provides a point-by-point comparison of selective plating with competitive processes, including tank plating.

Table 2 Deposit hardness attainable with selective plating versus bath plating

Metal type	**Microhardness, DPH**	
	Bath plating	**Selective plating**
Cadmium	30-50	20-27
Chromium	750-1100[a]	850-1100
Cobalt	180-440	510
Copper	53-350	140-210
Gold	40-100	140-150

Lead	4-20	7
Nickel	150-760	280-580
Palladium	85-450	375
Rhodium	550-1000	800
Silver	42-190	70-140
Tin	4-15	7
Zinc	35-125	40-54

Source: Ref 2

(a) Usual range, but hardnesses of 280-1200 DPH are possible.

Table 3 Selective plating versus other processes

Characteristic	**Selective plating**	**Welding**	**Flame spray or plasma metallizing**	**Electroplating**
Precision buildup capability	Excellent	Poor	Poor	Fair to good
Quality of bond	Excellent	Excellent	Fair to good	Good
Heat distortion or stresses	None	Frequently	Sometimes	None
Heat cracking	None	Frequently	Sometimes	None
Speed of deposit	Fast	Very fast	Very fast	Slow
Density of deposit (porosity)	Very dense[(a)]	Very dense, but with blowholes	70-90% of theoretical density	Moderately dense
Portability	Yes	Yes	Sometimes, but over-spray precludes its use	No
Requirement for post-machining	Not required on thicknesses up to 0.254 mm (0.010 in.) on smooth surface	Always required	Almost always required	Usually required

Hydrogen embrittlement	No[b]	No	No	Yes

Source: Ref 1

(a) Generally 25% less porous than electroplating and 70% less porous than flame spray or plasma metallizing.

(b) Specific cadmium, nickel, and nickel-tungsten deposits have been tested on high-strength steel and were found to be nonembrittling. Other deposits may not cause embrittlement.

Besides electroplating, selective plating systems can perform several other ancillary operations:

- *Electrostripping* for deplating of many metals and alloys
- *Anodizing* for protecting aluminum and alloys
- *Electromilling* for removing base metal, as in chemical milling
- *Electroetching* for permanently identifying parts
- *Electropolishing* for refining a surface chemically

Depending on part size, dimensional considerations, and required surface characteristics, all of these operations can be done with the same equipment and similar electrodes. Only the solutions are different.

Selective plating of small parts is more the exception than the rule, and large volumes of small parts are more economically plated by high-production-rate processes, such as barrel plating. Plating of entire components with complex geometries is better left to processes such as tank plating, which is more economical because solutions are less costly and throughput is higher. Another limitation is deposit rate; both flame spraying and welding deposit metal at a considerably faster rate.

References cited in this section

1. M. Rubinstein, *Electrochemical Metallizing,* Vinmar Press, 1987
2. J.C. Norris, Brush Plating: Part I, *Metal Finishing,* July 1988, p 44-48

Applications

In many cases, an operator brush plates only one part at a time. Nevertheless, selective plating is an effective and economical electroplating process when used in application for which it is designed. These include plating of parts that are too large to immerse in solution, plating a small area of a larger component, and touchup and repair of components, large or small, that would cost too much to strip and remanufacture. The largest parts ever plated are building domes and church steeples, up to about 1390 m^2 (15,000 ft^2), in copper, nickel, and gold. The smallest are cells on rotogravure rolls, 0.076 by 0.038 mm (0.003 by 0.0015 in.). The process can also perform at high production volumes, such as 4,000,000 parts/day for nickel-plated brass electrical contacts on alkaline batteries.

Cosmetic or decorative applications involve parts that range in size from jewelry to large exterior structural domes and lobby interiors.

Corrosion protection applications allow touchup of small rusted or corroded areas without disassembly. Examples include aircraft landing gears, virtually all kinds of machinery, mixing vats, and tanks. Parts too large to fit into plating tanks are almost always good candidates.

Repair of electronic parts is usually done with precious metals, such as gold, silver, and rhodium. Typical applications are repair of broken circuits and small circuit board contacts, and application of conductive coatings on high-

voltage sources. Selective plating minimizes scrap, allows immediate repair on site, and does not require immersion of the entire part in solution.

Restoration of large parts is a natural application for selective plating if the parts are permanent fixtures that cannot be removed or disassembled. The process makes it possible to repair and restore dimensions or apply a wear-resistant or corrosion-resistant surface to just about any part. Portable systems allow access to parts at great elevations and in remote areas, such as protecting the inside surface of a large mixing vessel and repairing critical equipment on ships at sea.

Specialized applications of selective plating involve unusual environments or the need for certain properties, such as conductivity or impact resistance. Examples include blocking radio frequency interference with a soft, radiowave-resistant material such as tin; plating aluminum to facilitate soldering; plating machinery components to ensure initial lubrication; and even plating test probes to resist extreme environmental conditions.

Following are examples of specific applications of selective plating and anodizing:

- *Adhesive-bonded aircraft parts:* anodizing (phosphoric acid) used to prepare aluminum skins and frames for adhesive repair of damaged skins
- *Aircraft engine components:* sulfamate nickel on high-temperature nickel alloys used as a prebrazing operation for second-stage turbine vanes, blades, and stator segments; also used for restoration of bearing area on turbine exhaust case, bearing housing and support, and cooling air duct
- *Aircraft landing gears:* cadmium touchup; on 2014 aluminum, hard coat on inner diameter of oil air strut used to accommodate press fit of bronze bearing
- *Aircraft skins:* anodizing (chromic acid or sulfuric acid) used to repair damaged chromic-acid and sulfuric-acid coatings, respectively
- *Aircraft wheel:* anodizing (sulfuric acid) used to correct a mismachined bearing bore
- *Bus bars:* silver on copper or aluminum used for electrical contacts
- *Electric motors:* nickel and copper used for dimensional restoration of motor shafts and bearing end caps; tin used for low-power motors to reduce vibration; and platinum, gold, or rhodium used to increase wear life and reduce arcing of commutators and slip rings
- *Hydraulics:* copper, nickel, cobalt, or chrome used to repair steel- or chrome-plated hydraulic components, often without disassembly
- *Metal recovery systems:* platinum coating used on titanium permanent anodes
- *Missile launch rail:* hard coat used on a 6061-T6 surface to bring dimensions into tolerance and provide wear resistance and corrosion resistance
- *Mold repair:* gold plating used on plastic molds where corrosive gases attack existing chrome; final plating of chrome used to repair rubber molds; copper, nickel, and cobalt used to repair other types of molds
- *Printed circuit boards:* gold over copper used on contact tabs, fingers, etc.
- *Printing presses:* copper, silver, nickel, cobalt, or chrome plating used to repair cylinders; in-press overhaul plating of side frame used for bearing retention and to correct out-of-concentricity condition
- *Railroad axles:* nickel used for dimensional restoration on bearing journals and sealing wear ring grooves
- *Space shuttle manifolds:* up to 0.5 mm (0.20 in.) of copper used to increase wall strength of a nickel-electroformed hydrogen-oxygen manifold for the prototype "Columbia" engine
- *Steel mill coating line:* cadmium, zinc, or nickel-zinc used to increase the thickness of the protective coating on steel sheet moving at 137 m/min (450 ft/min)
- *Submarines:* rhodium and gold used on copper slip rings
- *Turbines:* cobalt, nickel, nickel/cobalt, or chrome used to restore dimensions on bearing and seal surfaces; silver used to repair steam cuts on horizontal seal surfaces

Equipment

Typical selective plating systems include a power pack, plating tools (called *styli* or *anodes*), anode covers, specially formulated plating solutions, and any auxiliary equipment required for the particular application. To achieve optimum deposits, equipment should be designed expressly for selective plating. Although tank plating solutions and rectifiers are

occasionally used, they are not usually recommended because the resultant deposits are thin and quality is typically below par.

Power packs (rectifiers) supply the direct current and are specially designed with the features and/or controls required by the process. Output voltage can typically be varied from 0 to between 25 and 30 V, compared to the usual 6 to 12 V for tank-plating power packs. Power packs are available in a variety of ratings to suit specific applications (Table 4).

Table 4 Commercially available power packs

Alternating current input, V	Phase	Maximum output current, A[a]
115 or 230	1	30
115 or 230	1 or 3	60
230 or 460	1 or 3	100
230 or 460	1 or 3	150
230 or 460	1 or 3	200
230 or 460	3	500

Source: Ref 2

(a) At 25 V dc.

Voltage control is extremely important because it regulates the current supplied to the process. In turn, the amount of current consumed over time, measured in ampere-hours (A · h), determines the deposit thickness. Ampere-hour requirements vary widely for different types of electroplates, as indicated by the energy factors in Table 1.

Stepless voltage control is a typical feature of selective plating power packs; most can be adjusted from 0 to 100%. The magnitude of power required depends on the part size, the deposit thickness required, and the plating type. For example, for delicate electronics parts, an output of 5 A and 12 V should be ample, whereas plating of large areas with thick buildups requires a much larger source.

A voltmeter and an ammeter should be available and should show 0 to 100% ranges. The voltmeter permits monitoring of the voltage required to plate a given part. The ammeter displays the amount of current flowing between the anode and the cathode, allowing calculation of the current density.

A polarity-reversing switch allows the operator to automatically change current flow direction, which is necessary in preparatory operations (e.g., etching and desmutting) and in stripping, when the current must run opposite to the direction used in electroplating. Otherwise, the connections to the anode and cathode must be changed manually, slowing down the entire process. Indicator lights to show polarity direction may also be incorporated.

Safety circuit breakers instantly shut off the current should a short circuit occur between the anode and the workpiece. Typically, shutdown is within one-half cycle (1/120 s), preventing workpiece damage and injury to the operator.

Energy counters (ampere-hour meters) are required by many industrial and government specifications. Besides keeping track of the energy being used, these meters make it possible to control the thickness of the deposit. Counters may incorporate set points with visual and/or audio warnings to indicate when the desired thickness has been reached.

Optional microprocessor-controlled systems reduce the chance of miscalculation and allow continuous monitoring of the process via an alphanumeric readout. The amount of energy required for an area to be plated to the desired thickness and the applicable parameters are determined by a microprocessor, not the operator. Such equipment is also of merit for plating multiple parts to the same specifications. In some systems, the software prompts the operator for data entry for a particular operation, then displays the correct process parameters.

The plating tool (stylus) must have an insulating handle and an anode material that is inert, insoluble in plating solutions, and able to carry high current. Graphite is by far the most practical choice for anode material. High purity is preferred; any additive used to harden the graphite or give it a different physical characteristic interferes with its beneficial qualities. Graphite can be machined or shaped to fit the contour of the part being processed. Stainless steel is much more durable, but it dissolves in some plating solutions, and after a short time it changes the characteristics of the electrolyte being used. Platinum-iridium, platinum-clad niobium, and platinum-clad titanium are inert to all of the electrolytes used in selective plating operations, and they are used for smaller-diameter anodes. Their disadvantages are increased cost and high hardness, which makes shaping difficult.

The anode covers (wrapping materials) serve as an insulator between the anode and cathode and help ensure smooth deposits at high current densities. Because they hold the electrolyte, they must be absolutely free of oil and foreign materials. Any substance that contaminates the electrolyte has a detrimental effect on the plating. For example, any oil contamination whatsoever results in poor adhesion. Consequently, in a machine shop or other environment where oil is widely used, the work area should be carefully selected. When necessary, applicable part surfaces can be solvent or vapor degreased or go through a separate cleaning cycle.

Various fiberlike materials make suitable covers. Cotton works very well if it is sterile, long fiber. Synthetic fibers, such as polyester and nylon, do not wet or hold electrolytes as well as cotton, but this does not preclude their use. Polyester felt is typically selected when the same anode will be used for numerous parts or for heavy deposits. Most of these materials work well in the form of tube gauze ("bandage covers") as covers over cotton. Scotch-Brite has been used when heavy/hard deposits are required, and it can also function as a burnishing tool, improving the surface as plating continues. If a surface is soft and easily scratched, a different wrap should be chosen.

Reference cited in this section

2. J.C. Norris, Brush Plating: Part I, *Metal Finishing,* July 1988, p 44-48

Key Process Elements

Anode-Cathode Motion. Controlling continuous movement between the anode and the workpiece, or cathode, is a key element in obtaining high-quality brush-plated deposits. However, quality also depends on plating within a specific current density range, so both variables affect ultimate deposit quality. This relationship is illustrated in Fig. 2. Solution suppliers routinely recommend ranges of anode-cathode speeds and current density values for each solution; a representative list is given in Table 5.

Table 5 Anode-cathode motion and current density for selective plating solutions

Selective plating solution	Anode-cathode motion		Current density	
	m/s	ft/min	A/dm^2	A/ft^2
Cadmium (acid)	0.26-0.561	50-110	86.4	864
Cadmium LHE (low hydrogen embrittlement formula)	0.20-0.41	40-80	86.4	864

Chromium	0.02-0.03	4-6	86.4	864
Cobalt (machinable)	0.13-0.26	25-50	115.2	1152
Copper (high speed, acid)	0.20-0.51	40-100	144.0	1440
Gold	0.15-0.31	30-60	28.8	288
Lead	0.15-0.26	30-50	86.4	864
Nickel (acid)	0.10-0.26	20-50	86.4	864
Nickel (high speed)	0.20-0.41	40-80	144.0	1440
Nickel-tungsten alloy	0.10-0.15	20-30	72.0	720
Rhodium	0.03-0.05	5-10	43.2	432
Silver (heavy build)	0.10-0.31	20-60	72.0	720
Tin (alkaline)	0.10-0.41	20-80	86.4	864
Zinc (alkaline)	0.15-0.612	30-120	115.2	1152

Data courtesy of SIFCO Selective Plating

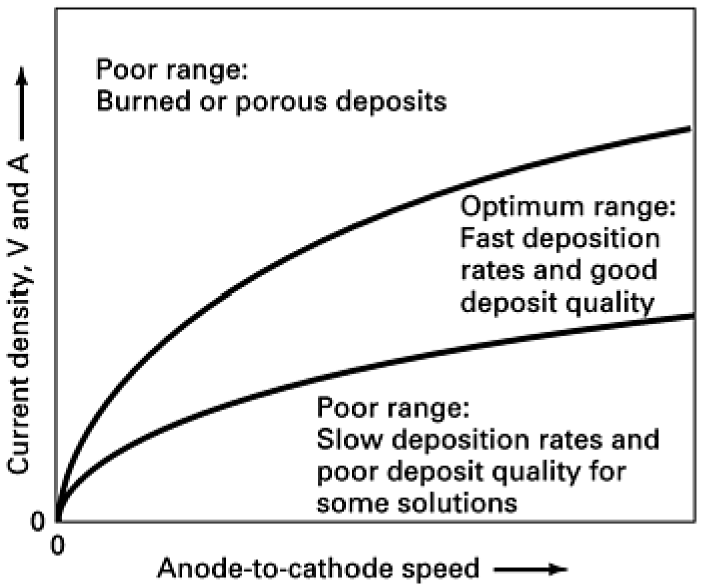


Fig. 2 Relationship between current density and anode-to-cathode speed. Source: Ref 3

The visual appearance of the electroplate is also an indicator of quality. A dark gray or black color usually corresponds to a burnt deposit, which results from too high a current density or insufficient movement. In contrast, inadequate current density or too much movement produces a generally shiny surface.

Anode-to-cathode movement may be achieved manually or mechanically, such as by using turning equipment to provide a constant rotational speed for cylindrical parts (Fig. 3) or by using specially designed tilting turntables to rotate large parts at controlled speeds. Another option is the rotostylus (Fig. 4), which rotates the anode instead of the workpiece.

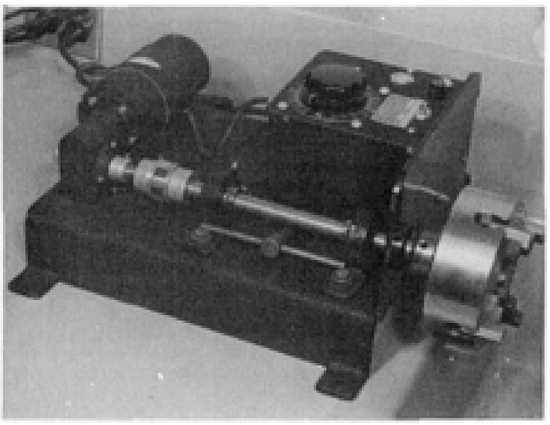


Fig. 3 Turning head. Courtesy of SIFCO Selective Plating

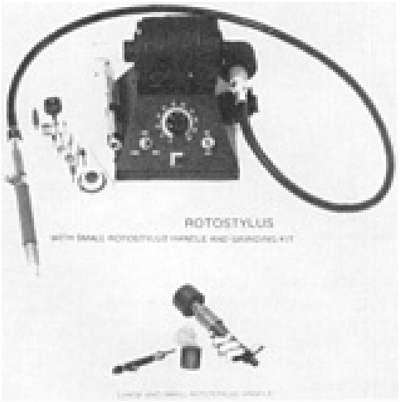


Fig. 4 Rotostylus. Courtesy of SIFCO Selective Plating

Anodes and Flowthrough. For the plating process to be efficient, the plating solution must flow between the anode and the area being plated. Solution can be supplied by periodically dipping the plating tool into the electrolyte. However, the most efficient method is to pump the solution through the block anode and into the interface between the anode and the workpiece (Fig. 5). Plating of large areas at high currents *requires* the use of a pump to recirculate the solution. This keeps the solution from overheating, results in thicker buildups on large areas, and allows the use of higher current densities. In addition, the entire process is faster. Various types of pumps can be used, depending on the amperage and on whether preheating and/or filtering is necessary for the solution used.

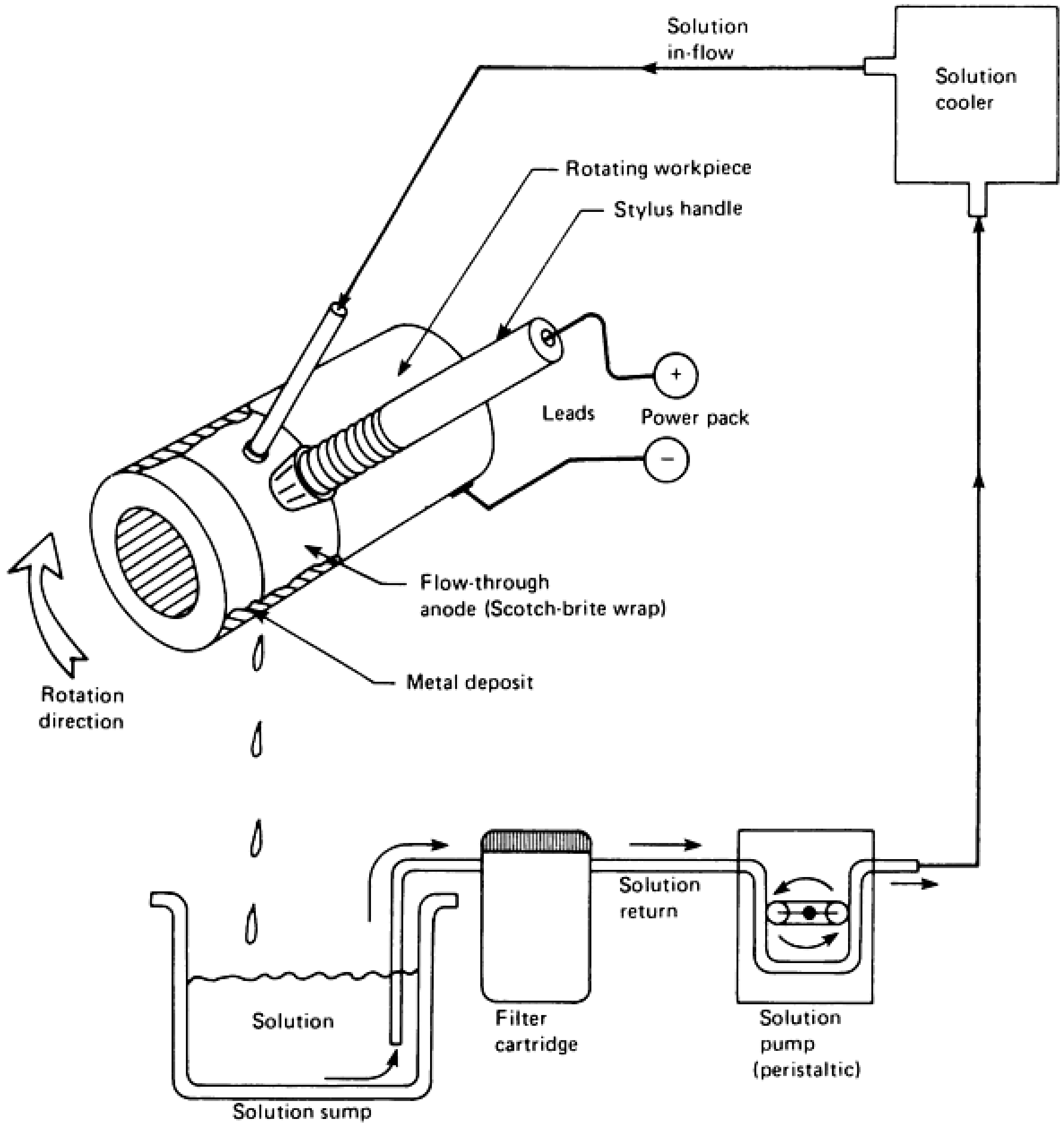


Fig. 5 Flow-through deposition. Courtesy of Vanguard Pacific, Inc.

Solutions. Three basic types of solutions are used in selective plating: preparatory, plating, and special-purpose. Table 6 shows the most common solutions and their uses. The base metal and the type of plating generally dictate which solutions are appropriate.

Table 6 Typical selective plating solutions

Preparatory solutions
Activating (for industrial hard chromium)
Cadmium activator
Chromium activator (for decorative applications)
Cleaning (for most materials)

Desmutting (for cast iron, carbon and alloy steels, copper alloys)
Etching (for aluminum alloys, steels, cast iron)
Etching and activating (for high-temperature nickel-base alloys and stainless)

Plating solutions for ferrous and nonferrous metals

Nickel (acid strike)
Nickel (alkaline)
Nickel (dense)
Nickel (ductile, for corrosion protection)
Nickel (neutral, for heavy buildup)
Nickel (sulfamate, hard, low stress)
Nickel (sulfamate, moderate hardness)
Nickel (sulfamate, soft, low stress)
Antimony
Bismuth
Cadmium (acid)
Cadmium (alkaline)
Cadmium (no-bake)
Chromium (hexavalent)
Chromium (trivalent)
Cobalt (for heavy buildup)
Copper (acid)
Copper (alkaline)
Copper (high-speed acid)
Copper (high-speed alkaline for heavy buildup)
Copper (neutral)
Iron
Lead (alkaline)
Lead (for alloying)
Tin (alkaline)
Zinc (acid)
Zinc (alkaline)
Zinc (bright)
Zinc (neutral)

Plating solutions for precious metals

Gallium
Gold (acid)
Gold (alkaline)
Gold (neutral)
Indium
Palladium
Platinum
Rhenium
Rhodium
Silver (hard)
Silver (noncyanide)
Silver (soft)

Plating solutions for alloys

Babbitt Navy Grade 2
Babbitt SAE 11
Brass
Cadmium-tin
Cobalt-tungsten
Nickel-cobalt
Nickel-tungsten

Tin-indium Tin-lead-nickel
Special-purpose solutions
Anodizing (chromic) Anodizing (hard coat) Anodizing (sulfuric) Chromate treatment Electropolishing solution

Source: Ref 2

Preparatory solutions clean the substrate surface so that it can effect a better bond with the electroplate. Preparation typically involves precleaning, electrocleaning, and electroetching; some base materials also require desmutting, activation, and preplate operations. Parts with heavy corrosion, lubricants, oil, and so on ordinarily require more aggressive cleaning, such as vapor/solvent degreasing or grit blasting, prior to precleaning.

Plating solutions used for selective plating have a much higher concentration of metal, usually as organometallic salts, than do solutions used for tank plating. This higher metal content permits the use of higher current densities, which results in faster deposition, better bond strength, and less porosity than in tank plating.

Two basic kinds of plating solutions are used. One deposits a thin preplate ("strike") that boosts adhesion on certain metals and alloys, and the other builds up the coating to its functional thickness. Suppliers usually offer a choice of solution for each type of electroplate, because different properties are required for different applications (e.g., high hardness and wear resistance for one, ductility for another).

Special-purpose solutions include those used for post-treatment, anodizing, and electropolishing.

Thickness Control. The thickness of a deposit can be controlled by monitoring the ampere-hour meter. Each solution has a prescribed energy factor, which indicates how many ampere-hours are required to deposit a given metal thickness on a given area:

$$\mathrm{A \cdot h} = F \times A \times T$$

where A · h is the ampere-hours required, *F* is the energy factor, *A* is the area to be plated (in square centimeters), and *T* is the thickness of the deposit (in microns). The calculation yields a fixed value that can be monitored on the meter (or set on the ampere-hour counter, if the power pack is so equipped). If needed, simple additional calculations can also be performed to determine the optimum current, plating time, volume of plating solution, and even rotational speed (Ref 4).

References cited in this section

2. J.C. Norris, Brush Plating: Part I, *Metal Finishing,* July 1988, p 44-48

3. DALIC Process Instruction Manual, 5th ed., SIFCO Selective Plating, 1990

4. J.C. Norris, Brush Plating: Part II, *Metal Finishing,* Aug 1988, p 45-47

Specifications

Since the mid 1950s, when the first commercial selective plating specification was introduced, the number of specifications has surpassed 100. The following list includes some of the more important industrial, government, and military specifications:

- MIL-STD-865C (U.S. Air Force)
- MIL-STD-2197SH (U.S. Navy)

- BAC 5849, 5854 (Boeing)
- DPS 9.89 (Douglas Aircraft)
- MPS 1118A (Lockheed Aircraft)
- SS 8413, 8494 (Sikorksy Aircraft)
- BPSFW 4312 (Bell Helicopter)
- FPS 1046 (General Dynamics)
- HA 0109-018 (North American Rockwell)
- GSS PO60B (Grumman)
- Standard Practice Manual 70-45-03 and T.M. No. 72-191 (General Electric)
- PS 137, Issue 1 (Dowty Rotol Ltd., England)
- ITF 40-839-01 (Messier-Hispano, France)
- TCMK-5 (Saab-Scania, Sweden)
- Report NAEC-AML 1617 (Naval Air Engineering Center, Philadelphia)
- M-967-80 (Association of American Railroads)
- AC 43.13-1A, Chg. 1 (Federal Aviation Administration)
- AMS 2439, 2441, 2424C
- SPOP 321 (Pratt & Whitney)

In addition to the above specifications, many U.S. Navy and U.S. Air Force activities have generated instructions for selective plating of specific hardware or components at specific military facilities.

In the electronics field, the repair of printed circuit boards for military applications is authorized by MIL-STD-865C. For commercial applications, the Institute for Interconnecting and Packaging Electronic Circuits approves the use of selective plating for repair of both bare and assembled printed circuit boards (Ref 5). In addition, many electronics companies have issued their own specifications for in-house repair of circuit boards and other electronic components.

Reference cited in this section

5. *Modification and Repair for Printed Boards and Assemblies,* Manual IPC-R700B, Institute for Interconnecting and Packaging Electronic Circuits

Health and Safety Considerations

There are two safety issues in selective plating: the chemicals and the equipment used to apply the chemicals. Overall, the process meets the safety requirements set by the Occupational Safety and Health Administration (OSHA) for in-plant use. Electrical protection of the power pack, workpiece, and operator are provided by a direct current circuit breaker within the power pack. This circuit breaker trips when an overload occurs. If the anode shorts out by contacting the part, or if the power pack exceeds its amperage rating, the breaker almost instantly stops power flow.

Today, manufacturers provide material safety data sheets (MSDS) with solutions, in conformance with OSHA requirements. The solutions are industrial chemicals and should be handled as such. Ventilation to remove fumes is recommended, and conventional safety guidelines, including the use of safety glasses and rubber gloves, should be routinely followed. Reviewing the MSDS will alert personnel to any special handling or other safety precautions required.

Pulsed-Current Plating

Chuck VanHorn, Enthone-OMI, Inc.

Introduction

CONVENTIONAL PULSED-CURRENT PLATING (commonly referred to as *pulse plating*) can be defined simply as metal deposition by pulsed electrolysis. In its simplest form, it involves using interrupted direct current to electroplate parts. This is accomplished with a series of pulses of direct current, of equal amplitude and duration in the same direction,

separated by periods of zero current. The pulse rate (frequency) and "on" and "off" times (duty cycle) can be controlled to meet the needs of a given application. The ideal shape of the pulsed current is shown in Fig. 1(a). An oscilloscope should be used to reveal how well the equipment controls the output (Fig. 1b).

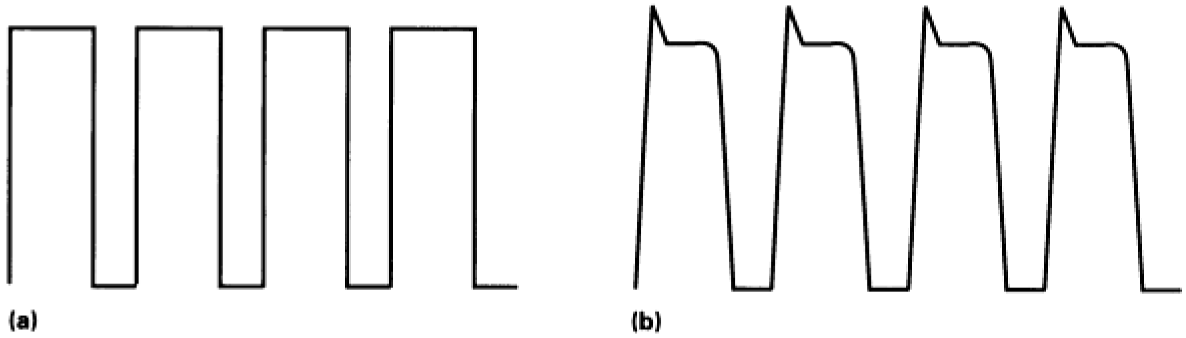


Fig. 1 Current patterns in conventional pulsed-current plating. (a) Ideal pattern. (b) Typical pattern as seen using an oscilloscope

Pulse plating has gained acceptance in a number of metal finishing industries, especially the electronics industry. With the advent of solid state pulse plating power supplies, the imprecision has been taken out of the process. The amount of time the current is on and off is set directly on digital thumb-wheel switches or via programmable software. Two different modes of operation are used: constant current and constant voltage. Figure 2 illustrates the constant-current mode of operation. The tops of the current pulses are kept flat by allowing the voltage to vary during the pulse on-time. In the constant-voltage mode (Fig. 3), the tops of the voltage pulses are kept flat by varying the current. Because of the shape of the current pulse in the constant-voltage mode, the peak current is not useful for controlling the plating rate. An amp-minute controller is needed to accurately control the plating thickness.

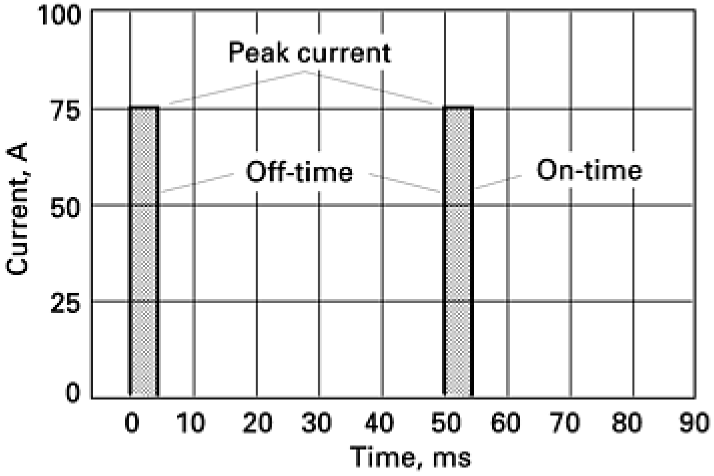


Fig. 2 Constant-current pulse plating with an on-time of 5 ms, an off-time of 45 ms, and a peak current of 75 A. Because the current is on one-tenth of the time, the average current is 7.5 A.

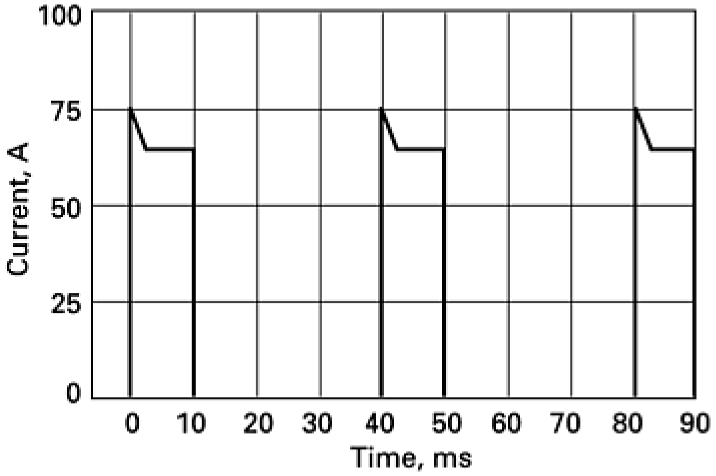


Fig. 3 Typical current pattern for constant-voltage pulse plating. The current falls during the on-time because of the increasing resistance of the cathode. On-time, 10 ms; off-time, 30 ms

Metals that are commonly deposited using pulsed current include gold and gold alloys, nickel, silver, chromium, tin-lead alloys, and palladium. Pulsed current is also used for anodizing and, in select cases, for etching, electrocleaning, and electroforming.

The advantages of pulse plating vary from one application to the next. The most common (relative to plating with conventional continuous current) include the following:

- Deposits are smooth, dense, fine-grained, and almost completely free of pinholes.
- Variation in plate thickness from one part to the next is considerably reduced.
- Plating speeds can normally be increased.
- Current efficiency generally is improved.
- Use of organic additives, in most cases, can be reduced by 50 to 60%. Deposits are free from dendritic growth even if additives are not used.
- For some electrodeposits, such as gold, less metal is required in the plating solution to meet end-use specifications.

The limitations of pulse plating include the fact that the cost of a pulsed-current rectifier is greater than that of a conventional dc unit. Also, optimization of results requires planning and experimentation, and plating equipment may need to be redesigned or upgraded.

Process Principles

The theory behind pulse plating is simple (Ref 1, 2). The cathode film is kept as rich in metal ions as possible and as low in impurities as possible. During the period when the current is on, the metal ions next to the cathode are depleted and a layer rich in water molecules is left. During the portion of the cycle when the current is off, the metal ions from the bulk of the plating solution diffuse into the layer next to the cathode. Then the process is repeated again. Also during the time the current is off, gas bubbles and impurities that have been adsorbed on the cathode have a chance to desorb.

Typical on-time range from 0.1 to 9.9 ms, and typical off-times range from 1 to 99 ms. If an ammeter is inserted into a pulsed-current plating circuit, it responds to the average current. In order to have the same plating rate using pulsed current as with conventional continuous current, the average current must be the same. This can be achieved by adjusting the peak current, the on-time, or the off-time. The physical and chemical properties of deposits can be very precisely controlled through the careful selection of pulse-plating parameters.

Concepts and Terminology. Selected terms that have special meaning when applied to pulse plating are defined as follows:

- *Cathodic (forward) and anodic (reverse)* are used to describe current direction; *cathodic* indicates flow is in the normal (plating) direction, *anodic* indicates flow is in the reverse (deplating) direction. In normal operation of a reversing pulse unit, current direction alternates in a controllable forward and reverse pattern.
- *Envelope* is the time span during which current may flow in only one direction. The time spans of the forward envelope and the reverse envelope are set individually.
- *Pulse train* is a regularly interrupted current flow in either the cathodic or anodic direction. A pulse train exists within the envelope.
- *Pulse* is the individual interval in a pulse train, consisting of one "on and off" period.
- *Pulse rate* is the number of times the current is switched on in a given period of time (usually 1 *s*).
- *Duty cycle* is the ratio of time an individual pulse is on compared to the total (on and off) pulse time. For example, 5 ms on and 5 ms off is a 50% duty cycle, 4 ms on and 1 ms off is an 80% duty cycle, and so on. (*Note:* if the duty cycle is 100%, there is no off time; the current is on for the duration of the envelope and there is no pulse or frequency.)
- *Frequency* is the pulse rate expressed as hertz units (e.g., 100 Hz = 100 pulses/s).
- *Pulse width* is the time span of the on portion of a pulse. Pulse width is a function of both frequency and duty cycle. For example, a 1000 Hz pulse with a duty cycle of 50% has a pulse width of 0.5 ms.

References cited in this section

1. H.Y. Chen, *J. Electrochem. Soc.,* Vol 118, 1971, p 551
2. R.J. Tedeschi, *Met. Finish.,* Nov 1971, p 49

Process Control

Microprocessor-controlled modulation of applied direct current to improve the electrodeposition process has found use in reel-to-reel selective plating, automatic tab plating, barrel line plating, still plating, electroforming, anodizing, electrocleaning, electropolishing, and electromachining. It recently has been adapted for use with semiconductor bump and wafer plating technologies.

The use of this sophisticated power control can result in greatly increased plating speeds, improved deposit distribution, lower deposit stress, finer grain structure, increased ductility, improved adhesion, increased micro-throwing power, reduced susceptibility to hydrogen embrittlement, and a markedly decreased need for additives.

The use of modulated dc power supplies with advanced electronic circuitry enables the user to control output patterns with extreme precision. A high-quality unit will superimpose periodic reverse on a high-frequency pulse. The power pattern that results is quite complex, with a wide range of profiles. The output--a series of pulses with controllable amplitude, frequency, duration, and polarity--influences the deposition characteristics of any solution. The characteristics obtained with modulated power supplies are quite different from those obtained with conventional pulse or periodic-reverse equipment. By "tuning" or shaping the output power pattern to a given plating application, the operator can dramatically enhance the rate of deposition and the character of the deposit.

In periodic-reverse plating, the polarity of a constant dc output is switched back and forth in a regular pattern. Figure 4(a) depicts the ideal output; Figure 4(b) shows the actual output from a slow-response control unit.

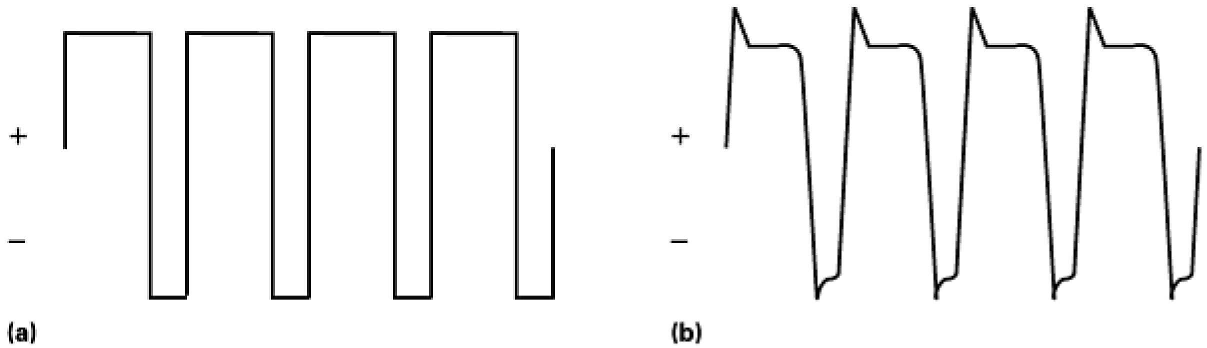


Fig. 4 Current patterns in periodic-reverse pulsed-current plating. (a) Ideal pattern. (b) Pattern of a slow-response control unit as seen using an oscilloscope

The sharpness of the output current pattern as revealed by an oscilloscope depends on the degree of ripple in the rectifier output and the quickness of response in the internal switching circuitry of the controller. High-quality units produce extremely sharp square-wave patterns (Fig. 3 and 4). Figure 5 illustrates the wave form of the forward (cathodic) and reverse (anodic) output of a high-quality unit.

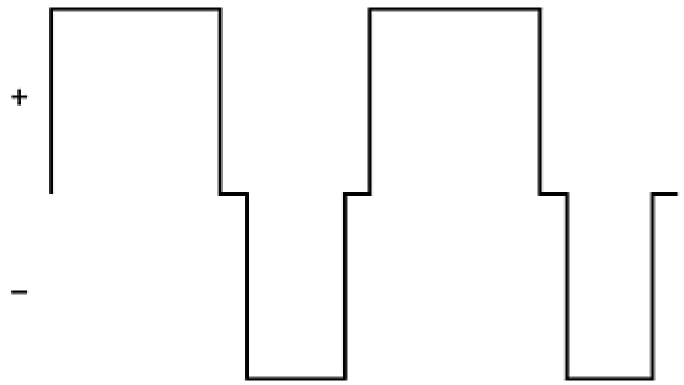


Fig. 5 Square-wave current pattern of the forward and reverse envelopes in periodic-reverse pulse plating

The duration of the current in each direction (the forward and reverse envelopes) can be individually controlled from 0.1 ms to 99.99 s. (A zero current delay of less than 0.1 ms between forward and reverse is a design feature of high-quality units that serves to prevent transistor failure due to "shoot through.") The simple, square-wave pattern shown in Fig. 5 is the result of a precisely controlled periodic-reverse output; pulse frequencies can then be superimposed upon this output pattern. Within each envelope, a square-wave pulse is generated (Fig. 6). The frequency and the duration of the pulses are set independently for the forward and reverse envelopes; frequencies range from 10 to 9999 Hz. Duty cycle settings in percentages determine the on and off times for each pulse.

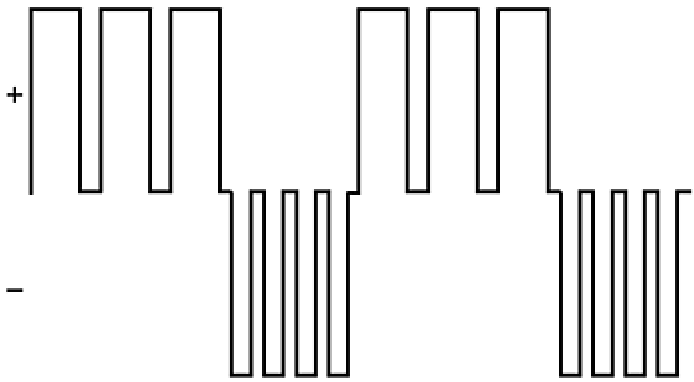


Fig. 6 Current pattern for periodic-reverse pulse plating in which pulse frequencies have been superimposed on the forward and reverse envelopes

On some models, forward and reverse amplitude can be controlled individually (Fig. 7). This permits, for example, a higher current density in the reverse (deplating) stage than in the forward (plating) stage, which is highly desirable for some applications. (More complete explanation of output control with specific units is available in the operation manuals supplied by their manufacturers.)

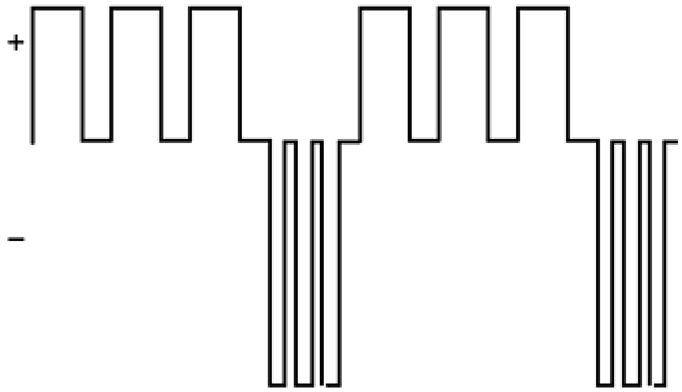


Fig. 7 Current pattern for periodic-reverse pulse plating in which pulse frequencies of different current densities have been superimposed on the forward and reverse envelopes

Solution Composition and Operating Conditions

With the changes that take place in the plating tank when a modulated periodic reverse pulse is impressed on the electrolyte, changes in the other operating conditions or even in the formulation may be required. Generally speaking, better results are obtained with simple, rather than sophisticated, formulations (Ref 3). Typical solutions used in pulse plating are given in Table 1.

Table 1 Typical solutions used in pulsed-current plating

Constituent or condition	Amount or value
Watts nickel solution for reel-to-reel plating	
Nickel sulfate, g/L (oz/gal)	650 (87)

Boric acid, g/L (oz/gal)	50 (7)
Temperature, °C (°F)	60 (140)
pH	3-4
Anodes[a]	Platinized niobium (insoluble)
Organic additives	None
Pure gold	
Potassium citrate, g/L (oz/gal)	150 (20)
Citric acid, g/L (oz/gal)	15 (2)
Potassium phosphate, g/L (oz/gal)	26 (3)
Boric acid, g/L (oz/gal)	72 (10)
Gold metal, g/L (oz/gal)	8.2 (1)
Temperature, °C (°F)	60 (140)
pH	3.5-4.0
Anodes	Platinized titanium
Hard gold	
Citric acid, g/L (oz/gal)	65 (9)
Potassium citrate, g/L (oz/gal)	50 (7)
Cobalt, g/L (oz/gal)[b]	0.5-0.6(0.07-0.08)
Gold, g/L (oz/gal)	8.2 (1)
pH	3.8-4.0
Temperature, °C (°F)	32-38 (90-100)

(a) When using soluble nickel anodes with reversing pulse modes, the use of an anode activator such as chloride is not required because the reversing current keeps the anode active and soluble.

(b) The higher voltage of pulse plating relative to continuous dc plating favors the deposition of the alloying agent. The operator should analyze the deposits to determine if the amount of cobalt in the solution should be adjusted. In most cases, the amount of available cobalt (or other alloying agent) should be reduced (from the amount used with continuous current) to obtain the desired properties.

Additives. The polarization imposed by the power pattern on the bath reduces, or even eliminates, the need for some addition agents. In many cases, additives can actually inhibit the effectiveness of the pulsed-current pattern. For example, large-molecule additives do not respond as they do under conventional power; in a high-frequency pulse field, their molecular size is a disadvantage. Small-molecule organics or inorganics will generally function well as additives. In many cases, the use of brighteners can be reduced as much as 90% without diminishing the brightness of the deposit because of the improved grain structures. If brightener levels are not reduced, longer pulses--i.e., lower frequencies and/or higher duty cycles--may be required (Ref 3).

Electrolyte conductivity must be maintained at a high level to allow the peak pulse current to be completely effective. If the conductivity is not high enough, an excess in voltage will be required to attain the desired peak current. Such peaks are power-inefficient and less effective.

Anode-to-cathode ratios for pulse plating are rarely the same as those for conventional power applications. Generally speaking, in acid or alkaline nonchelating formulations, the anode area should be reduced. In cyanide or other chelating formulations, the reverse is generally the case, and a greater anode area is required.

Temperature and agitation conditions for conventional processes may also have to be altered for modulated power pattern plating. Unfortunately, no general rule applies; each application has its own requirements, and optimum conditions must be established on a case-by-case basis.

Reference cited in this section

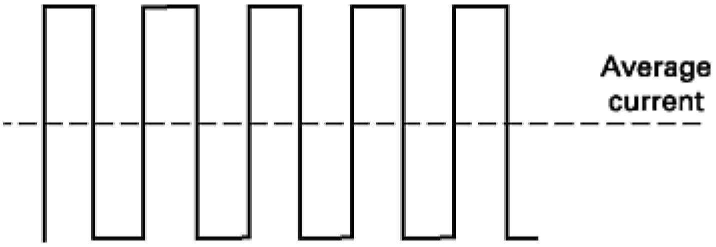
3. J. Padden, J. Lochet, and C. VanHorn, "Improvement of Electrodeposition through Modulated dc Power Patterns," 1981

Equipment Modification

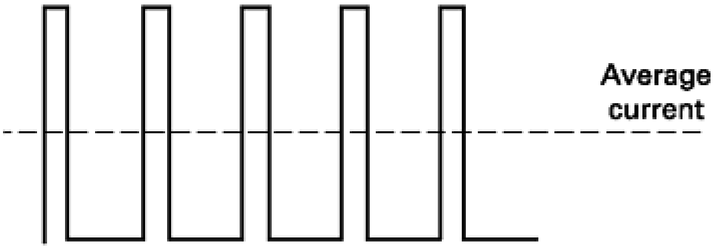
One factor that should always be checked when planning a change from conventional to pulsed-current power is the tank electrical contact system. Some anode and/or cathode contacts that may be perfectly suitable for conventional plating may present unwanted resistance to high-frequency peak currents. Overlooking this factor may prevent the realization of the full benefits of a modulated power supply.

The major consideration, of course, is the power system itself. Existing rectifiers may or may not be suitable for use with modulated periodic reverse or direct pulse units. For pulse plating, a high-voltage, quick-response rectifier is required, and the lower the ripple, the more precise and predictable the output. Although pulse units are available for use with existing power supplies, models with self-contained rectifiers give greater assurance that full benefit of the control system will be realized.

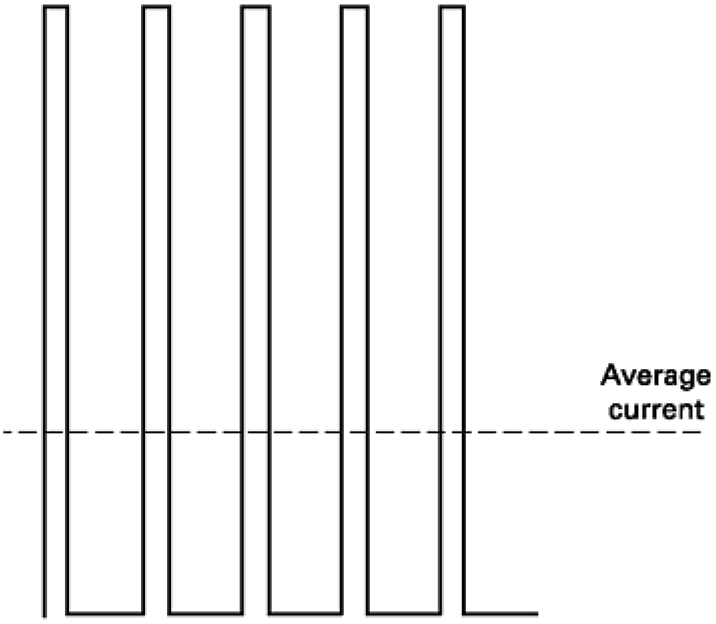
Pulse units with self-contained power can be operated in either a constant-average-current or constant-voltage mode. The significance of this option is illustrated in Fig. 8. Figure 8(a) depicts a pulse train with a 50% duty cycle. The *average* current delivered is 50% of the *peak* value. Figure 8(b) shows the effect of reducing the duty cycle to 25% when in a constant-voltage mode. The peak current remains the same, but the average current changes directly with the duty cycle, in this case dropping to half its former value. The current density of the pulsed current remains the same, but twice as much real time is required to deliver the same amp-minutes of current. Figure 8(c) shows the effect of reducing the duty cycle from 50 to 25% when operating in constant-average-current mode. In this case, the peak current changes inversely to the duty cycle, increasing in value to maintain the same average current delivered as before but in shorter pulses.



(a)



(b)



(c)

Fig. 8 Effect of changes in the duty cycle on constant-average-current and constant-voltage pulsed-current plating. (a) 50% duty cycle, with average current 50% of the peak value. (b) Duty cycle reduced to 25% in constant-voltage mode; average current drops with duty cycle. (c) Duty cycle reduced to 25% in constant-current mode; the peak current changes inversely to the duty cycle.

Although a change in frequency also changes the pulse width, it does not effect either peak or average current, regardless of output mode (Fig. 9). Unlike conventional plating rectifiers, which are rated by average current capacity (ignoring the ripple), modulated periodic reverse pulse units are normally rated by their peak current capacity. Because both peak and average current values are intrinsic to modulated power pattern plating, both output capacities must be considered. Depending on the internal circuitry of the unit, the average current output capacity of some models can be as low as 25 or 30% of the peak capacity. With such a low value for average current, the rated peak current output would be attained even at average current capacity only if a duty cycle as low as 25 or 30% was used. Attempting to push average current up would drastically shorten the life of the unit. Experience has shown that effective duty cycles are usually not less than 50% (although they can be as low as 10% for pure precious metals), and most units are designed to deliver an average

current capacity of 50 to 60% of the peak current capacity rating. However, any desired duty cycle can be used or specified, but the operator must keep in mind that the average current is the percentage (duty cycle) of the peak rating.

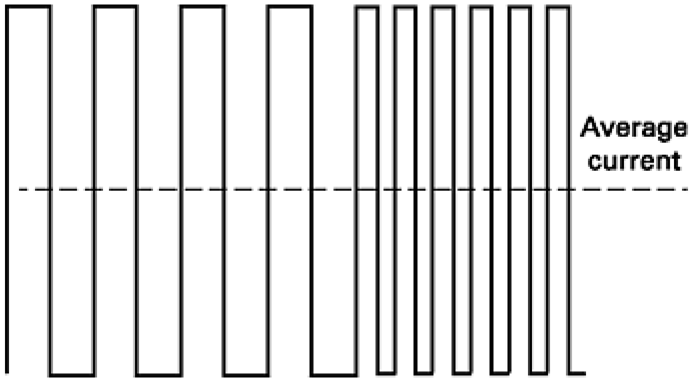


Fig. 9 Effect of change of frequency on current pattern in pulsed-current plating. Only pulse width is altered; peak current, average current, and duty cycle remain constant.

Electroforming

Glenn Malone, Electroformed Nickel, Inc.; Myron E. Browning, Matrix Technologies

Introduction

ELECTROFORMING is the process by which articles or shapes can be exactly reproduced by electrodeposition on a mandrel or form that is later removed, leaving a precise duplicate of the original. In certain applications, the mandrel is designed to remain as an integral part of the final electroformed object. Electroforms themselves may be used as parents or masters, usually with special passivating treatments so the secondary electroform can be easily removed. The same or similar electrodeposition additives as those used for electroplating are required for electroforming to control deposit stress, grain size, and other resultant mechanical properties in order to produce high-quality electroforms.

Early Applications

Electroforming was developed by a Prof. Jacobi of the Academy of Sciences in St. Petersburg, Russia in 1838 while working with an engraved copper printing plate. While Prof. Jacobi had much difficulty in trying to separate the replicated layer, he did note that once it was released the copper piece gave a perfect match of the original.

Prof. Boettger of Germany used nickel plating in the 1840s to produce exacting replicates of art objects by the electroforming process. Electroformed articles, including sculpture, bas-reliefs, and statues from nickel, iron, or copper were produced prior to 1870. Of special interest were the huge electroformed street lamps found in downtown Paris, the production of which might be considered an enormous world-record accomplishment for electrodeposition. Iron electroforming had early applications in the duplication of printing plates for coinage and currency because of its facility to produce the highest accuracy in copying engraved masters.

Modern Applications

Today, the electroforming industry sees a number of high-tech uses for nickel, copper, iron, and alloy deposits to electrofabricate exceedingly important components such as the main combustion chamber for the Space Shuttle, heart pump components, body joint implants (prosthetic devices), high-precision optical scanners and holographic masters (for credit cards, etc.), and recording masters. Fabrication of duplicating plates such as electrotypes, video disc stampers, and currency embossing plates is manufacturing technology of today that employs electroforming. High-precision parts such as molds and dies, where tolerances of internal surfaces are critical, are pieces for which electroforming can be used advantageously. Optical memory disc mold cavities, including those for compact discs (CD and video discs) rely on the virtually perfect surface reproduction found with the electroforming process. The average optical disc requires

impressions having a mean diameter of about 0.2 μm, which is well within the range of the electroforming processes practiced today. One of the most widely used applications today is nickel disc mold electroforming.

Examples of electroforming applications are almost limitless, but a few of the more exacting examples are:

- Delicate, thin-wall components such as lightweight heat or cold shields for aerospace applications, hypodermic needles, foil, fine-mesh screen, and seamless tubing
- Parts that would be difficult to make by any other means, such as electronic waveguides, regeneratively cooled thrust chambers for rocket engines, musical instruments, Pitot tubes, surface roughness gages, and complex metal bellows
- Electroform joining (cold welding) of dissimilar metals that are difficult, if not impossible, to join by thermal means

Electroforming provides unique production advantages for precision operation in the textile, medical, aerospace, communication, electronics, photocopying, automotive, and computer industries, and a number of other industries and is used in the manufacturing of items such as textile printing screens, molds and dies, mesh products, bellows, compact disc stampers, radar wave guides, and optical components.

Electroforming Determinants

Once the conceptual design for a part or component is developed, it is necessary to determine the fabrication process that best meets the functional requirements of the hardware with least cost impact. The following advantages of electroforming might be weighed:

- Parts can be mass produced with identical tolerances from one part to the next, provided that mandrels can be made with adequate replication.
- Fine detail reproduction is unmatched by any other method of mass fabrication. Examples are the electroforming of microgroove masters and stampers for the record and compact disc industries, surface roughness standards, and masters and stampers for holographic image reproduction.
- Mechanical properties of electroformed articles can be varied over a wide range by selecting a suitable plating electrolyte and adjusting operating conditions. In some instances properties can be created in electroformed metals that are difficult, if not impossible, to duplicate in wrought counterparts.
- Some shapes, particularly those with complex internal surfaces or passages, cannot be made by any other method without excessive machining costs and scrap losses. These shapes are often easily electroformed. Examples of such hardware are regeneratively cooled thrust chambers and waveguides with compound curves.
- Gearing up to high-volume production is relatively easy in many electroforming applications. For example, a number of first-generation positive replicas can be made from which a large number of second-generation negatives can be electroformed. Such technology lends itself to many molds, stamping devices, and optical surfaces requiring volume production.
- The size and thickness of parts electroformed is not limited. Larger size can be accommodated by increasing the tank volume in which the electrolyte is contained. Thickness may vary from micrometers, as in foils, to one or more centimeters, as is common in rocket thrust chamber shells.
- Without the use of thermal joining techniques, metal layers can be applied by electroforming to provide sandwich composites having a variety of functional properties. Waveguides having an inner silver electroformed layer for high electrical conductivity and an outer electroformed structural layer of copper, nickel, nickel-cobalt, or other electrodepositable alloys are examples.

There are also some disadvantages of electroforming that must be considered, such as:

- Electroforming is generally an expensive manufacturing method and is chosen when other methods are more expensive or impractical to produce the desired hardware.

- Thick electroforming is very time-consuming. Some deposits require days, or even weeks, to produce the desired thickness. However, unlike precision machining, which is also very time-consuming, electroforming is not labor-intensive once the deposition process is started.
- Design limitations exist in that deep or narrow recesses and sharp angles cause problems. Sudden and severe change in cross section or wall thickness must be avoided unless subsequent machining can be permitted.
- Most electrodeposits have some degree of stress in the as-deposited condition that may cause distortion after the mandrel is separated. Stress relieving and special attention to electrolyte chemistries and operating parameters can lessen this problem.
- Any degradation in the mandrel surface quality will be reproduced in the electroform made from it.

The Electroforming Process

Electroforming is very similar to conventional electroplating as far as facilities and electrolytes are concerned. However, the controls are more stringent, because the process consumes much more time and the product must be mechanically sound and have low internal stress for dimensional acceptance. With long deposition times, high current densities at edges and surfaces closer to the anodes result in significant buildup, leading to nodules and uncontrolled growth. This results in further current density variations that can seriously affect the mechanical properties of the deposit.

In electroforming nickel, cobalt, or iron there is significant hydrogen codeposition that, if not removed, causes pits in the deposit surface. Pumping filtered electrolyte through sprays over the surfaces being electroformed will minimize the problem and aid in maintaining a smooth deposit. Areas of high current density showing excessive and rough buildup can be corrected by using nonconducting shields as baffles to improve the current distribution. Where recessed areas exist, low current density will be experienced. Undesired trace metal impurities will codeposit in such locales, leading to inferior mechanical properties and surface appearance. Auxiliary or bipolar anodes may be necessary to overcome the low-current problem.

Electroforming solutions may be used with one or more additives to control stress, brightness, leveling (smoothness), and microstructure. When mechanical properties (including high ductility) or good electrical or thermal conductivity are important in the deposit, it is advisable to use nonadditive electrolytes. Because most additives are organic compounds, they are subject to decomposition if the deposit is subjected to elevated temperatures.

Stress-reducing agents are often used in nickel, iron, and cobalt plating baths to produce neutral or compressive residual stresses. Such agents are usually grain-refining compounds also. These deposits are generally harder, have higher yield strength, and exhibit less ductility than conventional deposits of the same metal. Advantages in neutral or compressively stressed deposits are ease of removal of electroforms from mandrels and inhibition of growth of cracks in deposits should they occur from impact. A problem with stress reducers in nickel is that sulfur codeposits form when the agent reacts at the cathode, because most stress reducers contain sulfur. Brazing or welding such deposits causes sulfur to react with nickel to form a nickel sulfide liquidus in the range of 483 °C (901 °F) to about 650 °C (1200 °F). This leads to the effect known as "hot shortness" experienced in wrought nickels. Such deposits can be alloyed with as little as 1500 ppm Mg to counter the problem.

Copper Electroforming. Acid sulfate electrolytes are the industry standard for copper electroforming. Additives are usually employed for grain refining, leveling, and brightening. The mechanical property improvements achieved are mostly a result of grain refining. Organic compounds capable of reducing copper oxides at the cathode may also be used to produce an oxygen-free, high-conductivity copper equivalent (<10 ppm oxygen). Decomposition products from copper bath additives will codeposit to degrade ductility. Without additives, acid sulfate baths produce copper with grain size increasing proportionally to deposit thickness. Intergranular voids are created that seriously degrade mechanical properties. A plating technique known as periodic current reversal will promote deposition of a copper deposit having uniform grain size and excellent mechanical properties for thicknesses of 0.5 cm (0.2 in.) or greater. This procedure requires plating in a conventional direction for a given period of time, followed by a reversal of current direction for a lesser period of time. Although the process results in a slow rate of deposition, the benefits of good mechanical properties, relatively smooth deposit surfaces, and ability to plate dense, thick deposits make this technique most useful.

Mandrel Types and Selection

Mandrels are either permanent or expendable. Permanent mandrels are usually metallic, but they can also be made of a conductive plastic. They can be used repeatedly until surface wear or scratching renders them useless. The most widely used permanent mandrels are made of metals that are resistant to adherent bonding by the metal being electroformed. The 300-series stainless steels are the preferred materials for permanent mandrels because of the naturally passive surfaces. Substrates such as copper, brass, or steel may also be used, but these must be plated with chromium to provide a passive surface for ease of separation. It is also possible to use copper or brass for engravure mandrels if they are chemically passivated to prevent electroform bonding. Nickel is frequently employed for producing multiple first-generation replicas for mass production of second-generation electroforms. Adherence on nickel is unpredictable, so it is advisable to passivate the surfaces chemically.

Plastics are suitable for permanent mandrels where flat electroforms are involved and separation is relatively simple. Such mandrels are made conductive by the silver reduction method (Ref 1) or by use of silver-filled paint. Plastic mandrels are often used for the electroforming of Fresnel lenses. Glass plates can also be used as permanent mandrels containing holographic imagery.

Expendable mandrels may consist of cast fusible metals, plaster, plastics, waxes, soluble metals, or wood. Fusible metals are commonly alloys of tin, lead, bismuth, antimony, and cadmium. Aluminum is a popular expendable mandrel material because it is easily machined and polished to close surface and dimensional tolerances. It is also easy to dissolve in caustic solutions.

Reference cited in this section

1. H. Narcus, *Metallizing of Plastics,* Reinhold Publishing Company, 1960

Mandrel Design and Preparation

Mandrels may be made to reproduce accurately external or internal surfaces. The reproduced surface will be precisely the same as the surface upon which plating is initiated. The final plated surface will be rougher as the plated thickness increases. Design features of importance are avoidance of deep grooves or recesses, avoidance of sharp internal angles, and maintenance of liberal radii on corners. Figure 1 illustrates mandrel design considerations that should be followed.

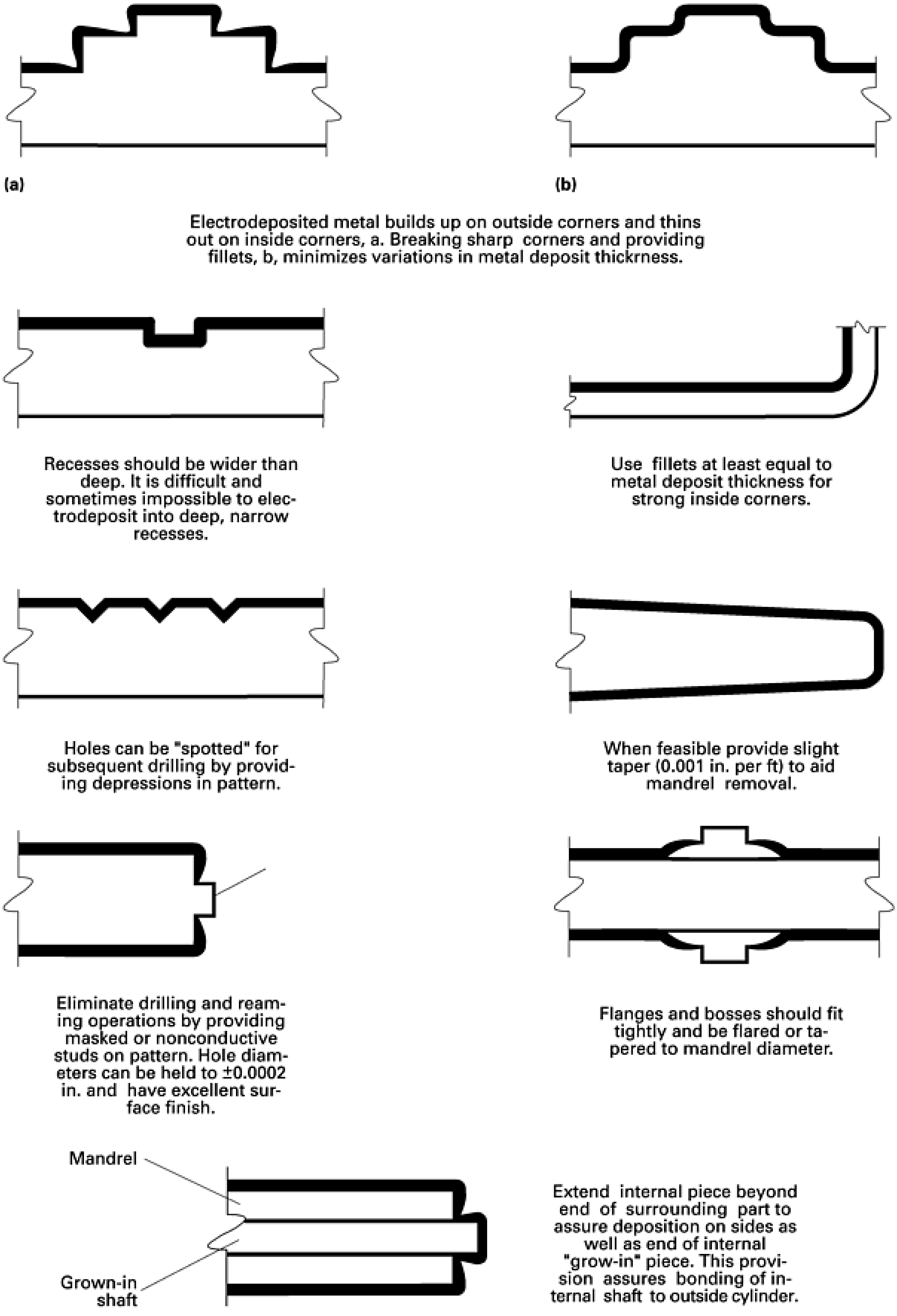


Fig. 1 Factors to consider in electroforming mandrel design. Source: Ref 2

Permanent mandrels for electroforming concentric shapes must be designed with a draft or taper to permit removal of the mandrel without damaging the electrodeposit or the mandrel. If this is not possible, expendable mandrels must be considered. ASTM B 450 provides more guidelines in the design of electroformed articles (Ref 3). Preparation of mandrels for electroforming is detailed in ASTM B 431 (Ref 4). Special design considerations are often given to permanent mandrels being developed for complex parts that are to be produced in mass quantities or are of a complex nature, requiring speedy release from the mandrel. In these cases, knockout blocks or key release sections are designed into the mold, mandrel, or matrix to ensure quick and positive release and multiple uses of the master form.

References cited in this section

2. A. Squitero, Designing Electroformed Parts, *Machine Design,* 9 May 1963
3. ASTM B 450, "Standard Practice for Engineering Design of Electroformed Articles," ASTM
4. ASTM B 431, "Standard Practice for Processing of Mandrels for Electroforming," ASTM

Electroforming Solutions and Operating Variables

Nickel Electroforming Solutions. Nickel, the most commonly electroformed metal, is plated from Watts, fluoborate, and sulfamate solutions. The last is the most widely used due to lower stresses in the deposits and ease of operation. Nickel is deposited from most baths with moderate to high tensile stress. If uncontrolled, this stress can make removal of the mandrel difficult, can result in distorted parts after mandrel separation, and can even result in deposit cracking. In general, the chloride-free sulfamate bath produces the lowest internal stresses of all the nickel baths. Typical nickel sulfamate electrolyte compositions, operating conditions, and deposit mechanical properties are shown in Table 1. Effects of changes in operating variables on mechanical properties of nickel sulfamate deposits are described in Table 2. Similar information for all commonly used nickel electroforming baths is given in ASTM B 503 (Ref 5).

Table 1 Nickel electroforming solutions and selected properties of the deposits

Parameter	Watts nickel	Nickel sulfamate
Electrolyte composition, g/L (oz/gal)	$NiSO_4 \cdot 6H_2O$--225-300 (30-40)	$Ni(SO_3NH_2)_2$--315-450 (42-60)
	$NiCl_2 \cdot 6H_2O$--37.5-52.5 (5-7)	H_3BO_3--30-45 (4-6)
	H_3BO_3--30-45 (4-6)	$NiCl_2 \cdot 6H_2O$--0-22.5 (0-3)
Operating conditions		
Temperature, °C (°F)	44-66 (115-150)	32-60 (90-140)
Agitation	Air or mechanical	Air or mechanical
Cathode current density, A/dm^2 (A/ft^2)	270-1075 (25-100)	50-3225 (5-300)
Anodes	Soluble nickel	Soluble nickel
pH	3.0-4.2	3.5-4.5
Mechanical properties		

Tensile strength, MPa (ksi)	345-482 (50-70)	410-620 (60-90)
Elongation, %	15-25	10-25
Hardness, HV_{100}	130-200	170-230
Internal tensile stress, MPa (ksi)	125-186 (18-27)	0-55 (0-8)

Table 2 Variables affecting mechanical properties of deposits from nickel sulfamate electrolytes

Property	**Operational effects**	**Solution composition effects**
Tensile strength	Decreases with increasing temperature to 49 °C, then increases slowly with further temperature increase. Increases with increasing pH. Decreases with increasing current density.	Decreases slightly with increasing nickel content.
Elongation	Decreases as the temperature varies in either direction from 43 °C. Decreases with increasing pH. Increases moderately with increasing current density.	Increases slightly with increasing nickel content. Increases slightly with increasing chloride content.
Hardness	Increases with increasing temperature within operating range suggested. Increases with increasing solution pH.Reaches a minimum at about 13 A/dm^2.	Decreases slightly with increasing concentration of nickel ion. Decreases slightly with increasing chloride content.
Internal stress	Decreases with increasing solution temperature. Reaches a minimum at pH 4.0-4.2. Increases with increasing current density.	Relatively independent of variation in nickel ion content within range. Increases significantly with increasing chloride content.

Copper electroforming solutions of significance are the acid sulfate and fluoborate baths. Table 3 lists typical compositions, operating conditions, and mechanical properties for these baths. Changes in operating variables will affect mechanical properties of copper sulfate deposits, as noted in Table 4. Similar information for effects of variable changes on copper fluoborate deposits are found in ASTM B 503 (Ref 5).

Table 3 Copper electroforming solutions and selected properties of deposits

Parameter	**Copper sulfate**	**Copper fluoborate**
Electrolyte composition, g/L (oz/gal)	$CuSO_4 \cdot 5H_2O$--210-240 (28-32)	$Cu(BF_4)_2$--225-450 (30-60)
	H_2SO_4--52-75 (7-10)	HBF_4--To maintain pH at 0.15-1.5
Operating conditions		
Temperature, °C (°F)	21-32 (70-90)	21-54 (70-129)

Agitation	Air or mechanical	Air or mechanical
Cathode current density, A/dm^2 (A/ft^2)	1-10 (9.3-93)	8-44 (75-410)
Anodes	Oxygen-free, high-conductivity copper or phosphorized copper	Soluble copper
Mechanical properties		
Tensile strength, MPa (ksi)	205-380 (30-55)	140-345 (20-50)
Elongation, %	15-25	5-25
Hardness, HV_{100}	45-70	40-80
Internal tensile stress, MPa (ksi)	0-10 (0-1.45)	0-105 (0-15)

Table 4 Variables affecting mechanical properties of deposits from acid copper sulfate electrolytes

Property	Operational effects	Solution composition effects
Tensile strength	Decreases slightly with increasing solution temperature. Increases significantly with increase in cathode current density.	Relatively independent of changes in copper sulfate concentration within the range suggested. Relatively independent of changes in sulfuric acid concentration within the range suggested.
Elongation	Decreases with increasing solution temperature. Increases slightly with increasing cathode current density.	High acid concentrations, particularly with low copper sulfate concentration, tend to reduce elongation slightly.
Hardness	Decreases slightly with increasing solution temperature. Relatively independent of change in cathode current density.	Relatively independent of copper sulfate concentration. Increases slightly with increasing acid concentration.
Internal stress	Increases with increasing solution temperature. Increases with increasing cathode current density.	Relatively independent of copper sulfate concentration. Decreases very slightly with increasing acid concentration.

Iron Electroforming Solutions. Iron electroforming, while not in major industrial production today, is technically usable if precautions are followed. Three types of electroforming baths exist as slightly acidic systems: sulfate, fluoborate, and sulfamate systems. A fourth system is the highly acidic chloride system, which uses ferrous chloride/calcium chloride operating between 88 and 99 °C (190 and 210 °F). Table 5 presents condensed details of the four baths and primary operating conditions. Except for deposits from the chloride bath, all other baths produce iron deposits brittle in nature and not usable without special thermal treatment, stress-reducing additives, or backup deposits to protect the brittle nature of the iron films. The chloride deposits can be best used with a postplating heat treatment of 260 °C (500 °F) or above to ensure ductility.

Table 5 Iron electroforming solutions and operating conditions

Parameter	Value
Chloride bath	
Ferrous chloride (dihydrate), g/L (oz/gal)	300-450 (40-60)
Calcium chloride, g/L (oz/gal)	150-185 (20-25)
Temperature, °C (°F)	90-99 (190-210)
pH (HCl)	0.2-1.8
Current density, A/dm^2 (A/ft^2)	
Without agitation	2-8.5 (20-80)
With agitation	2-21 (20-200)
Sulfate bath	
Ferrous sulfate, g/L (oz/gal)	240 (32)
pH	2.8-3.5
Temperature, °C (°F)	32-65 (90-150)
Current density, max, A/dm^2 (A/ft^2)	
at 32 °C (90 °F)	4.3 (40)
at 65 °C (150 °F)	10 (100)
Surface tension, dynes/cm	40
Cathode agitation	Desirable
Fluoborate bath	
Iron fluoborate, g/L (oz/gal)	227 (30.3)

Metallic iron, g/L (oz/gal)	55.2 (7.37)
Sodium chloride, g/L (oz/gal)	10.0 (1.34)
Baumé, degrees, at 27 °C (80 °F)	19-21
pH (colorimetric)	3.0-3.4
Temperature, °C (°F)	57-63 (135-145)
Current density (cathode-average), A/dm^2 (A/ft^2)	2-10 (20-90)
Tank voltage, avg	2-6
Sulfamate bath	
Ferrous iron, g/L (oz/gal)	75 (10)
Ammonium sulfamate, g/L (oz/gal)	30-37 (4-5)
Sodium chloride, g/L (oz/gal)	37-45 (5-6)
Temperature, °C (°F)	50-60 (120-140)
Current density, A/dm^2 (A/ft^2)	5.4 (50)
pH	2.7-3.0

Reference cited in this section

5. ASTM B 503, "Standard Practice for Use of Copper and Nickel Electroplating Solutions for Electroforming," ASTM

Process Controls

Because of the exacting products desired during electroforming, the controls are apt to be more stringent. Controlling metal distribution, internal stress, nodular growth, and roughness are among the potential problems that are often found in electroforming. Some of these problems are handled by using various addition agents, but special attention is often required to monitor conditions during deposition. Other significant aspects of the electroforming process that demand special consideration include the following.

Metal distribution relates to nonuniform deposition due to changes in mandrel configuration, throwing power of the bath selected, placement in the plating tank, and other features of the deposits being produced. Attempting to retain the best properties of the metal being deposited and at the same time maintain excellent throwing power is most difficult. One can improve metal distribution by using proper racking designs, employing "thieves," "robbers," shields, or auxiliary or

conforming anodes, and completely mapping out the electrical requirements of the mandrel. Computer software programs exist that aid in the design of cathode distribution systems.

Internal deposit stress is most important to control during, before, and after deposition. Before deposition it may develop within the mandrel, resulting in unwarranted partial liftoff of the electroform before it is complete. During deposition, symptoms of internal deposit stress are problems trying to separate the electroform from the mold, buckling or blistering of the deposits, and cracking of the deposit during deposition or while it is separated from the master. Most of these manifestations come from either the bath itself, impurities permitted in the bath (incomplete filtration), or lack of control of the additives needed for the bath. Careful monitoring of all operating conditions is also important for deposit stress control.

Roughness and "treeing" are conditions that may appear during electroforming if care is not taken. To minimize roughness, the electroformer must watch the filtration rates, because even small dirt particles can be the nucleation sites for rough deposits. Filtration rates may need to be as high as whole-solution-volume recycling once or more per hour. Other aids in preventing roughness include using positive pressure of an inch or so with filtered air, plus keeping the electroforming room in extra-clean condition.

The phenomenon of treeing occurs near the edges or corners of the mandrel or attachment areas. These can be minimized by the use of shields, improved racking, or "thieving" to prevent excess current in unwanted areas. Leveling agents and nodule suppressants may also be useful to reduce treeing. Often it becomes necessary to stop the electroforming, remove the part, and machine off the excess deposit. One must remember to reactivate the electroform when replacing it in the plating tank.

One other factor worthy of considering in minimizing roughness, pitting, burning, and sometimes treeing is to constantly check solution agitation, whether by air, mechanical, cathode rod, or other means. Make sure that no grease, wear particles, or other outside dirt enters the electroforming system by virtue of the agitation system.

Alloy Electroforming

Alloy electroforming using high-strength materials, such as nickel-cobalt, cobalt-tungsten, and even more complex alloys involving tungsten and the iron group metals, has made some inroads for special applications. Microfabrication of sensors, maskless jet systems, miniature computer components, and a host of newer devices rely on the properties of many electrodeposited alloys and the precision of electroforming to produce such items. Bath chemistries, deposition parameters (in some cases requiring pulse plating control), and fixturing are all very critical to control for optimal production of these advanced products.

Future Applications

Such developments as composition-modulated alloys, nanophase composites, nonaqueous plating baths, and advanced pulsed current controls are expected to open the field of electroforming to more complex and innovative applications.

Electroless Nickel Plating

Revised by Donald W. Baudrand, MacDermid Inc.

Introduction

ELECTROLESS NICKEL PLATING is used to deposit nickel without the use of an electric current. The coating is deposited by an autocatalytic chemical reduction of nickel ions by hypophosphite, aminoborane, or borohydride compounds. Two other methods have been used commercially for plating nickel without electric current, including (1) immersion plating on steel from solutions of nickel chloride and boric acid at 70 °C (160 °F) and (2) decomposition of nickel carbonyl vapor at 180 °C (360 °F). Immersion deposits, however, are poorly adherent and nonprotective, while the decomposition of nickel carbonyl is expensive and hazardous. Accordingly, only electroless nickel plating has gained wide acceptance.

Since gaining commercial use in the 1950s, electroless nickel plating has grown rapidly and now is an established industrial process. Currently, hot acid hypophosphite-reduced baths are most frequently used to plate steel and other

metals, whereas warm alkaline hypophosphite baths are used for plating plastics and nonmetals. Borohydride-reduced baths are also used to plate iron and copper alloys, especially in Europe.

Electroless nickel is an engineering coating, normally used because of excellent corrosion and wear resistance. Electroless nickel coatings are also frequently applied on aluminum to provide a solderable surface and are used with molds and dies to improve lubricity and part release. Because of these properties, electroless nickel coatings have found many applications, including those in petroleum, chemicals, plastics, optics, printing, mining, aerospace, nuclear, automotive, electronics, computers, textiles, paper, and food machinery (Ref 1). Some advantages and limitations of electroless nickel coatings include:

Advantages

- Good resistance to corrosion and wear
- Excellent uniformity
- Solderability and brazeability
- Low labor costs

Limitations

- Higher chemical cost than electroplating
- Brittleness
- Poor welding characteristics due to contamination of nickel plate with nickel phosphorus deposits
- Need to copper strike plate alloys containing significant amounts of lead, tin, cadmium, and zinc before electroless nickel can be applied
- Slower plating rate, as compared to electrolytic methods

Reference

1. K. Parker, "Recent Advances in Electroless Nickel Deposits, 8th Interfinish Conference," 1972 (Basel)

Bath Composition and Characteristics

Electroless nickel coatings are produced by the controlled chemical reduction of nickel ions onto a catalytic surface. The deposit itself is catalytic to reduction, and the reaction continues as long as the surface remains in contact with the electroless nickel solution. Because the deposit is applied without an electric current, its thickness is uniform on all areas of an article in contact with fresh solution.

Electroless nickel solutions are blends of different chemicals, each performing an important function. Electroless nickel solutions contain:

- A source of nickel, usually nickel sulfate
- A reducing agent to supply electrons for the reduction of nickel
- Energy (heat)
- Complexing agents (chelators) to control the free nickel available to the reaction
- Buffering agents to resist the pH changes caused by the hydrogen generated during deposition
- Accelerators (exultants) to help increase the speed of the reaction
- Inhibitors (stabilizers) to help control reduction
- Reaction byproducts

The characteristics of an electroless nickel bath and its deposit are determined by the composition of these components.

Reducing Agents

A number of different reducing agents have been used in preparing electroless nickel baths, including sodium hypophosphite, aminoboranes, sodium borohydride, and hydrazine.

Sodium Hypophosphite Baths. The majority of electroless nickel used commercially is deposited from solutions reduced with sodium hypophosphite. The principal advantages of these solutions over those reduced with boron compounds or hydrazine include lower cost, greater ease of control, and better corrosion resistance of the deposit.

Several mechanisms have been proposed for the chemical reactions that occur in hypophosphite-reduced electroless nickel plating solutions. The most widely accepted mechanism is illustrated by the following equations:

$$(H_2PO_2)^- + H_2O \xrightarrow[Heat]{Catalyst} H^+ + (HPO_3)^{-2} + 2H_{abs} \qquad \textbf{(Eq 1)}$$

$$Ni_2 + 2H_{abs} \rightarrow Ni + 2H^+ \qquad \textbf{(Eq 2)}$$

$$(H_2PO_2)^- + H_{abs} \rightarrow H_2O + OH^- + P \qquad \textbf{(Eq 3)}$$

$$(H_2PO_2)^- + H_2O \rightarrow H^+ + (HPO_3)^{2-} + H_2 \qquad \textbf{(Eq 4)}$$

In the presence of a catalytic surface and sufficient energy, hypophosphite ions are oxidized to orthophosphite. A portion of the hydrogen given off is absorbed onto the catalytic surface (Eq 1). Nickel at the surface of the catalyst is then reduced by the absorbed active hydrogen (Eq 2). Simultaneously, some of the absorbed hydrogen reduces a small amount of the hypophosphite at the catalytic surface to water, hydroxyl ion, and phosphorus (Eq 3). Most of the hypophosphite present is catalytically oxidized to orthophosphite and gaseous hydrogen (Eq 4) independently of the deposition of nickel and phosphorus, causing the low efficiency of electroless nickel solutions. Usually 5 kg (10 lb) of sodium hypophosphite is required to reduce 1 kg (2 lb) of nickel, for an average efficiency of 37% (Ref 2, 3).

Early electroless nickel formulations were ammoniacal and operated at high pH. Later, acid solutions were found to have several advantages over alkaline solutions. Among these are higher plating rate, better stability, greater ease of control, and improved deposit corrosion resistance. Accordingly, most hypophosphite reduced electroless nickel solutions are operated between 4 and 5.5 pH. Compositions for alkaline and acid plating solutions are listed in Table 1 (Ref 2, 3, 4, 5).

Table 1 Hypophosphite-reduced electroless nickel plating solutions

Constituent or condition	Alkaline			Acid		
	Bath 1	Bath 2	Bath 3	Bath 4	Bath 5	Bath 6
Composition						
Nickel chloride, g/L (oz/gal)	45 (6)	30 (4)	30 (4)	. . .	. . .	. . .
Nickel sulfate, g/L (oz/gal)	. . .	. . .	. . .	21 (2.8)	34 (4.5)	45 (6)
Sodium hypophosphite, g/L (oz/gal)	11 (1.5)	10 (1.3)	10 (1.3)	24 (3.2)	35 (4.7)	10 (1.3)
Ammonium chloride, g/L (oz/gal)	50 (6.7)	50 (6.7)	. . .	. . .	. . .	. . .
Sodium citrate, g/L (oz/gal)	100 (13.3)	. . .	. . .	. . .	. . .	. . .

Ammonium citrate, g/L (oz/gal)	. . .	65 (8.6)	. . .	. . .	. . .	. . .
Ammonium hydroxide	To pH	To pH	. . .	. . .	. . .	. . .
Lactic acid, g/L (oz/gal)	. . .	. . .	. . .	28 (3.7)	. . .	. . .
Malic acid, g/L (oz/gal)	. . .	. . .	. . .	. . .	35 (4.7)	. . .
Amino-acetic acid, g/L (oz/gal)	. . .	. . .	. . .	. . .	. . .	40 (5.3)
Sodium hydroxyacetate, g/L (oz/gal)	. . .	. . .	10 (1.3)	. . .	. . .	. . .
Propionic acid, g/L (oz/gal)	. . .	. . .	. . .	2.2 (0.3)	. . .	. . .
Acetic acid, g/L (oz/gal)	. . .	. . .	. . .	. . .	. . .	10 (1.3)
Succinic acid, g/L (oz/gal)	. . .	. . .	. . .	. . .	10 (1.3)	. . .
Lead, ppm	. . .	. . .	. . .	1	. . .	. . .
Thiourea, ppm	. . .	. . .	. . .	. . .	1	. . .
Operating conditions						
pH	8.5-10	8-10	4-6	4.3-4.6	4.5-5.5	4.5-5.5
Temperature, °C (°F)	90-95 (195-205)	90-95 (195-205)	88-95 (190-205)	88-95 (190-205)	88-95 (190-205)	88-95 (190-205)
Plating rate, μm/h (mil/h)	10 (0.4)	8 (0.3)	10 (0.4)	25 (1)	25 (1)	25 (1)

Aminoborane Baths. The use of aminoboranes in commercial electroless nickel plating solutions has been limited to two compounds: N-dimethylamine borane (DMAB)-$(CH_3)_2$ $NHBH_3$, and H-diethylamine borane (DEAB)--$(C_2H_5)_2$ $NHBH_3$. DEAB is used primarily in European facilities, whereas DMAB is used principally in the United States. DMAB is readily soluble in aqueous systems. DEAB must be mixed with a short chain aliphatic alcohol, such as ethanol, before it can be dissolved in the plating solution.

Aminoborane-reduced electroless nickel solutions have been formulated over wide pH ranges, although they are usually operated between 6 and 9 pH. Operating temperatures for these baths range from 50 to 80 °C (120 to 180 °F), but they can be used at temperatures as low as 30 °C (90 °F). Accordingly, aminoborane baths are very useful for plating plastics and nonmetals, which is their primary application. The rate of deposition varies with pH and temperature, but is usually 7 to 12 μm/h (0.3 to 0.5 mil/h). The boron content of the deposit from these baths varies between 0.4 and 5%. Compositions and operating conditions for aminoborane baths are listed in Table 2 (Ref 2, 5, 6).

Table 2 Aminoborane- and borohydride-reduced electroless nickel plating solutions

Constituent or condition	Aminoborane		Borohydride	
	Bath 7	Bath 8	Bath 9	Bath 10
Composition				
Nickel chloride, g/L (oz/gal)	30 (4)	24-48 (3.2-6.4)	. . .	20 (2.7)
Nickel sulfate, g/L (oz/gal)	. . .	. . .	50 (6.7)	. . .
DMAB, g/L (oz/gal)	. . .	3-4.8 (0.4-0.64)	3 (0.4)	. . .
DEAB, g/L (oz/gal)	3 (0.4)	. . .	. . .	. . .
Isopropanol, mL (fluid oz)	50 (1.7)	. . .	. . .	. . .
Sodium citrate, g/L (oz/gal)	10 (1.3)	. . .	. . .	. . .
Sodium succinate, g/L (oz/gal)	20 (2.7)	. . .	. . .	. . .
Potassium acetate, g/L (oz/gal)	. . .	18-37 (2.4-4.9)	. . .	. . .
Sodium pyrophosphate, g/L (oz/gal)	. . .	. . .	100 (13.3)	. . .
Sodium borohydride, g/L (oz/gal)	. . .	. . .	. . .	0.4 (0.05)
Sodium hydroxide, g/L (oz/gal)	. . .	. . .	. . .	90 (12)
Ethylene diamine, 98%, g/L (oz/gal)	. . .	. . .	. . .	90 (12)
Thallium sulfate, g/L (oz/gal)	. . .	. . .	. . .	0.4 (0.05)
Operating conditions				
pH	5-7	5.5	10	14
Temperature, °C (°F)	65 (150)	70 (160)	25 (77)	95 (205)
Plating rate, μm/h (mil/h)	7-12 (0.5)	7-12 (0.5)	. . .	15-20 (0.6-0.8)

Sodium Borohydride Baths. The borohydride ion is the most powerful reducing agent available for electroless nickel plating. Any water-soluble borohydride may be used, although sodium borohydride is preferred.

In acid or neutral solutions, hydrolysis of borohydride ions is very rapid. In the presence of nickel ions, nickel boride may form spontaneously. If the pH of the plating solution is maintained between 12 and 14, however, nickel boride formation is suppressed, and the reaction product is principally elemental nickel. One mol of sodium borohydride can reduce approximately one mol of nickel, so that the reduction of 1 kg (2 lb) of nickel requires 0.6 kg (1 lb) of sodium borohydride. Deposits from borohydride-reduced electroless nickel solutions contain 3 to 8 wt% B.

To prevent precipitation of nickel hydroxide, complexing agents, such as ethylene diamine, that are effective between 12 to 14 pH must be used. Such strong complexing agents, however, decrease the rate of deposition. At an operating temperature of 90 to 95 °C (195 to 205 °F), the plating rate of commercial baths is 25 to 30 μm/h (1 to 1.2 mil/h). Compositions of a borohydride-reduced electroless nickel bath are also shown in Table 2 (Ref 6).

During the course of reduction, the solution pH decreases, requiring constant additions of an alkali hydroxide. Spontaneous solution decomposition may occur if the bath pH is allowed to fall below 12. Because of the high operating pH, borohydride plating baths cannot be used for aluminum substrates (Ref 2, 5, 7).

Hydrazine Baths. Hydrazine has also been used to produce electroless nickel deposits. These baths operate at 90 to 95 °C (195 to 205 °F) and 10 to 11 pH. Their plating rate is approximately 12 μm/h (0.5 mil/h). Because of the instability of hydrazine at high temperatures, however, these baths tend to be very unstable and difficult to control.

Whereas the deposit from hydrazine-reduced solutions is 97 to 99% N, it does not have a metallic appearance. The deposit is brittle and highly stressed with poor corrosion resistance. The stress and brittleness are likely due to codeposition of small amounts of basic nickel salts, $Ni(OH)_2$, and nitrogen. Unlike hypophosphite- and boron-reduced nickels, hardness from a hydrazine-reduced electroless nickel has very little commercial use (Ref 2).

Energy

The amount of energy or heat present in an electroless nickel solution is one of the most important variables affecting coating deposition. In a plating bath, temperature is a measure of its energy content.

Temperature has a strong effect on the deposition rate of acid hypophosphite-reduced solutions. The rate of deposition is usually very low at temperatures below 65 °C (150 °F), but increases rapidly with increased temperature (Ref 5). This is illustrated in Fig. 1, which gives the results of tests conducted using bath 3 in Table 1 (Ref 7). The effect of temperature on deposition in boron-reduced solutions is similar. At temperatures above 100 °C (212 °F), electroless nickel solutions may decompose. Accordingly, the preferred operating range for most solutions is 85 to 95 °C (185 to 205 °F).

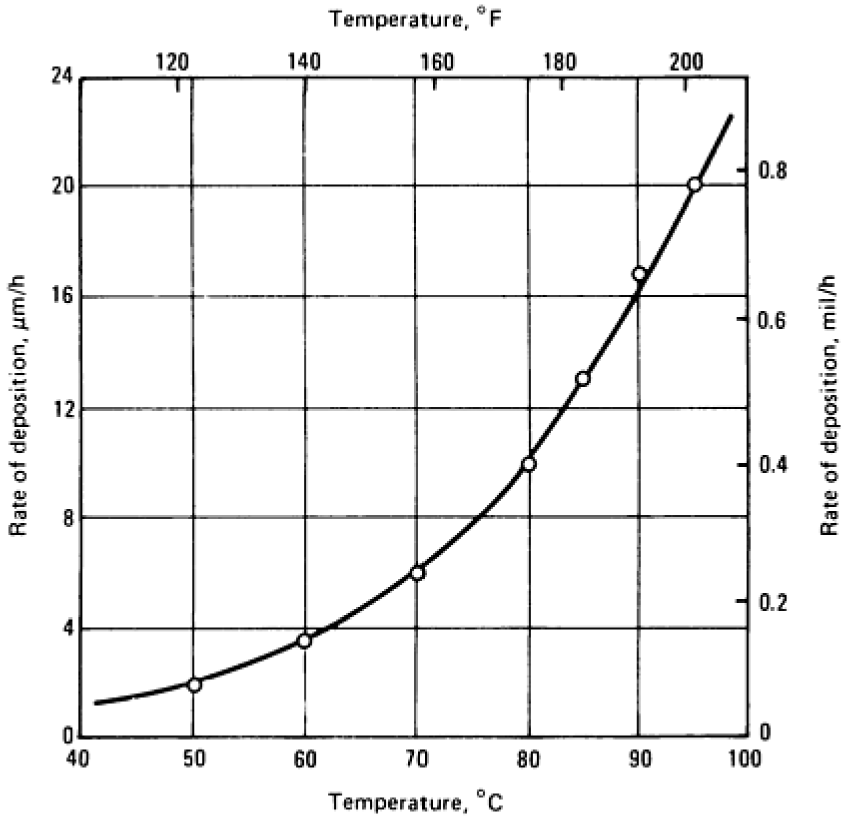


Fig. 1 Effect of solution temperature on the rate of deposition. Tests conducted on bath 3 at 5 pH

Complexing Agents

To avoid spontaneous decomposition of electroless nickel solutions and to control the reaction so that it occurs only on the catalytic surface, complexing agents are added. Complexing agents are organic acids or their salts, added to control the amount of free nickel available for reaction. They act to stabilize the solution and to retard the precipitation of nickel phosphite.

Complexing agents also buffer the plating solution and prevent its pH from decreasing too rapidly as hydrogen ions are produced by the reduction reaction. Ammonia, hydroxides, or carbonates, however, may also have to be added periodically to neutralize hydrogen.

Original electroless nickel solutions were made with the salts of glycolic, citric, or acetic acids. Later baths were prepared using other polydentate acids, including succinic, glutaric, lactic, propionic, and aminoacetic. The complexing ability of an individual acid or group of acids varies, but may be quantified by the amount of orthophosphite that can be held in solution without precipitation (Ref 2, 8). This is illustrated in Fig. 2, which shows the maximum solubility of orthophosphite in solutions complexed with citric and glycolic acids as a function of pH (Ref 9). The complexing agent used in the plating solution can also have a pronounced effect on the quality of the deposit, especially on its phosphorus content, internal stress, and porosity (Ref 8).

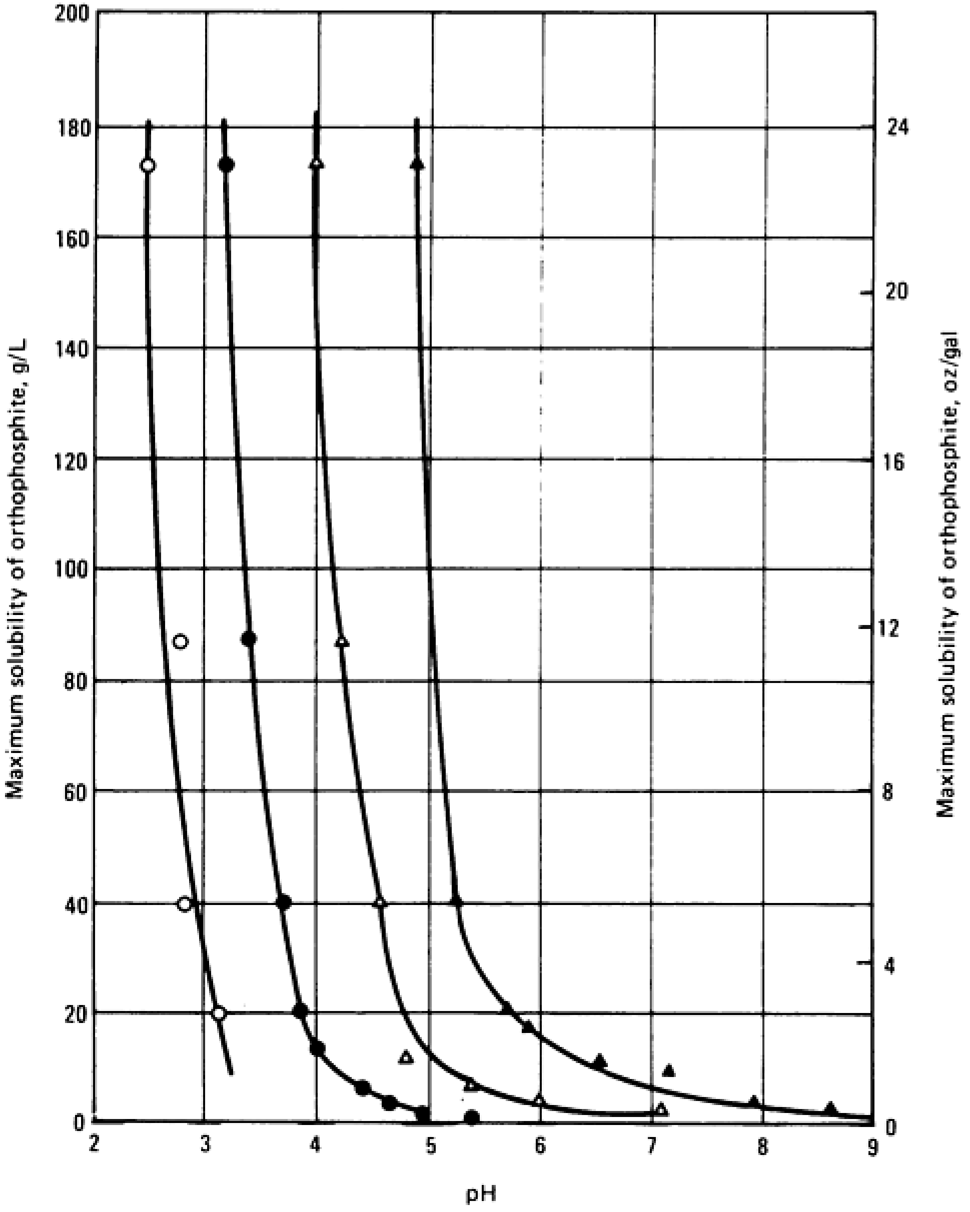


Fig. 2 Limits of solubility for orthophosphite in electroless nickel solutions. Solutions contain 30 g/L (4 oz/gal) nickel chloride ($NiCl_2$) and 10 g/L (1.3 oz/gal) sodium hypophosphite (NaH_2PO_2). d , without a complexing agent; •, with 15 g/L (2 oz/gal) citric acid; V , with 39 g/L (5.2 oz/gal) glycolic acid; ▲, with 78 g/L (10 oz/gal) glycolic acid.

Accelerators

Complexing agents reduce the speed of deposition and can cause the plating rate to become uneconomically slow. To overcome this, organic additives, called accelerators or exultants, are often added to the plating solution in small amounts. Accelerators are thought to function by loosening the bond between hydrogen and phosphorous atoms in the hypophosphite molecule, allowing it to be more easily removed and absorbed onto the catalytic surface. Accelerators activate the hypophosphite ion and speed the reaction shown in Eq 1 (Ref 2, 3). In hypophosphite-reduced solutions, succinic acid is the accelerator most frequently used. Other carbonic acids, soluble fluorides, and some solvents, however, have also been used (Ref 2). The effect of succinate additions upon deposition rate is illustrated in Fig. 3 (Ref 3).

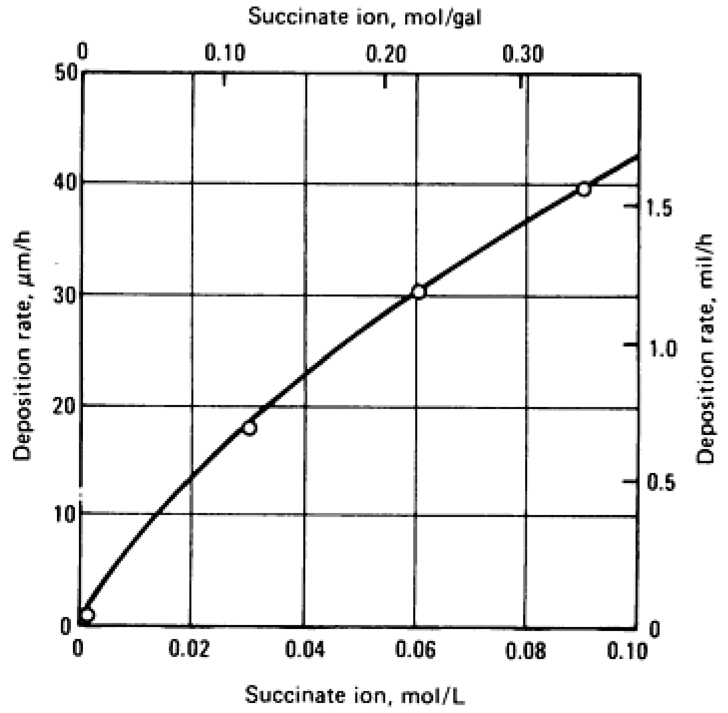


Fig. 3 Effect of succinate additions on the plating rate of an electroless nickel solution. Solutions contain 16 g/L (2.1 oz/gal) nickel chloride ($NiCl_2$) and 24 g/L (3.2 oz/gal) sodium hypophosphite (NaH_2PO_2). 5 g/L (0.7 oz/gal) ammonium hydroxide (NH_4OH) and 1 mg/L (4 mg/gal) lead at 5 pH and 95 °C (205 °F).

Inhibitors

The reduction reaction in an electroless nickel plating bath must be controlled so that deposition occurs at a predictable rate and only on the substrate to be plated. To accomplish this, inhibitors, also known as stabilizers, are added. Electroless nickel plating solutions can operate for hours or days without inhibitors, only to decompose unexpectedly. Decomposition is usually initiated by the presence of colloidal, solid particles in the solution. These particles may be the result of the presence of foreign matter (such as dust or blasting media), or may be generated in the bath as the concentration of orthophosphite exceeds its solubility limit. Whatever the source, the large surface area of the particles catalyzes reduction, leading to a self-accelerating chain reaction and decomposition. This is usually preceded by increased hydrogen evolution and the appearance of a finely divided black precipitate throughout the solution. This precipitate consists of nickel and either nickel phosphide or nickel boride.

Spontaneous decomposition can be controlled by adding trace amounts of catalytic inhibitors to the solution. These inhibitors are absorbed on any colloidal particles present in the solution and prevent the reduction of nickel on their surface. Traditionally, inhibitors used with hypophosphite-reduced electroless nickel have been of three types: sulfur compounds, such as thiourea; oxy anions, such as molybdates or iodates; and heavy metals, such as lead, bismuth, tin, or cadmium. More recently, organic compounds, including oleates and some unsaturated acids, have been used for some functional solutions. Organic sulfide, thio compounds, and metals, such as selenium and thallium, are used to inhibit aminoborane- and borohydride-reduced electroless nickel solutions.

The addition of inhibitors can have harmful as well as beneficial effects on the plating bath and its deposit. In small amounts, some inhibitors increase the rate of deposition and/or the brightness of the deposit; others, especially metals or sulfur compounds, increase internal stress and porosity and reduce ductility, thus reducing the ability of the coating to resist corrosion and wear (Ref 2, 3, 5).

The amount of inhibitor used is critical. The presence of only about 1 mg/L (4 mg/gal) of HS^- ion completely stops deposition, whereas at a concentration of 0.01 mg/L (0.04 mg/gal), this ion is an effective inhibitor. The effect of lead additions on a hypophosphite-reduced succinate bath at pH 4.6 and 95 °C (205 °F) is shown in Fig. 4 (Ref 3). The tests illustrated in Fig. 4 also showed that baths containing less than 0.1 mg/L (0.4 mg/gal) Pb^{2+} decomposed rapidly, whereas baths containing higher concentrations were stable. Excess inhibitor absorbs preferentially at sharp edges and corners, resulting in incomplete coverage (edge pull back) and porosity.

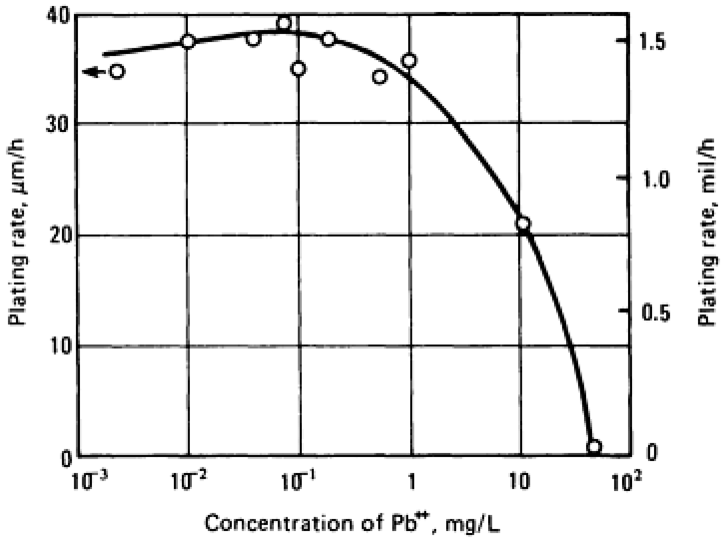


Fig. 4 Effect of lead additions on plating rate in a hypophosphite-reduced succinate-based bath. Bath at 4.6 pH and 95 °C (205 °F). Solutions containing less than 0.1 mg (0.4 mg/gal) Pb^{2+} were unstable.

Reaction Byproducts

During electroless nickel deposition, the byproducts of the reduction, orthophosphite or borate and hydrogen ions, as well as dissolved metals from the substrate accumulate in the solution. These can affect the performance of the plating bath.

Orthophosphite. As nickel is reduced, orthophosphite ion (HPO_3^{2-}) accumulates in the solution and at some point interferes with the reaction. As the concentration of orthophosphite increases, there is usually a small decrease in the deposition rate and a small increase in the phosphorus content of the deposit. Ultimately the accumulation of orthophosphite in the plating solution results in the precipitation of nickel phosphite, causing rough deposits and spontaneous decomposition. Orthophosphite ion also codeposits with nickel and phosphorus, creating a highly stressed, porous deposit.

The solubility of phosphite in the solution is increased when complexing agents, such as citric or glycolic acids, are added. This effect is shown in Fig. 2. However, the use of strong complexors, in other than limited quantities, tends to reduce the deposition rate and increase the porosity and brittleness of the deposit (Ref 8).

Borates. The accumulation of metaborate ion (BO_2^-) from the reduction of borohydride or of boric acid (H_3BO_3) from the reduction of aminoboranes has little effect on electroless nickel plating baths. Both borohydride and aminoborate baths have been operated through numerous regenerations with only a slight decrease in plating rate and without decomposing. With aminoborane-reduced solutions, the solubility of boric acid is probably increased by the presence of amine through the formation of a complex aminoborate (Ref 10).

Hydrogen ions (H^+), produced by the reduction reaction, cause the pH of the bath to decrease. The amount of hydrogen produced, however, depends on the reducing agent being used. Because they are less efficient, hypophosphite-reduced solutions tend to generate more hydrogen ions than those reduced with boron compounds.

The pH of the bath has a strong effect on both solution operation and the composition of the deposit. This is illustrated in Fig. 5, which shows the plating rate and deposit phosphorus content resulting from varying solution pH values in a bath containing 33 g/L (4.4 oz/gal) of nickel sulfate and 20 g/L (2.7 oz/gal) of sodium hypophosphite at 82 °C (180 °F) (Ref 11).

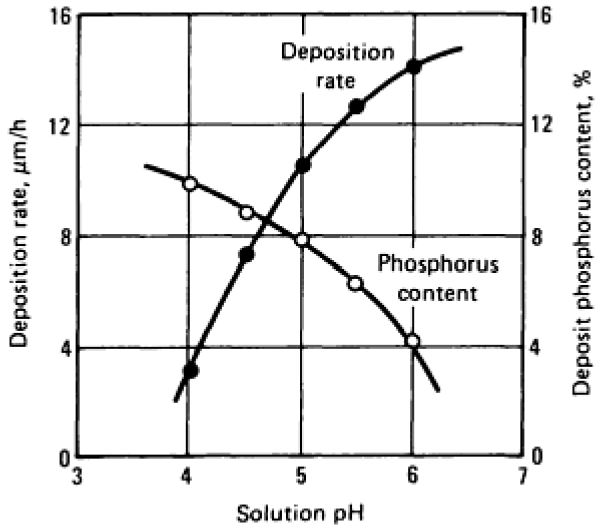


Fig. 5 Effect of solution pH on deposition rate and deposit phosphorus content

To retard pH changes and to help keep operating conditions and deposit properties constant, buffers are included in electroless nickel solutions. Some of the most frequently used buffers include acetate, propionate, and succinate salts. Additions of alkaline materials, such as hydroxide, carbonate solutions, or ammonia, are also required periodically to neutralize the acid formed during plating.

References cited in this section

2. G.G. Gawrilov, *Chemical (Electroless) Nickel Plating,* Portcullis Press, Redhill, England, 1979
3. G. Gutzeit, An Outline of the Chemistry Involved in the Process of Catalytic Nickel Deposition from Aqueous Solution, *Plat. Surf. Finish.,* Vol 46 (No. 10), 1959, p 1158
4. A. Brenner and G. Riddell, Deposition of Nickel and Cobalt by Chemical Reduction, *J. Res. Natl. Bur. Stand.,* Vol 39 (No. 11), 1947, p 385
5. G.O. Mallory, The Electroless Nickel Plating Bath, Electroless Nickel Conference, Cincinnati, Nov 1979
6. K. Stallman and H. Speckhardt, Deposition and Properties of Nickel-Boron Coatings, *Metalloberfl.; Angew. Elektrochem.,* Vol 35 (No. 10), 1981, p 979
7. K.M. Gorbunova and A.A. Nikiforova, *Physicochemical Principles of Nickel Plating,* Izdatel'stvo Akademii Nauk SSSR, Moscow, 1960
8. G.O. Mallory, Influence of the Electroless Plating Bath on the Corrosion Resistance of the Deposits, *Plating,* Vol 61 (No. 11), 1974, p 1005
9. C.E. deMinjer and A. Brenner, Studies on Electroless Nickel Plating, *Plating,* Vol 44 (No. 12), 1957, p 1297
10. G.O. Mallory, The Electroless Nickel-Boron Plating Bath; Effects of Variables on Deposit Properties, *Plating,* Vol 58 (No. 4), 1971, p 319
11. C. Baldwin and T.E. Such, The Plating Rates and Physical Properties of Electroless Nickel/Phosphorus Alloy Deposits, *Trans. Inst. Met. Finish.,* Vol 46 (No. 2), 1968, p 73

Temperature, °C (°F)	22-30 (72-86)	43-60 (110-140)
Current density, A/dm^2 (A/ft^2)	1.0-3.0 (10-30)	1.0-7.0 (10-70)
Cathode efficiency	. . .	95-100%
Voltage at tank, V	2-5	2-6
pH, electrometric[(a)]	8.0-8.5	8.0-8.7
Anodes[(b)]	Copper	Copper
Anode:cathode ratio	2:1	2:1

(a) May be maintained with pyrophosphoric acid and potassium hydroxide.

(b) OFHC anodes

Copper pyrophosphate bath characteristics are intermediate between those of cyanide and acid baths and are very similar to those of the high-efficiency cyanide bath. Electrode efficiencies are 100%; throwing power and plating rates are good. The bath also operates at an almost neutral pH. Deposits from pyrophosphate baths are fine-grain and semibright. For pyrophosphate plating on steel, zinc die castings, magnesium, or aluminum, a preliminary strike should be used. For striking, a dilute cyanide or pyrophosphate copper, nickel, or other solution may be used.

References cited in this section

1. B. Smith, W. Rapacki, and T. Davidson, Heat Treatment Maskant Materials--Evaluation of Non-cyanide Containing Electrolytes, *Plating and Surface Finishing,* Vol 79 (No. 8), 1992, p 11
2. U.S. Patent No. 3,475,293, 1969
3. L.C. Tomaszewski and R.A. Tremmel, *Proc. of the 72nd AES Annual Tech. Conf.,* American Electroplating Society, 1985

Acid Plating Baths

Electrodeposition of copper from acid baths is used extensively for electroforming, electrorefining, and decorative electroplating. Acid copper plating baths contain copper in the bivalent form and are more tolerant of ionic impurities than alkaline baths. They also have less macro throwing power and poorer metal distribution. Acid baths have excellent micro throwing power, resulting in the ability to fill or level scratches, grooves, or other substrate conditions, and additionally they are effective in sealing porous substrates. In most instances the smooth deposits produced by these solutions reduce or eliminate the need for mechanical smoothing for various substrates. A cyanide, noncyanide copper, or nickel strike must be applied to steel or zinc-alloy die castings before they are plated in acid copper solutions. Acid copper solutions cannot be used directly over substrates that are attacked by the high acidity or those where the copper forms an immersion deposit. Immersion deposits usually have poor adhesion to the substrate. Concentration limits and operating conditions of acid copper plating baths are given in Table 4.

Table 4 Compositions and operating conditions of acid copper plating baths

Constituent or condition	Copper sulfate bath		Copper fluoborate bath	
	General	**Printed circuit through-hole**	**Low copper**	**High copper**
Bath composition, g/L (oz/gal)				
Copper sulfate, $CuSO_4 \cdot 5H_2O$	200-240 (27-32)	60-110 (8-15)	. . .	. . .
Sulfuric acid, H_2SO_4	45-75 (6-10)	180-260 (24-35)	. . .	. . .
Copper fluoborate, $Cu(BF_4)_2$	. . .	. . .	225 (30)	450 (60)
Fluoboric acid, HBF_4	. . .	. . .	To pH	40 (5)
Bath analysis, g/L (oz/gal)				
Copper	50-60 (7-8)	15-28 (2-4)	8 (1)	16 (2)
Sulfuric acid	45-75 (6-10)	180-260 (24-35)	. . .	. . .
Specific gravity at 25 °C (77 °F)	. . .	. . .	1.17-1.18	1.35-1.37
Operating conditions				
Temperature, °C (°F)	20-50 (68-120)	20-40 (68-105)	20-70 (68-160)	20-70 (68-160)
Current density, A/dm^2 (A/ft^2)	2.0-10.0 (20-100)	0.1-6.0 (1-6)	7.0-13.0 (70-130)	12-35 (120-350)
Cathode efficiency, %	95-100	95-100	95-100	95-100
Voltage, V	6	6	6	6-12
pH	. . .	. . .	0.8-1.7	<0.6
Anodes	Copper[(a)]	Copper[(a)]	Copper[(b)]	Copper[(b)]

(a) Phosphorized copper (0.02-0.08% P) is recommended.

(b) High-purity, oxygen-free, nonphosphorized copper is recommended.

The copper sulfate bath is the most frequently used of the acid copper electrolytes and has its primary use in electroforming. In this application, the advantages of acid copper lie in its strength and ductility. Acid copper sulfate is used to plate thick deposits over 150 μm (6 mils) on large nickel-plated rolls; it is then engraved to electroform textile printing screens. It is also used extensively for the application of copper as an undercoating for bright nickel-chromium plating, especially for automotive components. Plates and rolls have been plated with acid copper sulfate for graphic arts and rotogravure printing where thicknesses of 500 μm (20 mils) or more are not uncommon. Bright acid copper sulfate baths are used extensively as an underlayer in decorative plating of the plastic trim found on automobiles, appliances, and various housewares. By altering the composition of the copper sulfate bath, it can be used in through-hole plating of printed circuit boards where a deposit ratio of 1 to 1 in the hole-to-board surface is desired. In some applications, acid copper sulfate solutions are used to plate over electroless deposited copper or nickel. With additives, the bath produces a bright deposit with good leveling characteristics or a semibright deposit that is easily buffed. Where copper is used as an undercoating, deposit thicknesses will generally range up to about 50 μm (2 mils).

The copper fluoborate bath produces high-speed plating and dense deposits up to any required thickness, usually 500 μm (20 mils). This bath is simple to prepare, stable, and easy to control. Operating efficiency approaches 100%. Deposits are smooth and attractive. Deposits from the low-copper bath operated at 49 °C (120 °F) are soft and are easily buffed to a high luster. The addition of molasses to either the high copper or the low copper bath operated at 49 °C (120 °F) results in deposits that are harder and stronger. Good smoothness of coatings up to 500 μm (20 mils) thick can be obtained without addition agents. For greater thicknesses, addition agents must be used to avoid excessive porosity.

Surface Preparation Considerations

Careful cleaning and preparation of the substrate material being plated is required for the effective electrodeposition of copper. Surface oils and greases, buffing compounds, rust, scale, and oxides, especially around weld or solder areas must be thoroughly removed before copper plating to ensure adhesion and to minimize contamination of the plating bath. However, before considering any preparation, it is important to know the type of substrate being used as well as any substrate surface conditions that may be present. This information is important because the preparation cycles used prior to copper plating can vary considerably, depending on the alloy or type of substrate. Also, substrate heat treatment variations can contribute to complications in surface preparation. Because there are also variations in organic and inorganic soil conditions on the work to be plated, preparation cycles should include adequate cleaning, rinsing, and activation steps to ensure quality deposits. Some of the cleaning methods used to prepare substrate surfaces prior to copper plating include soak or electrolytic alkaline cleaning, alkaline derusting, vapor degreasing, and solvent cleaning.

Good rinsing between preparation steps is a very important and often-overlooked step in the preparation cycle. Time, temperature, and concentration considerations should be applied to rinsing techniques as well as to the cleaning processing solutions. Often, rinse times are too short, immersion temperatures are too cold, and the water flow rate is too low to adequately rinse cleaner films from the surfaces.

The activation step is usually carried out with the use of an acid to remove inorganic soils, oxides, or cleaner films from the surfaces. The acid used depends on the type of substrate to be plated. The most commonly used acids in preplate processes are hydrochloric acid and sulfuric acid. More information about the techniques used in these preparation processes is found in the Section "Surface Cleaning" in this Volume. Specifications and practices for copper electroplating are given in Table 5.

Table 5 Specifications and standards for copper electroplating

Specification	Uses
Copper plating	
AMS 2418	Copper plating
MIL-C-14550 (Ord)	Copper plating

ASTM B 503	Recommended practice for use of copper and nickel electroplating solution for electroforming
Copper plating in multiplate systems	
ASTM B 456	Specification for electrodeposited coatings of copper plus nickel plus chromium and nickel plus chromium
ASTM B 200	Specification for electrodeposited coatings of lead and lead-tin alloys on steel and ferrous alloys
AMS 2412	Plating silver, copper strike, low bake
AMS 2413	Silver and rhodium plating
AMS 2420	Plating, aluminum for solderability, zincate process
AMS 2421	Plating, magnesium for solderability, zincate process
QQ-N-290	Nickel plating (electrodeposited)
Surface preparation	
ASTM A 380	Practice for cleaning and descaling stainless steel parts, equipment, and systems
ASTM B 183	Practice for preparation of low-carbon steel for electroplating
ASTM B 242	Practice for preparation of high-carbon steel for electroplating
ASTM B 252	Recommended practice for preparation of zinc alloy die castings for electroplating
ASTM B 253	Practice for preparation of aluminum alloys for electroplating
ASTM B 254	Practice for preparation of and electroplating on stainless steel
ASTM B 281	Practice for preparation of copper and copper-base alloys for electroplating and conversion coatings
ASTM B 319	Guide for preparation of lead and lead alloys for electroplating
ASTM B 322	Practice for cleaning metals prior to electroplating
ASTM B 480	Practice for preparation of magnesium and magnesium alloys for electroplating
ASTM B 481	Practice for preparation of titanium and titanium alloys for electroplating

MIL-HDBK-132 (Ord)	Military handbook, protective finishes

Cyanide Baths. Although the dilute cyanide and Rochelle cyanide baths exert a significant cleaning action on the surface of the parts during the plating operation, thorough cleaning of parts to be plated in these baths is still necessary.

The high-efficiency sodium cyanide and potassium cyanide electrolytes have virtually no surface-cleaning ability during plating because of the absence of hydrogen evolution. Parts to be plated in these electrolytes must be thoroughly cleaned. Parts also must receive first a dilute cyanide copper strike about 1.3 μm (0.05 mil) thick.

Noncyanide Alkaline Baths. Unlike cyanide baths, noncyanide alkaline baths do not offer any cleaning, and parts plated in these electrolytes must first be thoroughly cleaned, rinsed, and activated. If being used as a strike prior to acid copper or other similar deposit, a minimum thickness of 5.2 μm (0.2 mil) is desired. These systems can be plated directly on properly prepared steel, brass, stainless steel, zincated aluminum, lead-tin, and most high-quality, properly prepared zinc-base die castings (Ref 4, 5). One advantage of the noncyanide electrolyte is the fact that accidental drag-in of acids poses no hazard of the evolution of poisonous cyanide gas, which could occur with cyanide copper electrolytes.

Pyrophosphate Baths. If pyrophosphate electrolytes are to be used, conventional cleaning cycles are generally satisfactory. A preliminary strike should be applied to steel, zinc-base die castings, magnesium, and aluminum. The strike solution may be a dilute cyanide copper, dilute pyrophosphate copper, or nickel. If a cyanide copper strike is used, adequate rinsing or, preferably, a mild acid dip following the strike is recommended before final pyrophosphate copper plating.

Acid Baths. When sulfate or fluoborate copper is to be deposited, steel or zinc must first receive a cyanide or noncyanide alkaline copper or nickel strike. With complete coverage, the strike may be as thin as 2 μm (0.08 mil). After the strike, the parts should be dipped in a dilute solution of sulfuric acid to neutralize solution retained from the alkaline strike bath. The parts should be rinsed thoroughly before acid copper plating. Nickel or nickel alloy parts, when surface activated by reverse-current etching in sulfuric acid, can be plated directly, provided contact is made to the work with the current or power on before immersion into the acid copper solution.

References cited in this section

4. "Cupral Alkaline Non-cyanide Copper," Operating Technical Data Sheet, Enthone/OMI, Warren, MI
5. "E-Brite 30/30 Alkaline Non-cyanide Copper," Operating Technical Data Sheet, Electrochemical Products, Inc., New Berlin, WI

Bath Composition and Operating Variables

The compositions and analyses given in Tables 1, 2, 3, and 4 for cyanide, noncyanide alkaline, pyrophosphate, and acid copper plating baths may be varied within the control limits to satisfy requirements for specific applications.

Current density can be altered to effect more efficient control and to increase the deposition rate of copper. The data in Table 6 can be used as a guide to the selection of current density.

Table 6 Estimated time required for plating copper (valence 1) to a given thickness at 100% cathode efficiency

Cyanide baths contain copper with a valence of 1. For baths containing copper with a valence of 2, such as noncyanide alkaline, sulfate, pyrophosphate, and fluoborate baths, double the time values given in this table. Values must be corrected for losses in cathode efficiency by adding the difference between the actual cathode efficiency and 100%; for example, for 70% cathode efficiency, add 30% to values in table to determine estimated time.

Thickness of plate	Plating time, min[(a)] at current density, A/dm^2 (A/ft^2)

µm	mils	1.0 (10)	1.5 (15)	2.0 (20)	2.5 (25)	3.0 (30)	3.5 (35)	4.0 (40)	4.5 (45)
2	0.08	4	3	2	2	2	1	1	1
5	0.2	11	8	6	5	4	3	3	2
10	0.4	23	15	11	9	8	6	6	5
20	0.8	45	30	23	18	15	13	11	9
30	1.2	68	45	34	27	23	19	17	14
40	1.6	90	60	45	36	30	26	23	18
50	2.0	113	75	57	45	38	32	28	23
60	2.4	136	90	68	54	45	39	34	27
70	2.8	158	106	79	63	53	45	40	32
80	3.1	181	120	90	72	60	52	45	36

(a) To nearest whole value

Impurities. The degree of control required to protect copper plating baths from impurities varies with the type of bath and the method of processing used. Known causes of roughness in copper deposits are:

- Dragover from cleaners, which results in the formation of insoluble silicates in the electrolyte
- Poor anode corrosion
- Insoluble metallic sulfides because of sulfide impurities
- Organic matter in the water used for composition, especially in rinse tanks
- Insoluble carbonates because of calcium and magnesium in hard water
- Oil from overhead conveyors
- Airborne dust or particles

If the level of impurities reaches a critical point, causing poor results, a batch carbon treatment or circulation through a carbon-packed filter may be required. For the noncyanide processes, a sulfur-free carbon pack must be maintained on the bath and changed weekly. Lead and cyanide are contaminants to these systems and tend to cause a black smutted deposit. When converting a plating line from a cyanide system to a noncyanide electrolyte, all associated equipment must be cleaned and thoroughly washed to ensure no cyanide contamination.

Caution: Cyanide remains in the system. Acids can be used only after all traces of cyanide have been eliminated.

Purity of Water Used in Composition. The purity of the water used in the composition of the baths is important for all plating operations. Iron in the water causes roughness in the deposit if the pH of the electrolyte is above 3.5 where iron

can be precipitated. Chlorides in concentrations greater than about 0.44 g/L (0.05 oz/gal) promote the formation of nodular deposits. Calcium, magnesium, and iron precipitate in the bath. Organic matter may cause pitting of deposits.

When plating in sodium or potassium, high-efficiency electrolytes and distilled, deionized, softened, or good quality tap water may be used for solution composition and for replenishment. Tap water with high contents of calcium and/or iron should not be used, because it may cause roughness of the deposit. Softened water should be used with care, especially in plating baths where chloride contents are critical, such as bright copper sulfate baths.

Agitation during plating permits the use of higher current densities, which create rapid deposition of copper. The amount of increase permissible in current density varies for the different baths. Preferred methods of agitation for the types of baths are:

Cyanide baths	Cathode movement, air agitation, or both
Pyrophosphate baths	Air agitation
Acid baths	Cathode movement, air agitation, or both
Noncyanide baths	Vigorous air agitation

When air agitation is used, all airline pipes should be made of inert material or coated with an inert material to prevent attack by the electrolytes. The air used for agitation must be clean to avoid bath contamination. Filtered air from a low-pressure blower is required.

Ultrasonic vibration also has been used for the agitation of copper plating baths. This method does not largely improve the properties or appearance of electroplates, but it can improve plating speed by permitting an increase in the current density without the hazard of burning the parts. Increased plating speed does not necessarily justify the increased cost and complexity of ultrasonic operation, because the high-speed baths can usually be operated with a fairly high current density at nearly 100% efficiency.

Plating in Dilute Cyanide Baths

In the dilute cyanide bath, corrosion of the anodes increases with increasing concentration of free cyanide. Low free-cyanide content may cause rough deposits due to anode polarization; however, excessive free cyanide lowers cathode efficiency, resulting in thinner deposits per unit of time. Modifications of the pH, or alkalinity, of the strike compositions are used for striking various substrates. For use on steel, additional NaOH or KOH improves the conductivity of the solution and aids in protecting steel anode baskets, tanks, and other steel fixtures from corrosion. For use on zinc-base die castings, the hydroxide concentration is kept in the range of 1.3 to 3.8 g/L (0.2 to 0.5 oz/gal). For use on zincated aluminum alloys, the pH should be reduced to approximately 9.7 to 10.0 with sodium bicarbonate. The operator should keep adding tartaric acid or sodium bicarbonate to the solution to maintain the desired pH range (e.g., 10.0 to 10.5 for plating on aluminum alloys.

The dilute copper cyanide bath can be operated at room temperature, but the general practice is to operate the bath between 32 and 49 °C (90 and 120 °F) to increase the rate of deposition and to improve anode dissolution. This electrolyte is usually operated with a cathode current density of 1 to 1.5 A/dm^2 (10 to 15 A/ft^2). The tank voltage is normally between 4 and 6 V.

Agitation of the bath produces more uniform composition throughout the electrolyte, more uniform anode corrosion, and an increase in current densities where the brightest deposits are obtained. Current densities in excess of 5 A/dm^2 (50 A/ft^2) have been applied successfully by using air agitation of the solution and agitating the work.

Continuous filtration is preferred for dilute cyanide baths. Organic contamination or suspended matter in the strike is frequently responsible for roughness of copper plate subsequently deposited in the cyanide copper plating bath. Hexavalent chromium in the strike causes blistering of the deposit. Proprietary additives can be used to improve the bath operation, as well as aid in the control of organic and inorganic contaminants. These proprietary additives consist of organic complexing agents, such as tartrate salts. Organic reducing agents are used to control impurities such as hexavalent chromium. Wetting agents (surfactants) are used to control organic contaminants and to lower the surface tension of the plating solution, to allow better throwing power of copper over substrate irregularities, and to aid drainage and rinsing.

Plating in Rochelle Cyanide Baths

Rochelle electrolytes with lower metal concentrations can be used both for striking applications and, with higher metal concentrations, for plating applications. Rochelle salts produce some grain refinement, reduce the effects of some metallic contaminants, and aid in anode corrosion by increasing the anode current density range before anode polarization occurs. The Rochelle electrolyte can also be used for periodic-reverse plating with good results. Barrel plating with a Rochelle bath requires a variation in the chemistry. When plating parts that tend to nest or stick together during the barrel rotation, it is necessary to increase the free cyanide to 25 to 30 g/L (3 to 4 oz/gal) or slightly higher to obtain adequate coverage on the nested parts.

Rochelle baths usually are operated at a current density between 2 and 5 A/dm^2 (20 and 50 A/ft^2). Substituting potassium salts for sodium salts in the baths with higher metal concentration, up to 38 g/L (5 oz/gal) copper, can increase the allowable current density to 6 A/dm^2 (60 A/ft ^{2}), with the penalty of lowering the cathode efficiency. The Rochelle baths are usually operated at between 54 and 71 °C (130 and 160 °F) for best efficiency. The rate of deposition is higher at the higher temperatures. A high-efficiency electrolyte having a higher metal concentration can be operated at up to 77 °C (170 °F). For copper plating zinc-base die castings, the electrolyte is best operated at 60 to 71 °C (140 to 160 °F), provided the pH of the bath is maintained between 11.6 and 12.3. An increase in the operating temperature of Rochelle cyanide baths increases the efficiency of the anode and cathode; however, free cyanide decomposes more rapidly, which increases carbonate formation. An increase in agitation causes an increase in anode efficiency, but this also increases carbonate formation. Carbonates are always present in cyanide copper solutions from oxidation of the cyanide and, also, from adsorption of carbon dioxide from the air that reacts with the alkali in solution. Carbonates from a sodium copper cyanide plating solution can be removed by cooling the solution, which precipitates the less soluble sodium carbonate. High carbonate concentrations lower the anode efficiency, which accelerates additional carbonate formation in addition to producing rough or porous plated deposits (Ref 6).

Rochelle copper baths should be maintained at a pH between 12.2 and 13.0. Anode efficiency may be prohibitively low if the pH is too high. Raising the pH also decreases the voltage drop across the anode film. Figure 1 shows a buffer curve for adjusting the pH of Rochelle electrolytes.

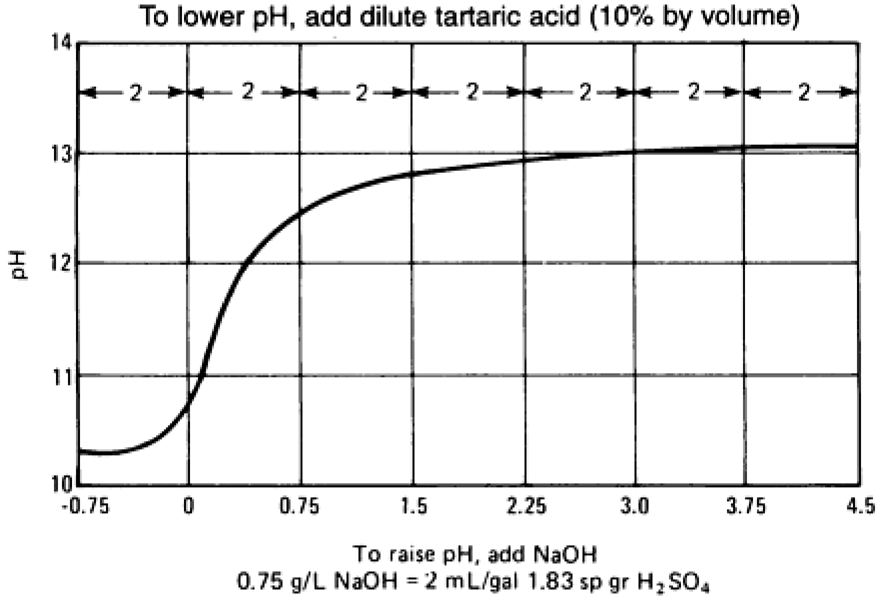


Fig. 1 Buffer curve for adjusting the pH of Rochelle electrolytes. Source: Ref 7

Conductivity of the bath is improved by raising the free alkali cyanide and the concentration of the copper complexes. When depositing copper directly on steel, brass, or copper, conductivity can be improved by the addition of 2 to 15 g/L ($\frac{1}{4}$ to 2 oz/gal) of sodium hydroxide. Sodium hydroxide concentrations should be reduced if the electrolyte is used to deposit copper onto zinc-base die castings, aluminum, or magnesium.

Rochelle baths can become contaminated during plating of zinc-base die castings. Zinc contamination can be removed by electrolysis of the bath at room temperature, at the current density that produces the most brassy or off-color deposit, usually 0.2 to 0.3 A/dm^2 (2 to 3 A/ft^2). Iron, which forms complexes with cyanide, cannot be removed readily from the bath and causes a reduction in current efficiency. Drag-in of chloride ion from acid dips must be kept very low to prevent iron buildup due to dissolution of steel equipment. Bipolarity of steel tanks or heat exchangers should be avoided.

The Rochelle bath is susceptible to organic contamination, which can be controlled by the use of wetting agents. Organic contaminants should be removed by periodic batch treatment of the electrolyte with activated carbon, followed by filtration. Organic contamination is especially high in barrel plating. A low-foaming, free-rinsing surfactant or a dispersion agent must be used in barrel plating baths to prevent organic contamination from adversely affecting the quality of the plated deposit. Organic contamination can be controlled with carbon treatment methods. Continuous filtration of cyanide electrolytes is recommended to eliminate particulate matter or salts, which can result in rough deposits.

Increase in the current density or the presence of lead in the Rochelle cyanide bath causes an increase in the stresses of copper plate. These stresses can be reduced by increasing the concentration of copper in Rochelle baths. The addition of 15 g/L (2 oz/gal) of potassium thiocyanate produces an expansion stress instead of the usual contraction stress. Figure 2 shows stress in thin copper electrodeposits plated from a cyanide solution onto stainless steel.

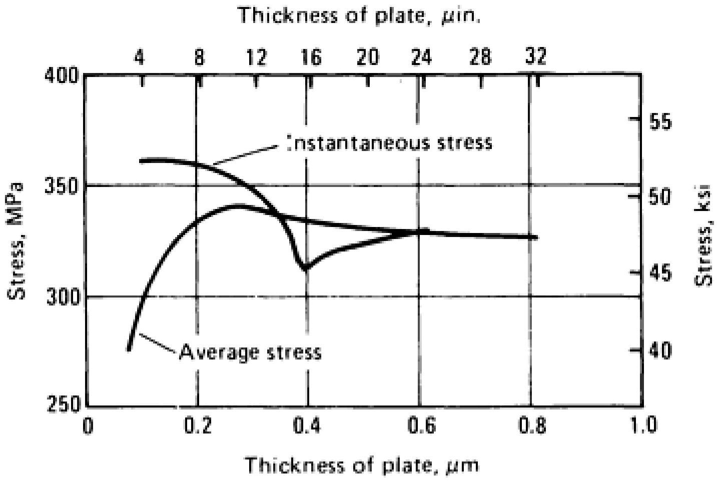


Fig. 2 Stress in thin copper plate deposited on stainless steel spirals. Stainless steel spirals are 0.127 mm (0.005 in.) thick. Source: Ref 8

References cited in this section

6. J. Horner, A Study of the Effects on Some Variables of the Speed and Distribution of Deposits from Cyanide Copper Plating Solutions, *Proc. of the 51st AES Annual Tech. Conf.,* American Electroplating Society, 1964
7. *Modern Electroplating,* Wiley, 1974, p 173
8. *J. Electrochemical Soc.,* Nov 1961

Plating in High-Efficiency Sodium and Potassium Cyanide Baths

High-efficiency sodium and potassium cyanide baths allow the use of higher current densities. Cyanide plating baths typically decrease in cathode efficiency, or speed of deposition, with increasing current, which accounts for the good plate distribution (throwing power). The cathode efficiency approaches 100% only at low current densities, often 10A/dm^2 or less. With more practical current densities of 2.0 to 3.0 A/dm^2, the cathode efficiency may drop 20%, especially with lower agitation rates. The sodium or potassium constituent improves the conductivity of the bath.

Operation of the sodium cyanide and potassium cyanide electrolytes at 66 to 74 °C (150 to 165 °F) produces quality deposits. Temperatures in excess of 74 °C (165 °F) allow the use of higher current densities, but breakdown of the cyanide becomes excessive at elevated temperatures. The anode current densities are limited by polarization, resulting in poor anode efficiency and higher voltage requirements. The cathode current densities are limited by burning of the deposit, resulting in reduced efficiency, loss of brightness, and roughness. These limits are higher in the potassium cyanide electrolyte.

Agitation of sodium cyanide and potassium cyanide high-efficiency baths is important for achieving maximum plating speed. Agitation can be accomplished by solution movement, cathode-rod movement, or use of air. Each type of agitation improves the maximum allowable current densities, with air agitation providing the greatest improvement. However, it should be noted that carbonate levels in air-agitated baths tend to increase at a greater rate than baths using mechanical agitation. All three types of agitation may be used within a single bath. Solution movement can be accomplished by mixing or by the flow of solution through filtration equipment. Cathode-rod movement of about 1 to 2 m/min (3 to 7 ft/min) allows increased plating rates. Gentle air agitation should be supplied by the use of a low-pressure blower that has a clean, filtered air source. Care must be taken to use clean, oil-free air for agitation to avoid contamination of the plating solution.

Filtration is also essential when operating high-efficiency cyanide copper electrolytes, especially for plating deposits thicker than 13 μm (0.5 mil). Filtration equipment should have the capability of one to two complete turnovers of the solution each hour while removing particulate matter from the electrolyte. Roughness of the copper deposits from particulate matter is often caused by faulty cleaning or by the formation of metallic copper or cuprous oxide particles at the anodes. Suspended dirt or solid matter in the cyanide copper electrolyte also causes surface roughness. Anode bags of proper size, material, weight, and weave are beneficial in retaining particulate matter formed at the anode. Other foreign particles introduced into the cyanide copper electrolyte are removed by the filtration equipment.

Carbonate buildup in high-efficiency copper cyanide baths can adversely affect the bath operation. High concentrations of carbonate reduce plating efficiency and speed. Excessive carbonates also affect the smoothness of the deposits. Carbonate contents of 120 to 150 g/L (16 to 20 oz/gal) or more may result in lower plating efficiency and plating speed. Excessive carbonates can also lower and reduce the acceptable plating range. These effects are more pronounced in a sodium cyanide bath than in a potassium cyanide bath.

The primary source of carbonate formation is the breakdown of cyanide as a result of poor anode efficiency. Operating cyanide electrolytes at temperatures above the recommended levels can also result in carbonate formation. Operating temperatures above about 74 °C (165 °F) cause decomposition of the cyanide ion. Air containing high levels of carbon dioxide should not be used in air-agitated systems, because the carbon dioxide is dissolved by the alkaline plating solution, also forming carbonate. The air source for air-agitated systems should be placed where it provides a clean, fresh supply.

Excessive carbonates can be removed by freezing or precipitation with lime or proprietary additives. Sodium cyanide baths can be treated either by precipitation or freezing. Potassium cyanide baths can only be treated by precipitation. Freezing is not effective for potassium cyanide baths because of the high solubility of the carbonate salts.

Current interruption cycles frequently improve the operating range of high-efficiency sodium or potassium copper cyanide plating solutions. Current interruption cycles generally allow the use of higher current densities while maintaining bath efficiency. Current interruption cycles also improve the brightness of the copper deposits, and in some cases they give excellent deposit brightness from bright plating baths that are so contaminated that acceptable deposits cannot be produced when using continuous direct current.

Current interruption cycles in the range of 8 to 15 s plating time followed by 1 to 3 s current interruption are generally used. Plating times of less than 8 s and current interruptions of more than 3 s lower the net plating rate. Plating times of more than 15 s and current interruption of less than 1 s reduce the benefits obtained by using a current interruption cycle.

The use of periodic current reversal can also be used to great advantage in high-efficiency copper cyanide plating solutions. This technique involves plating parts in the conventional manner for a selected time and then deplating for a shorter period by reversing the current. Shorter periodic reversal cycles, such as 2 to 40 s of plating followed by 1 to 10 s of deplating (reversal), result in improved deposit brightness similar to that obtained with current interruption. A major advantage in using periodic reversal is the degree of leveling that can be achieved, particularly when relatively long reversal cycles are used. These longer cycles, in excess of 45 s direct with reverse cycles in excess of 10 s, can provide leveling characteristics in excess of 50%. The use of periodic reversal permits the use of higher plating and deplating current densities.

The leveling characteristics of the deposit are improved by increasing the reversal current, whereas cycle efficiency is increased by lowering the reversal current. Figure 3 shows cycle efficiency for periodic-reverse plating. Figure 4 indicates thickness of deposit as a function of cycle efficiency.

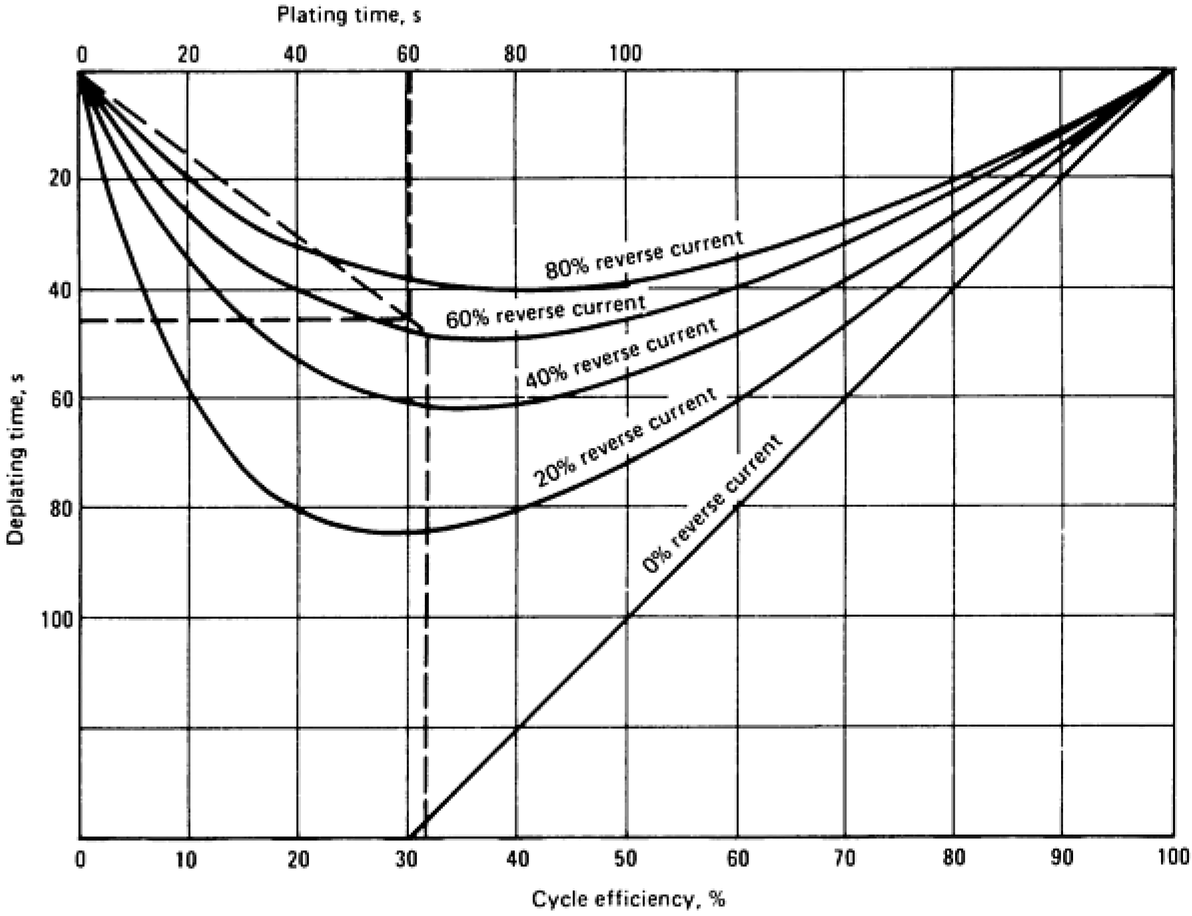


Fig. 3 Cycle efficiency during copper plating with periodic current reversal. Source: Ref 9

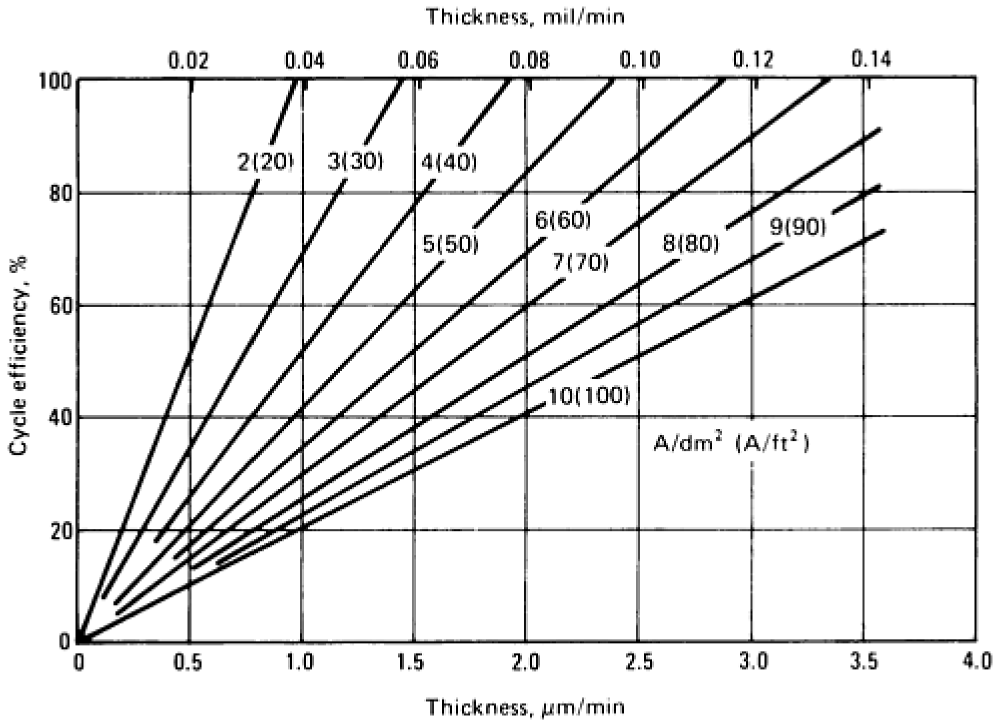


Fig. 4 Thickness of copper deposits as a function of cycle efficiency and current density during plating with periodic current reversal. Source: Ref 9

Another current-interrupting scheme being used for this and other copper plating systems is pulse plating. This normally involves a pulse power source (rectifier) that produces square-wave current pulses. *Square wave* conventionally suggests a pulse with a rise-and-fall time of approximately 10 to 85 μs and a standard frequency of 150 and 10,000 cycles. The periodic interruption of the current with proper time sequences allows much faster plating without surface burning, produces finer grain deposits, and increases throwing power and distribution.

Proprietary additives are used in high-efficiency copper cyanide baths to improve anode corrosion, increase both anode and cathode efficiencies, and control contamination. Organic and metallic additives are also used to improve deposit characteristics and brightness. These additives produce deposits ranging from matte to full-bright.

Reference cited in this section

9. *Electroplating Engineering Handbook*, Reinhold, 1971, p 748, 750

Plating in Noncyanide Copper Baths

The development and refinement of proprietary noncyanide copper baths continues today. The copper deposit from these systems is a fine-grain, dense deposit (Ref 3). The noncyanide copper systems exhibit excellent throwing and covering power, even in deeply recessed areas. In addition to eliminating the cyanide, these processes operate at much lower copper metal concentrations of 7.5 to 13.5 g/L (1 to 2 oz/gal). As a result, they offer additional savings in lowering waste treatment costs. Copper sulfate is the source of copper ions for these systems. The plating electrolytes producing these deposits are very stable compared to those of cyanide copper processes, because there is no decomposition of cyanide resulting in carbonate buildup.

Over the typical current density range of 0.5 to 3.5 A/dm^2 (5 to 35 A/ft^2), the cathode efficiency of noncyanide systems approaches 100%. The good efficiency tends to offset the lower deposition rate of divalent copper electrolysis compared to that of monovalent copper systems. Agitation has a dramatic effect on deposit appearance and cathode efficiency. To obtain a uniform, fine-grain deposit over a wide current density range, air agitation is required for these systems. Lack of agitation produces dull, burned deposits at average current densities of 1.5 to 2.0 A/dm^2 (15 to 20 A/ft^2).

Of the commercially available systems, one process is affected by the buildup of cuprous ions in the cupric phosphonate system, which results in rough, nonadherent copper deposits (Ref 10). To overcome this effect, the process uses continuous electrolysis carried out in an auxiliary tank with special ceramic or platinized anodes to oxidize the cuprous to cupric.

Because the operating pH of these systems is in the range of 9 to 10, these baths can be used as both strikes and plates. There are no special adjustments required for processing zinc diecast and zincated aluminum, as there are in cyanide copper plating. At pH values below 9, the deposits are brighter but adhesion is adversely affected. Values greater than 10 cause high-current-density dullness and can reduce the limiting current density.

These systems, unlike the cyanide systems, are more susceptible to metallic and organic contaminants. Iron, lead, and silver are critical impurities that should be removed by low-current-density electrolytic treatments. Organic impurities are treated using hydrogen peroxide and carbon treatments on a regular basis. Continuous filtration through a 10 μm retention-size cartridge is beneficial for the noncyanide systems. Occasional carbon filtration using a sulfur-free carbon can be used to control organic contamination. Noncyanide systems have very little tolerance to cyanide contamination. When converting cyanide plating lines to noncyanide processes, it is essential to clean and leach out all the cyanide from the tank linings, racks, filters, heaters, plating barrels, and any associated equipment.

References cited in this section

3. L.C. Tomaszewski and R.A. Tremmel, *Proc. of the 72nd AES Annual Tech. Conf.,* American Electroplating Society, 1985
10. D. Maule and B. Srinivasan, Alkaline Non-cyanide Plating, *Proc. of the 80th AESF Tech. Conf.,* American Electroplating and Surface Finishers, 1993

Plating in Pyrophosphate Baths

Copper pyrophosphate plating baths offer a number of desirable features. Copper pyrophosphate forms a highly soluble and conductive complex when dissolved in potassium pyrophosphate solution. Potassium salts are preferred because of their higher solubilities. Copper pyrophosphate plating baths operate at nearly 100% cathode efficiency and provide good throwing power. They are noncorrosive because the operating pH is near neutral. Concentration limits and operating conditions for copper pyrophosphate baths are given in Table 3.

Pyrophosphate forms a highly soluble complex with copper. Excess pyrophosphate is necessary to increase the conductivity of the bath and to effect proper corrosion of the anodes. Ammonia assists anode corrosion, helps enhance the luster of the deposit, and aids pH control. Nitrate allows the use of higher operating current densities by inhibiting the reduction of hydrogen at the upper end of the current density range. The pH of the pyrophosphate bath is maintained between 8.0 and 8.8. A high pH reduces anode efficiency, and a low pH reduces the throwing power of the solution and the stability of the complex compound in solution with the formation of orthophosphate. The pH of the bath can be lowered with pyrophosphoric acid and raised with potassium hydroxide. Good agitation is also essential for consistent operation. Air agitation provides for good performance of the anodes and cathodes and is preferred to cathode agitation.

Pyrophosphate electrolytes can be operated at current densities up to 7.0 A/dm^2 (70 A/ft^2) or higher. The operating current density can be increased by agitating the solution or by increasing the temperature of the bath. The anode current density should be maintained between 2 and 4 A/dm^2 (20 and 40 A/ft^2).

High bath temperatures should be avoided, because excessive formation of orthophosphate occurs. Orthophosphate formed by the hydrolysis of pyrophosphate is beneficial up to about 90 g/L (12 oz/gal), because it promotes anode corrosion and acts as a buffer. Above this concentration, conductivity and bright plating range are decreased and banded deposits are obtained. Orthophosphate cannot be removed chemically from the solution. The concentration can be reduced only by discarding the bath or diluting and rebuilding the pyrophosphate plating solution.

Copper pyrophosphate plating baths are susceptible to organic contamination, including oil and excess or decomposed addition agents. These are removed by treatment with activated carbon and filtration. Cyanide and lead also contaminate the bath. Cyanide is removed by treatment with hydrogen peroxide and lead by electrolysis. Precautionary methods, such as proper cleaning, adequate rinsing, and good solution control and maintenance, prevent these contaminants from

entering or building up in the bath, avoiding the need for frequent purification. Copper pyrophosphate solutions are tolerant of other metallic contamination.

Proprietary brighteners are available that refine the grain structure, impart leveling characteristics, and act as brighteners. However, decomposition products from an excessive additive concentration cause stress and brittle deposits. Thus, for quality deposits, additives should be added to the bath on an as-consumed basis.

Plating in Acid Sulfate Baths

The chemical composition of acid sulfate baths is simple. Copper sulfate pentahydrate and sulfuric acid are the primary constituents of the copper sulfate electrolyte. The metal ions are furnished by the copper sulfate. Sulfuric acid increases solution conductivity and helps prevent the formation of basic cuprous or cupric crystals on the anodes and the tank, which causes poor anode corrosion and roughness. Low sulfuric acid contents produce more high-current-density burn, poorer leveling, more low-current-density dullness, and more nodular deposits. High sulfuric acid has less effect on the deposit but increases the anode dissolution. With cathode efficiencies of 95 to 100%, the copper sulfate bath is easy to operate and control.

Many copper sulfate plating solutions require the use of additives to produce smooth, fine-grain, bright, leveled, and ductile deposits. Most of the addition agents used in copper sulfate plating solutions are proprietary formulations. These proprietary additives are capable of producing the desired characteristics in the copper deposit, and deposit hardness can be increased where necessary.

In copper sulfate systems that produce bright deposits, a catalyst must be added in addition to the primary constituents to avoid streaky deposits. This catalyst is chloride, which is maintained between 0.02 to 0.1 g/L (0.003 to 0.01 oz/gal), or 20 to 100 ppm. The chloride, usually added as hydrochloric acid, inhibits rough nodular plate from forming. Low chloride can cause dark deposits on the edges and high-current-density areas of the work, loss of leveling, loss of brightness, pitting, and poor anode corrosion. High chloride causes streaks, increased brightener usage, and loss of leveling and brightness in the bright bath formulations. High chloride can be reduced with zinc dust treatments or precipitation with silver.

If solution agitation or work movement is minimal, current densities should not exceed about 4.5 A/dm^2 (45 A/ft^2), because excessive anode polarization may occur and the deposits can be spongy. Where higher current densities are desired, such as for electrotypes or wire plating, air agitation is used. Air agitation is necessary to accelerate ionic diffusion and produce high-quality, fine-grain deposits where current densities are in excess of 10 A/dm^2 (100 A/ft^2).

The effect of temperature changes on the grain structure and surface smoothness of deposits plated from the copper sulfate bath is less significant than the effect of changes in cathode current densities. An increase in temperature results in higher conductivity and reduced anode and cathode polarization. Increased temperature also reduces the tensile strength of deposits and increases grain size. Excessive temperatures should be avoided in copper sulfate baths where proprietary brightener formulations are used, because reduced plating ranges, excessive additive use, and solution contamination from additive breakdown result.

Care must be taken to avoid accelerated buildup of copper metal, as in cases where dragout rates are low or improper anode-to-cathode ratios are maintained. An increase in the concentration of the copper sulfate increases the solution resistivity and slightly reduces the anode and cathode polarization. Copper sulfate concentrations in excess of 248 g/L (33 oz/gal) may result in salt crystallization in the plating solution. Normal bath composition is restored by discarding a portion of the bath and adding water and sulfuric acid.

To improve the throwing power of some bright copper sulfate baths used for plating printed circuit boards, a low copper sulfate and high sulfuric acid electrolyte is used. The use of this electrolyte allows a nearly equal deposit distribution when plating the through-holes of the printed circuit board.

In sulfate electrolytes, impurities such as silver, gold, arsenic, and antimony can codeposit with copper. Arsenic and antimony cause copper deposits to be brittle and rough, and silver may cause roughness. Nickel and iron impurities reduce the conductivity of the plating bath. Lead impurities do not codeposit with copper; however, they precipitate in the electrolyte. Soluble silicates may precipitate onto the work. Organic contamination from decomposition products of addition agents, tank linings, and anode bags can cause brittle or discolored deposits. These organics can be removed from the electrolyte by treating it with activated carbon.

Plating in Fluoborate Baths

Copper fluoborate and fluoboric acid are the primary constituents of the copper fluoborate electrolyte. The metal ions are furnished by the copper fluoborate, which is more soluble than copper sulfate used in the sulfate bath, and the anode current density is not critical. Therefore, the metal-ion concentration in the fluoborate bath can be more than twice that in the copper sulfate solution, and this permits higher cathode current densities. The cupric salts in the fluoborate bath are highly ionized, except for small amounts of less ionized complex salts formed with certain addition agents.

In the copper fluoborate bath, the anode current density can be as high as 40 A/dm^2 (400 A/ft^2) without excessive anode polarization. The effect of temperature changes on the grain structure and surface smoothness of deposits plated from the copper fluoborate bath is less significant than the effect of changes in cathode current density.

Agitation is preferred for the fluoborate bath, although acceptable deposits 25 μm (1 mil) thick have been produced in a high-concentration bath without agitation and with current density maintained at 35 A/dm^2 (350 A/ft^2). When agitation is used, a low-concentration bath operated at a current density of 4 to 5 A/dm^2 (40 to 50 A/ft^2) is preferred.

Although fluoborate baths containing no additives can produce dense and smooth deposits up to 500 μm (20 mils) thick, additives may be used to aid in the deposition of brighter or more uniform coatings or to assist in control of plating conditions. Although deposits from fluoborate baths are easily buffed to a high luster, brighteners of acetyl thiourea can be added to the electrolyte to produce bright coatings. The addition of free acid to the bath increases solution conductivity, reduces anode and cathode polarization, and prevents the precipitation of basic salts. Hard deposits and minimum edge effects result when molasses (1 mL/L, or 0.1 fluid oz/gal) is added to the electrolyte. If the pH of these baths exceeds 1.7, deposits become dull, dark, and brittle.

The resistivity of fluoborate electrolytes is reduced if the concentration of fluoboric acid exceeds 15 g/L (2 oz/gal) or if the concentration of copper fluoborate exceeds 220 g/L (29 oz/gal). In the fluoborate bath, the metal-ion concentration can be more than double that in a copper sulfate solution containing 50 to 75 g/L (6.7 to 10 oz/gal) of sulfuric acid.

In the fluoborate electrolytes, silver, gold, arsenic, and antimony may co-deposit with copper, but the effects of such impurities in this electrolyte have not been reported. Lead is the only metallic impurity known to interfere with the deposition of ductile copper deposits. Additions of sulfuric acid precipitate the lead. As with the sulfate electrolytes, organic impurities sometimes cause deposits to be brittle or discolored. They can be removed by treating the bath with activated carbon

Wastewater Control and Treatment

Increasing regulations governing discharge water have led to improved techniques for reducing the quantities of wastes that must be treated. These techniques have not only reduced the quantity of wastewater to be treated, but have also reduced the quantity of chemicals used and have lowered water consumption. These methods can be applied to any plating operation. Many references are available, including Ref 11, that cover waste treatment technologies.

The use of counterflow rinses has reduced water consumption and wastewaters while maintaining adequate rinsing between plating operations. Reduced dragout of plating electrolytes can be accomplished by allowing processed parts leaving the plating solution to drain into the plating solution. Drip pans also reduce the amount of electrolyte dragout.

Closed-loop systems have dramatically reduced wastewater, lowered water consumption, and diminished chemical usage. Closed-loop systems allow recovery of rinse waters and chemicals by evaporative, reverse osmosis, or ion exchange recovery methods. Care must be exercised when using closed-loop systems, especially with copper plating, to keep impurities and contaminants from preplate operations out of the copper plating bath where they will be trapped by the closed-loop operation.

In any plating operation, wastewaters must be treated to reduce the hazardous materials to meet regulations. The general procedures for treating copper plating electrolytes and rinse waters resulting from copper plating systems are:

- Cyanide-bearing solutions require oxidation of the cyanide with an oxidizing agent such as chlorine or hypochlorite, followed by precipitation of the heavy metals.
- Noncyanide alkaline solutions are pH-adjusted and have calcium chloride added to precipitate the

copper.

- Pyrophosphate wastes require low pH hydrolysis to orthophosphate, followed by precipitation of the heavy metals.
- Acid sulfate and fluoborate wastes are pH-adjusted to precipitate the copper.

Reference cited in this section

11. J.W. Patterson, *Industrial Waste Water Treatment Technology,* 2nd ed., Butterworth Publishers, 1985

Copper Plating Equipment

Construction materials for equipment are indicated in Table 7. Construction materials for racks and anodes are given in Table 8.

Table 7 Materials of construction for equipment basic to copper plating

Tank linings are of rubber or plastic[(a)], or Koroseal.

Plating bath	Heating coils	Filters	Filter aids
Dilute cyanide	Low-carbon steel Teflon[(b)]	Low-carbon or stainless steel; cast iron	Diatomite Cellulose
Rochelle cyanide	Low-carbon steel Teflon[(b)]	Low-carbon or stainless steel; cast iron	Diatomite Cellulose
High-efficiency cyanide	Low-carbon steel Teflon[(b)]	Low-carbon or stainless steel; cast iron	Diatomite Cellulose
Pyrophosphate	Stainless steel Teflon[(b)]	Stainless steel Rubber- or vinyl-lined steel	Diatomite Cellulose
Noncyanide alkaline[(c)]	Stainless steel Titanium	Stainless steel Rubber- or vinyl-lined steel	Diatomite Cellulose
Acid copper sulfate	Titanium[(d)] Teflon[(b)]	Rubber- or vinyl-lined steel	Diatomite Cellulose
Fluoborate	Carbon[(d)] Teflon[(b)]	Rubber- or vinyl-lined steel	Diatomite Cellulose

(a) Of approved compositions; in the absence of data on bath contamination and effects on deposits, compatibility tests are required.

(b) Dupont trademark.

(c) Polypropylene filter cartridges may be used.

(d) Also for cooling coils, if bath is used below 32 °C (90 °F)

Table 8 Materials for anodes and racks for use in copper plating

Racks are made of copper[(a)].

Plating bath	Anodes
Dilute cyanide	Copper; steel
Rochelle cyanide	Copper[(b)(c)(d)]
High-efficiency cyanide	Copper[(b)(c)(d)]
Noncyanide alkaline	Copper[(d)]
Pyrophosphate	Copper[(b)(c)(d)]
Acid copper sulfate	Copper[(e)]
Fluoborate	Copper[(d)]

(a) Racks are generally coated with an inert plastic coating to prevent plating.

(b) Cast copper, high purity.

(c) Rolled copper, high purity.

(d) Oxygen-free high-purity copper.

(e) Phosphorized copper

Tanks. For cyanide copper solutions, low-carbon steel tanks are suitable. Polypropylene tanks with adequate reinforcing may also be used, provided that the operating temperature is not excessive. Low-carbon steel tanks should be lined with rubber, polyvinylchloride, or another synthetic material that is not susceptible to attack by the cyanide plating solution. This will prevent bipolar effects, which may rob current from significant areas of the work. Tanks for alkaline noncyanide copper, copper pyrophosphate, acid copper sulfate, and copper fluoborate solutions should be of similar construction. Low-carbon steel tanks used for these solutions must be lined with the above materials to prevent the solutions from attacking the low-carbon steel, resulting in short tank life and immersion deposits. New tanks, as well as all other equipment coming in contact with the plating solution, should be leached before use to remove any materials that may leach into the plating solution and cause poor quality deposits. Leaching solutions should be similar to the plating solution to be used, such as a 15 to 30 g/L (2 to 4 oz/gal) caustic solution for copper cyanide or noncyanide copper equipment, or a 5 to 10% sulfuric acid solution for acid copper sulfate. When converting a tank or line that contained cyanide to a noncyanide electrolyte, it is essential to leach out all residual cyanide from the tank lining and any associated equipment.

Barrels. High-speed copper plating solutions for barrel plating are being used in product operations. Polypropylene barrels have been used successfully for prolonged periods.

Anodes. The types of copper anodes used in each of the copper plating solutions are indicated in Table 8. High-purity copper anodes are recommended. Anodes with a lesser purity may form heavy sludges during electrolysis and contribute appreciably to roughness of the deposit. Anodes used for acid copper plating solutions should be phosphorized. These contain a small percentage of phosphorus, which helps to control chemical dissolution and limits the buildup rate of copper in the acid solution. These types should not be used in alkaline cyanide or noncyanide electrolytes, because anode polarization will develop and cause deposit roughness and more difficult copper metal control.

Copper anodes are available in many forms, such as bars, balls, or chips. Bars are suspended from the anode bar. Balls or chips are placed in titanium baskets.

The anode area in a copper plating solution should be controlled and maintained. If the anode area is not maintained, it decreases as the copper is dissolved and the anode current density rises, resulting in increased polarization and formation of undesirable films. These films can restrict current flow or sluff from the anode and cause roughness in the plating solution.

Anode Bags. Bags made of cotton, Dynel, or polypropylene are used in copper plating solutions. Cotton bags are preferred for cyanide copper solutions, and Dynel or polypropylene are used in the acid copper solutions. Bags are used to keep the fine particles formed at the anode from migrating to the cathode, resulting in roughness. The weave and weight of the anode bag are most important. The bag material must be capable of retaining the particles formed at the anode and at the same time allow the plating solution to flow freely around the anode. Anode bags are not generally used in pyrophosphate baths, because they interfere with dissolution of the anode by decreasing the circulation of the solution around the anode.

Characteristics of Copper Plate

Variations in processing during surface preparation or during plating have significant effects on the quality of the copper electrodeposit. Certain variations can adversely affect the adhesion of copper to the substrate metal. Variations also can affect brightness, porosity, blistering, roughness, hardness, solderability, and leveling.

Brightness. Bright copper coatings are generally obtained by the addition of brighteners to the electrolyte, although buffing of the electrodeposited coating provides a high luster. Plating from high-concentration cyanide baths with current interruption or periodic reversal of current also improves the luster of the copper coating.

Buffing or electropolishing the work before plating it in an electrolyte not containing a brightener results in the deposition of a smooth and sometimes semibright coating. If an electrolyte containing a brightener is used, the luster of the coating is enhanced. The high cost of labor is a primary concern when buffing is considered as the method of brightening the coatings. Plating from high-efficiency cyanide baths with current interruption or periodic reversal of current also improves the luster of the deposits. Improved casting techniques and mechanical finishing before plating can improve the quality of the copper deposit.

Adhesion. Careful selection of substrate surface and proper preparation of the surface before plating are important for good adhesion. In general, cast and other porous surfaces are less receptive to good-quality electrodeposited coatings than wrought surfaces.

The kind of material to be electroplated with copper is another important consideration. For magnesium-base or aluminum-base die castings, the zincate layer between the substrate and the copper deposit is a critical control factor. For a properly activated stainless steel surface, a controlling factor for ensured adhesion of copper is the speed with which the workpiece is immersed in the bath. Some brighteners, especially organic brighteners, may adversely affect adhesion of subsequent electrodeposited coatings. Adhesion of copper electrodeposits from acid baths can be ensured only if a strike from a cyanide copper bath precedes copper plating.

Porosity. The degree of porosity in a copper coating can be controlled by the kind of copper plating bath selected, the composition and control of the electrolyte, the basis material to be plated, and the condition of the surface to be plated. The degree of porosity on the surface of the metal to be plated also dictates the techniques needed to minimize porosity in the coating. A porous surface has high surface area and requires high current density for efficient plating.

Blistering of copper plate, particularly when the plated work is subjected to heat, occurs mostly on zinc-base die castings. Blistering can also occur on parts made of magnesium or aluminum in any form, as a result of poor quality of castings, poor surface preparation, or both. Blistering of copper plate on zinc-base die castings plated in a cyanide strike electrolyte and then subjected to heat can be reduced by lowering the pH of the cyanide strike bath from the range of 12.0 to 12.6 to about 10. Caution must be used because operation at a pH value this low may result in the release of poisonous hydrogen cyanide gas. It is imperative that the plating bath be thoroughly vented.

Blistering of copper-plated magnesium and aluminum, especially during subsequent soldering or heating in service, is caused by poor adhesion at the zincate-copper interface. Unfortunately, blistering often does not become evident until subsequent electrodeposits have been applied and the coating has been subjected to heat. Exposing all copper-plated magnesium and aluminum parts to controlled heat representative of that to be subsequently encountered is good practice. This causes blistering before deposition of subsequent metal coatings if there is poor adhesion at the interface.

Roughness in copper deposits is often caused by foreign particles present in the bath as the result of faulty cleaning, or by the migration to the cathode of metallic copper or cuprous oxide particles that form at the anode. Such roughness is especially likely to occur with the sodium cyanide high-concentration electrolytes and can be prevented by using anode bags.

Solderability of the coating is good when the copper surface is free of oxide, the coating is thick enough, and the adhesion of the copper plate is superior. Direct soldering of electrodeposited copper is not unusual for parts that are subsequently contained in hermetically sealed units.

Soldering is a routine operation for aluminum and magnesium electronic parts used in aerospace applications. A copper strike and copper plate frequently comprise the initial metal coating over the zincated surfaces of these parts, after which electrodeposits of other metals are applied before soldering. A top coat of tin, or of cadmium plate that has been chromate conversion coated, is a particularly effective means of producing a good combination of solderability and corrosion resistance for parts exposed to the atmosphere.

Hardness. Without the use of addition agents, cyanide electrolytes produce harder coatings than acid baths. With the use of addition agents, the hardness of copper deposits from any electrolyte can be increased. Hardness of the electrodeposit is generally associated with fine grain, but hardness can be increased by introducing preferred crystal orientation in the absence of grain refinement. Changes in the copper sulfate or sulfuric acid concentration of acid baths have little effect on the hardness of copper plate.

Leveling has a significant effect on the appearance of the copper coating, as well as on the appearance of the final product when other metals are subsequently plated over the copper. Often, the substrate metal does not have the degree of smoothness that is desired of the plated surface. Metal substrate surfaces can be mechanically or chemically worked to reduce surface roughness before electroplating; however, some copper electrolytes can produce substantial leveling in the deposited coating, thus reducing cost related to elaborate prepolishing or other means of smoothing the surface. The high-concentration potassium cyanide electrolytes produce excellent leveling when certain addition agents are added and interrupted current or periodic reversal is used during plating. Although somewhat less effective, high-concentration sodium cyanide baths, mixed sodium and potassium electrolytes, and Rochelle cyanide electrolytes also have good leveling characteristics with interrupted or periodically reversed current. Acid copper sulfate electrolytes also provide very good leveling characteristics.

Copper in Multiplate Systems

Electrodeposited copper is widely used as a basis for subsequent plated coatings in multiplate systems. The use of copper plate in copper-nickel-chromium systems is discussed in the article "Decorative Chromium Plating" in this Volume.

Cost

The cost of copper plating is influenced largely by the type of installation. In a modern, automated, multiple-phase shop, brighteners and wetting agents probably are the greatest cost factor. In a still-tank operation, the cost of labor is of major importance. An increase in current density reduces cost because of the reduction in time required to deposit a given thickness of coating.

For a routine plating operation, the cost of the copper deposited can be estimated with the aid of Fig. 5. For example, Fig. 5 shows that 120 g (4 oz) of copper is required for plating an area of 0.7 m^2 (7 ft^2) with a coating 20 μm (0.8 mil) thick. The cost of the copper coating is obtained by multiplying the weight of copper required by the cost of copper anodes. For areas larger than 2.4 m^2 (10 ft^2), multiply by the proper factor.

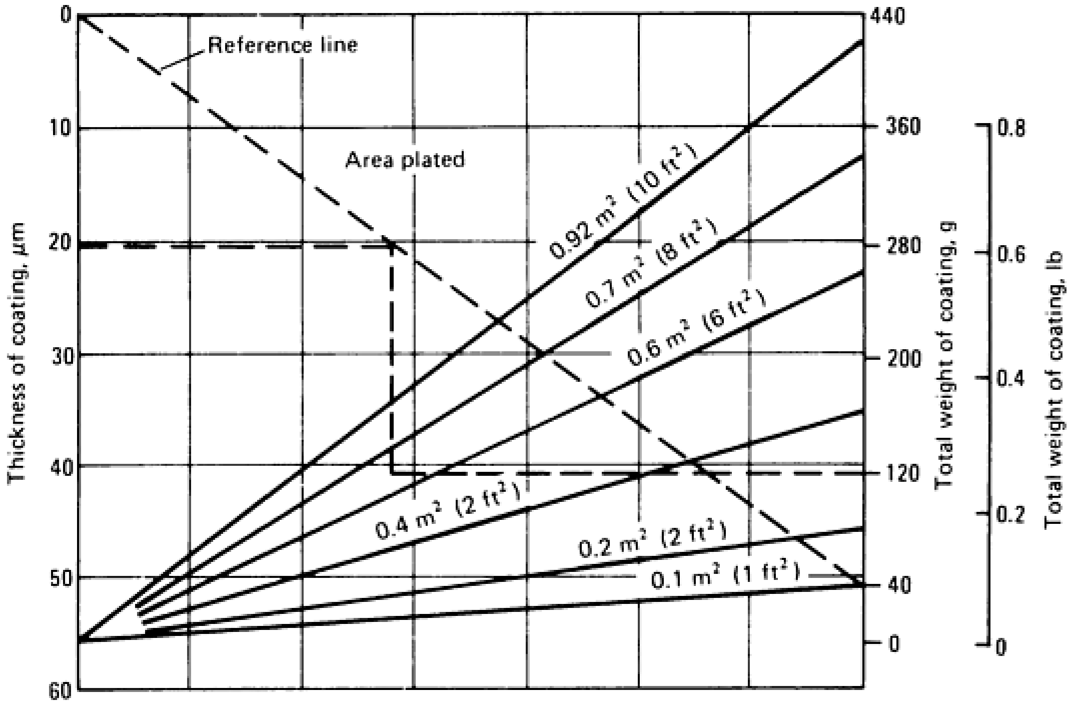


Fig. 5 Copper required for covering an area with a specific thickness

Industrial (Hard) Chromium Plating

Revised by Kenneth R. Newby, Atotech USA

Introduction

HARD CHROMIUM PLATING is produced by electrodeposition from a solution containing chromic acid (CrO_3) and a catalytic anion in proper proportion. The metal so produced is extremely hard and corrosion resistant. The process is used for applications where excellent wear and/or corrosion resistance is required. This includes products such as piston rings, shock absorbers, struts, brake pistons, engine valve stems, cylinder liners, and hydraulic rods. Other applications are for aircraft landing gears, textile and gravure rolls, plastic rolls, and dies and molds. The rebuilding of mismachined or worn parts comprises large segments of the industry. One specialized application is a thin chromium layer used as a lacquer adhesive layer in the manufacture of "tin" cans.

Hard chromium plating is also known as industrial, functional, or engineering chromium plating. It differs from decorative chromium plating in the following ways:

- Hard chromium deposits are intended primarily to increase the service life of functional parts by providing a surface with a low coefficient of friction that resists galling, abrasive and lubricated wear, and corrosion. Another major purpose is to restore dimensions of undersized parts.
- Hard chromium normally is deposited to thicknesses ranging from 2.5 to 500 μm (0.1 to 20 mils) and for certain applications to considerably greater thicknesses, whereas decorative coatings seldom exceed 1.3 μm (0.05 mil).
- With certain exceptions, hard chromium is applied directly to the base metal; decorative chromium is

applied over undercoats of nickel or of copper and nickel.

Principal Uses

The major uses of hard chromium plating are for wear-resistance applications, improvement of tool performance and tool life, and part salvage. Table 1 lists parts to which hard chromium plate is applied and representative data regarding plate thickness and plating times. Plating times can be reduced by using high-efficiency or mixed-catalyst solutions.

Table 1 Typical thicknesses and plating times for selected applications of hard chromium plating

Part	Base metal	Thickness of plate		Plating time[(a)]
		μm	mils	
Computer printer type	Carbon steel	25	1	60 min
Face seals	Steel or copper	75-180	3-7	10 h
Aircraft engine parts	Nickel-based alloys, high strength steel	75-180	3-7	10 h
Plastic molds	Tool steel	5-13	0.2-0.5	30 min
Textile guides	Steel	5-100	0.2-4	20-240 min
Piston rings	Steel or cast iron	150-255	6-10	8 h
Balls for ball valves	Brass or steel	7.5-13	0.3-0.5	20 min
Micrometers	Steel	7.5-13	0.3-0.5	20 min
Golf ball molds	Brass or steel	7.5-25	0.3-1	20-60 min
Lock cases	Brass	5-7.5	0.2-0.3	20 min
Cylinder	Cast iron	255	10	300 min
Bushing	1018 carburized, 56 HRC	25	1	45 min
Crankshafts	Steel	255-3800	10-150	. . .
Cutting tools	Tool steel	1.3	0.05	5 min
Forming and drawing dies	Steel	25	1	60 min

Part	Base metal	Thickness of plate		Plating time[a]
		µm	mils	
Gage	Steel	125	5	150 min
Gun barrels, 30 caliber[b]	Steel	25	1	40 min
Hydraulic cylinder	1045 steel	13	0.5	40 min
Pin	Steel	13	0.5	30 min
Pin	1045 steel, 60 HRC	125	5	40 min
Plug gage	1040 steel, 55 HRC	125	5	150 min
Relief-valve plunger	1113 steel, soft	100	4	60 min
Ring gage	Steel	205	8	240 min
Rolls	Steel	13-255	0.5-10	20-300 min

(a) Times shown are for conventional plating solutions; plating times for the proprietary fluoride-free solution are half of those shown.

(b) M-16 rifle, barrel and chamber

Wear Resistance. Extensive performance data indicate the effectiveness of chromium plate in reducing the wear of piston rings caused by scuffing and abrasion. The average life of a chromium-plated ring is approximately five times that of an unplated ring made of the same base metal. Piston rings for most engines have a chromium plate thickness of 100 to 200 µm (4 to 8 mils) on the bearing face, although thicknesses up to 250 µm (10 mils) are specified for some heavy-duty engines.

In the automotive industry, hard chromium is also applied to shock absorber rods and struts to increase their resistance to wear and corrosion. Valve stems are plated with a flash coating (about 2.5 µm, or 0.1 mil) to reduce wear. Hydraulic shafts for all kinds of equipment are plated with 20 to 30 µm (0.8 to 1.2 mil) of hard chromium to increase service life.

Tooling Applications. Various types of tools are plated with chromium to minimize wear, prevent seizing and galling, reduce friction, and/or prevent or minimize corrosion. Steel or beryllium copper dies for molding of plastics are usually plated with chromium, especially when vinyl or other corrosive plastic materials are to be molded. Plating thicknesses of 2.5 to 125 µm (0.1 to 5 mils) usually are recommended for preventing wear in parts sticking in molds and for reducing frequency of polishing when plastics that attack steel or beryllium copper are being molded. Chromium-plated dies should not be used when plastics containing fire-retardant chlorides are molded.

The service life of plug gages and other types of gages may be prolonged by hard chromium plating. Most gage manufacturers provide chromium-plated gages. Records in one plant indicate that plug gages made from hardened O1 tool

steel wore 0.0025 mm (0.0001 in.) after gaging 5000 cast iron parts. Hard chromium plating of these gages allowed the gaging of 40,000 parts per 0.0025 mm (0.0001 in.) of wear.

Worn gages can be salvaged by being built up with hard chromium plate. Also, chromium plate provides steel gages with good protection against rusting in normal exposure and handling. Chromium plating is not recommended, however, for gages that are subjected to impact at exposed edges during operation.

Deep drawing tools often are plated with chromium, in thicknesses up to 100 μm (4 mils), for improvement of tool performance and/or building up of worn areas. The life of draw rings and punches may be prolonged by plating. In addition, plating reduces frictional force on punches and facilitates removal of workpieces from punches in instances where sticking is encountered with plain steel surfaces. If deep drawing tools are chromium plated, the base metal should be harder than 50 HRC. Steel dies used for drawing bars and tubes are often plated with relatively heavy thicknesses (up to 250 μm, or 10 mils) of chromium to minimize die wear, reduce friction, and prevent seizing and galling.

The service life of cutting tools is often extended by chromium plate, in thicknesses ranging from less than 2.5 to 13 μm (0.1 to 0.5 mil). Taps and reamers are examples of tools on which chromium plate has proved advantageous. In one case, a flash plate on taps used to thread cold-worked 1010 steel improved tap life from 250 (for unplated taps) to 6000 parts per tap. The poor tool life of the unplated taps was caused by buildup of metal on the cutting edges. Hard chromium plating is not recommended for cold extrusion tools for severe applications where extreme heat and pressure are generated, because the plate is likely to crack and spall and may be incompatible with phosphate-soap lubricants.

Part Salvage. Hard chromium plating is sometimes used for restoring mismachined or worn surfaces. Since 1970, the use of this process for part salvage has been frequently replaced by thermal spraying and plasma coatings, which can be applied more quickly. The fact that a chromium deposit can significantly reduce fatigue strength must be considered in determining whether chromium plating can be safely used.

Hard chromium plating is used to restore to original dimensions the worn surfaces of large crankshafts for diesel and gas engines and for compressors. In these applications, in which coating thicknesses usually range from 125 to 1250 μm (5 to 50 mils), the excellent wearing qualities and low coefficient of friction of chromium are highly advantageous. The plate is prevented from depositing in fillet areas as a precaution against fatigue failure.

The extremely close dimensional tolerances specified for components of compressors for jet aircraft engines are not always correctly met in machining. Hard chromium plating is sometimes used to salvage mismachined parts. Most frequently mismachined are the diameters of rotor disks and spacers. The maximum thickness of plate on these components, which are made of 4130 and 4340 steels, generally does not exceed 380 μm (15 mils).

Other Applications. Hard chromium plate is applied to printing plates and stereotypes, especially to those intended for long runs, because compared to other materials or coatings used for this application, it wipes cleaner, provides sharper reproduction, and increases the length of press runs. It is used on press rams because of its excellent resistance to corrosion, seizing, galling, and other forms of wear.

Selection Factors

The decision to use hard chromium plating on a specific part should take into account the following characteristics:

- The inherent hardness and wear resistance of electrodeposited chromium
- The thickness of chromium required
- The shape, size, and construction of the part to be plated
- The type of metal from which the part is made
- Masking requirements (for parts that are to be selectively plated)
- Dimensional requirements (that is, whether or not mechanical finishing is required and can be accomplished in accordance with desired tolerances)

The hardness of chromium electrodeposits is a function of the type of chemistry selected and the plating conditions. In general, chromium plated in the bright range is optimally hard. Typically bright chromium deposits from conventional

plating solutions have hardness values of 850 to 950 HV; those from mixed-catalyst solutions have values of 900 to 1000 hV; and those from fluoride-free chemistries have values of 950 to 1100 HV or higher.

Size. Frequently, a very large part can be plated in sections or can be rotated so that only a portion of the part is immersed in the plating solution at any given time. The latter method has been used to plate large cylinders up to 4 m (12 ft) in diameter and up to 18 m (60 ft) long. When this technique is used, all of the surface to be plated that is exposed to the atmosphere must remain wet with plating solution.

Journal surfaces of the largest diesel crankshafts and bores of large naval guns and M-16 rifles are hard chromium plated on a production basis. Internal surfaces of very large cylinders have been plated by closing off the ends of each cylinder and retaining the plating solution with it.

Base Metal. Most hard chromium deposits are applied to parts made of ferrous alloys; however, numerous aerospace applications require the chromium plating of aluminum and nickel-base alloys. From the standpoint of processing, hard chromium plate may be applied to steels, regardless of their surface hardness or chemical composition, provided that the base metal is hard enough to support the chromium layer in service. Similarly, cast irons can be plated provided that the surface is capable of conducting the required current and is reasonably free of voids, pits, gross silicate inclusions, massive segregation, slivers, and feather edges.

Plating Solutions

Chromic acid is the source of metal in hard chromium plating solutions. However, a chromic acid solution does not deposit chromium unless a definite amount of catalyst is present. If there is either too much or too little catalyst, no chromium metal is deposited. Catalysts that have proved successful are acid anions, the first of which to be used was sulfate. Substitution of fluoride ions present in complex acid radicals for a portion of the sulfate improves the chromium-plating operation. In the late 1980s, a fluoride-free proprietary solution was developed. The secondary catalyst in this chemistry is a stable organic species. Reflecting this difference in catalyst, the principal types of solutions are designated as conventional sulfate (also called Sargent or Fink); mixed-catalyst, which refers to the sulfate and fluoride chemistry; and fluoride-free (proprietary) catalyst.

The fatigue limit of high-strength steel (steels with ultimate tensile strengths of 1240 MPa, or 180 ksi, and above) may be reduced by about 50% when chromium plated because of the inherent crack structure of hard chromium. However, special techniques using shot peening and postplate heat treatments may be used to retain most of the original fatigue strength.

Conventional Sulfate Solutions. Composition of conventional chromic acid solutions catalyzed by sulfate can vary widely, provided the ratio by weight of chromic acid to sulfate radical is within the range between 75 and 120 to 1. Throwing power, or distribution of plate, is optimum at ratios between 90 and 110 to 1; however, in the range between 75 and 90 to 1, brighter deposits are obtained, less burning occurs, and a higher current density can be used.

Solutions containing chromic acid in a concentration as low as 50 g/L (7 oz/gal) have been reported but are not practical for production because:

- Their plating range is too limited
- The solutions are more sensitive to contamination
- They have a higher electrical resistance
- They require a higher voltage for operation

Compositions and operating conditions for two chromic acid/sulfate solutions (low and high concentrations) for hard chromium plating are given in Table 2. The low-concentration solution is widely used for hard chromium plating because it minimizes dragout losses and associated environmental problems. The high-concentration solution has the advantage of being less sensitive to concentration changes; it is also easier to control and has better throwing power. Because the high-concentration solution is more conductive, it can be operated at lower voltages and heats up less in operation.

Table 2 Sulfate baths for hard chromium plating

Type of oath	Chromic acid[(a)]		Sulfate[(a)]		Current density		Bath temperature	
	g/L	oz/gal	g/L	oz/gal	A/dm^2	A/in.^{2}	°C	°F
Low concentration	250	33	2.5	0.33	31-62	2-4	52-63	125-145
High concentration	400	53	4.0	0.53	16-54	1-3.5	43-63	110-145

(a) Concentration usually can deviate ±10% without creating problems. It is recommended that adjustments be such that the concentrations listed above lie in the middle of the range permitted. For example, chromic acid can fluctuate by ±23 g/L (±3 oz/gal); therefore, the concentration range should be 225-270 g/L (30 to 36 oz/gal), rather than 205-250 g/L (27 to 33 oz/gal).

If available voltage is limited, it may be preferable to operate a solution with higher conductivity in the range of 300 to 405 g/L (40 to 54 oz/gal) of chromic acid, even though current efficiency is lower than with the less concentrated solutions. The lower current efficiency is offset by increased current density obtainable because of better solution conductivity. Usually, the best range of operation is from 195 to 300 g/L (26 to 40 oz/gal) of chromic acid. Even within this range, the solution containing 195 g/L (26 oz/gal) has the highest current efficiency, while the solution containing 300 g/L (40 oz/gal) has the best conductivity.

The mixed-catalyst solutions are similar to conventional sulfate solutions in conductivity, but they produce harder deposits and have higher intrinsic current efficiency than conventional solutions under identical conditions. They also have a higher current efficiency at higher concentration. Mixed-catalyst solutions can increase production rates 40 to 60% and more over those obtainable with conventional solutions, due to the greater current efficiencies of the mixed-catalyst solutions and their ability to operate at higher current densities without creating harmful effects on the deposit. One limitation of mixed-catalyst solutions is that they cause etching of unplated iron surfaces at areas of low current density, with a resulting increase in contamination that reduces the life of the solution. This etching can be prevented on significant surfaces by masking areas not to be plated. Mixed-catalyst solutions are seldom used on aluminum or copper substrates because of the attack by the fluoride chemicals.

Fluoride-free solution, a proprietary chemistry, is based on chromic acid, sulfate, and a stable organic catalyst. It provides deposit speeds and current density ranges slightly in excess of those obtained with mixed-catalyst solutions. Because the solution contains no fluorides or other halogens, it does not cause etching on exposed unplated surfaces or attack aluminum or copper substrates. These features alleviate the need for excessive protective masking operations. As with the mixed-catalyst chemistry, the fluoride-free solution provides much greater plating throughput while consuming about one-third less electricity than the conventional solution.

Deposit hardness and corrosion resistance improve as one moves from the conventional sulfate solution to the mixed-catalyst solution and on to the fluoride-free solution.

Solution Control

Chromium-plating solutions of all three types must be subjected to periodic chemical analyses for control of solution composition. With the exception of catalyst analysis, the species and methods are identical for all chemistries. Solution control can be simplified if a record is kept of the way a particular chromium solution changes in composition during its use. Change in chemical composition depends on the number of ampere-hours of current passed through the solution, the dragout of solution, and spray losses. Also, evaporation losses, if not compensated for, usually cause the concentration to change by about 2 to 5% during a day's operation. A complete solution analysis should be made at periodic intervals (weekly or monthly, depending on production rate) and the solution should be brought into proper balance.

Chromic acid content can be semi-quantitatively determined simply by placing a hydrometer in the plating solution, provided that other contaminants, such as iron or copper, are not present in significant quantities. Hydrometers calibrated in ounces of chromic acid per gallon at the operating temperature of the solution are available. Baumé hydrometers can be used in samples cooled to the calibration temperature marked on the hydrometer; the reading can be converted to

concentration by using Table 3. Impurities cause the Baumé reading to be higher than is warranted by the actual chromic acid content. Periodically, the chromic acid content should be quantitatively determined by chemical titration and a notation made of the differences between the contents as shown by chemical analysis and by hydrometer readings. Hydrometer readings should then be corrected by that amount. When a hydrometer reading shows 30 to 38 g/L (4 to 5 oz/gal) more chromic acid than is actually present, the solution should be discarded, because this is caused by a high metallic impurity level. Adjustments in chromic acid concentration are simplified by the use of Table 4.

Table 3 Determination of chromic acid in chromium baths with a Baumé hydrometer

Direct conversion of degrees Baumé to ounces of chromic acid per gallon, at 25 °C (77 °F)

°Bé	Chromic acid	
	g/L	oz/gal
10.5	113	15.0
11.0	119	15.8
11.5	124	16.5
12.0	130	17.3
12.5	137	18.2
13.0	144	19.1
13.5	149	19.8
14.0	153	20.4
14.5	159	21.2
15.0	165	22.0
15.5	172	22.9
16.0	178	23.7
16.5	184	24.5
17.0	191	25.4
17.5	198	26.3

18.0	204	27.2
18.5	211	28.1
19.0	218	29.0
19.5	224	29.8
20.0	230	30.9
20.5	237	31.5
21.0	244	32.4
21.5	250	33.3
22.0	257	34.2
22.5	264	35.1
23.0	271	36.0
23.5	279	37.1
24.0	287	38.2
24.5	294	39.1
25.0	301	40.0
25.5	308	4.09
26.0	315	41.9
26.5	323	42.9
27.0	331	44.0
27.5	338	45.0
28.0	346	46.0

28.5	354	47.1
29.0	362	48.2
29.5	370	49.2
30.0	378	50.2
30.5	387	51.5
31.0	399	53.0
31.5	406	54.0
32.0	415	55.2

Note: Impurities will cause the Baumé hydrometer reading to be higher than is warranted by the actual content of chromic acid.

Table 4 Conversion equivalents for chromic acid concentration in chromium baths

Values in table are based on the following formula, which may be used to compute values for which conditions are not given: Chromic acid required, kg(lb) = g/L(oz/gal) CrO_3 to be added × bath volume, in liters (gallons)/16

Chromic acid to be added		**Chromic acid required, kg (lb), at volume of bath, L (gal), of:**									
g/L	**oz/gal**	**380 (100)**	**760 (200)**	**1140 (300)**	**1510 (400)**	**1890 (500)**	**2270 (600)**	**2650 (700)**	**3030 (800)**	**3410 (900)**	**3790 (1000)**
4.0	0.5	1.4 (3.1)	2.9 (6.3)	4.3 (9.4)	5.7 (12.5)	7.1 (15.6)	8.5 (18.8)	9.9 (21.9)	11.3 (25.0)	12.7 (28.1)	14.2 (31.2)
7.5	1.0	2.8 (6.2)	5.7 (12.5)	8.5 (18.8)	11.3 (25.0)	14.2 (31.2)	17.0 (37.5)	19.9 (43.8)	22.7 (50.0)	25.5 (56.3)	28.3 (62.5)
11.0	1.5	4.3 (9.4)	8.5 (18.8)	12.8 (28.2)	17.0 (37.5)	21.3 (46.9)	25.5 (56.3)	29.8 (65.6)	34.0 (75.0)	38.3 (84.4)	42.5 (93.8)
15.0	2.0	5.7 (12.5)	11.3 (25.0)	17.0 (37.5)	22.7 (50.0)	28.3 (62.5)	34.0 (75.0)	39.7 (87.5)	45.3 (100.0)	51.3 (113.0)	56.7 (125.0)
19.0	2.5	7.1 (15.6)	14.2 (31.2)	21.3 (46.9)	28.3 (62.5)	35.4 (78.1)	42.5 (93.8)	49.4 (109.0)	56.7 (125.0)	61.0 (141.0)	70.8 (156.0)
22.0	3.0	8.5 (18.8)	17.0 (37.5)	25.5 (56.3)	34.0 (75.0)	42.6 (93.8)	51.3 (113.0)	59.4 (131.0)	68.0 (150.0)	76.7 (169.0)	85.3 (188.0)

26.0	3.5	9.9 (21.9)	19.8 (43.7)	29.8 (65.6)	39.7 (87.5)	49.4 (109.0)	59.4 (131.0)	69.4 (153.0)	79.4 (175.0)	89.4 (197.0)	99.3 (219.0)
30.0	4.0	11.3 (25.0)	22.7 (50.0)	34.0 (75.0)	45.3 (100.0)	56.7 (125.0)	68.0 (150.0)	79.4 (175.0)	90.7 (200.0)	102.0 (225.0)	113.0 (250.0)
34.0	4.5	12.7 (28.1)	25.5 (56.2)	38.3 (84.4)	51.3 (113.0)	64.0 (141.0)	76.7 (169.0)	89.4 (197.0)	102.0 (225.0)	115.0 (253.0)	127.0 (281.0)
37.0	5.0	14.2 (31.2)	28.3 (62.5)	42.5 (93.8)	56.7 (125.0)	70.8 (156.0)	85.3 (188.0)	99.3 (219.0)	113.0 (250.0)	128.0 (281.0)	142.0 (312.0)
41.0	5.5	15.6 (34.4)	31.2 (68.7)	46.7 (103.0)	62.6 (138.0)	78.0 (172.0)	93.4 (206.0)	109.0 (241.0)	125.0 (275.0)	140.0 (309.0)	156.0 (344.0)
45.0	6.0	17.0 (37.5)	34.0 (75.0)	51.3 (113.0)	68.0 (150.0)	85.3 (188.0)	102.0 (225.0)	119.0 (262.0)	136.0 (300.0)	153.0 (338.0)	170.0 (375.0)
49.0	6.5	18.4 (40.6)	36.8 (81.2)	55.3 (122.0)	73.9 (163.0)	92.1 (203.0)	111.0 (244.0)	129.0 (284.0)	147.0 (325.0)	162.0 (365.0)	184.0 (406.0)
52.0	7.0	19.8 (43.7)	39.7 (87.5)	59.4 (131.0)	79.4 (175.0)	99.3 (219.0)	119.0 (262.0)	139.0 (306.0)	159.0 (350.0)	179.0 (394.0)	198.0 (437.0)
56.0	7.5	21.3 (46.9)	42.5 (93.8)	64.0 (141.0)	85.3 (188.0)	106.0 (234.0)	128.0 (281.0)	149.0 (328.0)	170.0 (375.0)	191.0 (422.0)	213.0 (469.0)
60.0	8.0	22.7 (50.0)	45.4 (100.0)	68.0 (150.0)	90.7 (200.0)	113.0 (250.0)	136.0 (300.0)	159.0 (350.0)	181.0 (400.0)	204.0 (450.0)	227.0 (500.0)
64.0	8.5	24.1 (53.1)	48.1 (106.0)	72.1 (159.0)	96.6 (213.0)	121.0 (266.0)	145.0 (319.0)	169.0 (372.0)	193.0 (425.0)	216.0 (477.0)	241.0 (531.0)
67.0	9.0	25.5 (56.2)	51.3 (113.0)	76.7 (169.0)	102.0 (225.0)	127.0 (281.0)	153.0 (338.0)	179.0 (394.0)	204.0 (450.0)	230.0 (506.0)	255.0 (562.0)
71.0	9.5	26.9 (59.4)	54.0 (119.0)	80.7 (178.0)	108.0 (238.0)	135.0 (297.0)	161.0 (356.0)	189.0 (416.0)	215.0 (475.0)	243.0 (535.0)	269.0 (594.0)
75.0	10.0	28.3 (62.5)	56.7 (125.0)	85.3 (188.0)	113.0 (250.0)	142.0 (312.0)	170.0 (375.0)	199.0 (438.0)	227.0 (500.0)	255.0 (563.0)	284.0 (625.0)

Chromic acid content can also be determined by various analytical procedures. Some of these procedures use standard solutions that can be used for other determinations; this may be the deciding factor as to which procedure to use. The following procedure is simple and quite rapid:

Reagents

- *Acid mixture:* Mix 1 part sulfuric acid, 1 part phosphoric acid, and 1 part water.
- *Ferrous ammonium sulfate (FAS) 0.1 N:* Dissolve 40 g/L (5.3 oz/gal) FAS · $6H_2O$ and add 25 mL/L concentrated sulfuric acid. When in use, keep about 6500 mm^2 (10 $in.^2$) of aluminum metal in the container to maintain constant normality.
- Orthophenanthroline ferrous sulfate complex indicator
- *Potassium dichromate, 0.1000 N:* dissolve 4.900 g (0.173 oz) of $K_2Cr_2O_7$ (CP grade) and dilute to a liter.

Standardization of FAS

- 1. Pipette 25 mL of potassium dichromate standard into a 250 mL Erlenmeyer flask and dilute to 85 mL.
- 2. Add 15 mL of acid mixture and 3 drops of indicator.
- 3. Titrate with FAS to clear orange endpoint. Normality of FAS = 2.5 / (mL of FAS).

Procedure

- 1(a). Pipette 10 mL of chromium solution into a 250 mL volumetric flask and dilute to volume. Pipette a 10 mL aliquot into a 250 mL Erlenmeyer flask.
- 1(b). Pipette 0.4 mL of chromium solution sample into a 250 mL Erlenmeyer flask, using a 1 mL pipette graduated in hundredths of a milliliter.
- 2. Add 50 mL of water, 15 mL of acid mixture, and 3 drops of indicator.
- 3. Titrate with FAS to clear orange end point. Chromic acid in g/L = (mL of FAS) × (N of FAS) × (83.3). Chromic acid in oz/gal = (mL of FAS) × (N of FAS) (11.12).

Use either step 1(a) or 1(b), followed by steps 2 and 3. Step 1(b) is slightly less accurate than 1(a) but is much faster.

Sulfate in a chromium solution can be determined to a high degree of accuracy by a gravimetric method, or with reasonable accuracy using the much faster centrifuge method. Unless there is some reason for great precision, the centrifuge method is entirely satisfactory. Most graduated centrifuge tubes can be calibrated for sulfate; however, the technique should be checked regularly by analysis of a standard solution, or by the gravimetric technique.

With the centrifuge method, the amount of insoluble material in the sample must be determined before sulfate is precipitated. This can be done by running a blank sample or centrifuging the sample before precipitating the sulfate. Because sulfate determinations are made in duplicate, it is advisable to determine how closely the two tubes match in calibration. This can be done by pouring a small amount of mercury into first one tube and then the other. These tubes should be marked to be used together, and a notation should be made, if necessary, as to the amount of correction needed in the reading. Adjustments of sulfate concentration in chromium solutions can be simplified by using Table 5.

Table 5 Conversion equivalents for adjusting sulfate concentration in chromium baths

Values in table are based on the following formula, which may be used to compute values for which conditions are not given: Sulfuric acid (66 °Bé) fluid oz, = 0.522 × oz/gal H_2SO_4 to be added × bath volume, gal

Sulfuric acid to be added		Sulfuric acid (66 °Bé) required, mL (fluid oz), at volume of bath, L (gal), of:									
g/L	oz/gal	380 (100)	760 (200)	1140 (300)	1515 (400)	1890 (500)	2270 (600)	2650 (700)	3030 (800)	3410 (900)	3790 (1000)
0.08	0.01	15 (0.5)	30 (1.0)	47 (1.6)	62 (2.1)	77 (2.6)	92 (3.1)	109 (3.7)	124 (4.2)	139 (4.7)	154 (5.2)

0.15	0.02	30 (1.0)	62 (2.1)	92 (3.1)	124 (4.2)	154 (5.2)	186 (6.3)	216 (7.3)	249 (8.4)	278 (9.4)	308 (10.4)
0.22	0.03	47 (1.6)	92 (3.1)	139 (4.7)	186 (6.3)	231 (7.8)	284 (9.6)	323 (10.9)	370 (12.5)	417 (14.1)	465 (15.7)
0.30	0.04	62 (2.1)	124 (4.2)	186 (6.3)	249 (8.4)	308 (10.4)	370 (12.5)	432 (14.6)	494 (16.7)	556 (18.8)	619 (20.9)
0.37	0.05	77 (2.6)	154 (5.2)	231 (7.8)	308 (10.4)	385 (13.0)	462 (15.6)	539 (18.2)	619 (20.9)	696 (23.5)	773 (26.1)
0.45	0.06	92 (3.1)	186 (6.3)	284 (9.6)	370 (12.5)	462 (15.6)	556 (18.8)	648 (21.9)	740 (25.0)	835 (28.2)	926 (31.3)
0.53	0.07	110 (3.7)	216 (7.3)	323 (10.9)	432 (14.6)	539 (18.2)	648 (21.9)	758 (25.6)	864 (29.2)	974 (32.9)	1080 (36.5)
0.60	0.08	124 (4.2)	249 (8.4)	370 (12.5)	494 (16.7)	619 (20.9)	740 (25.0)	864 (29.2)	989 (33.4)	1113 (37.6)	1237 (41.8)
0.67	0.09	139 (4.7)	278 (9.4)	417 (14.1)	556 (18.8)	696 (23.5)	835 (28.2)	974 (32.9)	1143 (38.6)	1252 (42.3)	1391 (47.0)
0.75	0.10	154 (5.2)	308 (10.4)	465 (15.7)	619 (20.9)	773 (26.1)	926 (31.3)	1080 (36.5)	1237 (41.8)	1391 (47.0)	1545 (52.2)

Note: To neutralize excess sulfuric acid (thereby lowering the sulfate content) in a chromium bath, add approximately 1.5 g/L (0.2 oz/gal) of barium carbonate for each 0.8 g/L (0.1 oz/gal) of excess sulfuric acid. Additions of barium carbonate should be made slowly to the bath.

Contamination. In the operation of any chromium solution, the solution should be kept free of excessive amounts of contamination. Introduction of copper, iron, or trivalent chromium seriously decreases the conductivity of the solution and requires the use of a higher operating voltage to produce a given current density.

Trivalent chromium can be formed by the decomposition of organics, but more often it results from too low a ratio of anode-to-cathode area, a condition always encountered in plating interior surfaces cylinders. Trivalent chromium can be reoxidized to hexavalent chromium by electrolyzing the solution at 60 to 66 °C (140 to 150 °F), with an anode-to-cathode area ratio of about 30 to 1, and using a cathode current density of about 60 A/dm^2 (4 $A/in.^2$). About 50 A · h/L (200 A · h/gal) is required for reoxidizing 15 g/L (2 oz/gal) of trivalent chromium; ordinarily, this operation is performed during the weekend shutdown period.

Removal of copper, iron, and other contaminants is usually accomplished by disposing of part or all of the solution, or where permissible, by ion exchange or electrodialysis techniques. In addition to reducing the conductivity of the solution, impurities, particularly iron and trivalent chromium, also reduce current efficiency. (This is especially true for the mixed-catalyst type of chemistry because these contaminants reduce the activity of the fluoride catalyst.) Normally, the presence of 10 g/L (1.5 oz/gal) of iron in solution reduces cathode current efficiency by about 30%. Iron and trivalent chromium can produce rougher deposits with more treeing. Other contaminants affect the throwing power and coverage.

Mandrel Test. When difficulties are experienced with the hard chromium production solution, it may be useful to use the mandrel test, so named because it is usually performed by plating a low-carbon steel rod or mandrel (9.5 mm diameter

by 75 mm long, or $\frac{3}{8}$ in. diameter by 3 in. long) with a conforming circular anode to give uniform current distribution. A convenient procedure is to use 540 mL of the solution in a 600 mL beaker made of heat-resistant glass. The steel mandrel is buffed to a bright finish, and the top 25 mm (1 in.) that projects out of the solution and into a holder is stopped-off to indicate the exact size of the plating area.

The mandrel is immersed in the test solution, which is heated to 55 °C (130 °F) in a water solution, treated anodically at 15 A/dm^2 (1 A/in.^{2}) for 15 s, and then plated at 30 A/dm^2 (2 A/in.^{2}) for 1 h. The temperature of the water solution should be reduced to about 52 °C (125 °F) during plating to compensate for the heat generated by the current. The mandrel is then removed, rinsed, dried, and inspected.

Better temperature control through the plating process is obtained by using 1 L of solution in a 1.5 L beaker. The solution is heated with a 125 W quartz heater controlled by a thermoregulator and relay. The process operates at 55 °C (130 °F).

A hard chromium solution in proper adjustment gives a bright plate under these conditions. If the deposit is dull, the solution is contaminated or out of balance. Burning on the bottom edge of the mandrel also indicates that the solution is out of adjustment. A high content of trivalent chromium causes dullness and growth of metal whiskers from the bottom edge of the mandrel.

Current efficiency and plating speed can be checked with the same setup, but this is more conveniently done with a flat steel panel and flat anodes. A polished steel panel, 25 by 75 mm (1 by 3 in.), can be used, with the bottom 50 mm (2 in.) marked off as the plating area. Plating conditions would be 30 A/dm^2 (2 A/in.^{2}) for 15 min at 55 °C (130 °F), but other conditions can be tested as desired. The steel panel is accurately weighed before and after plating (without current reversal). Current efficiency, thickness of chromium, and plating speed are calculated as follows:

- Current efficiency, % = (weight, in grams, of chromium × 100) / (ampere-hours × 0.323)
- Thickness of deposit, mils = (weight, in grams, of chromium) / (4 × 0.116)
- Plating speed, mils/h = (thickness of deposit, in mils × 60) / plating time, min

Process Control

In addition to solution composition, the principal variables that must be controlled for satisfactory hard chromium plating are the anodes, the current density, and the solution temperature.

Anodes. In contrast to other plating solutions, which use soluble anodes to supply the solution with a large part of the metal ion being plated, chromium plating solutions are operated with insoluble lead alloy anodes. Usually about 7% Sn or Sb or a combination of the two are used to alloy the lead. As a consequence of using inert anodes, additions of chromic acid must be made to keep the plating solution supplied with chromium metal ions.

A coating of lead peroxide forms on the lead alloy anodes during electrolysis. This coating is usually dark charcoal brown, which indicates that the anodes are functioning correctly. The presence of an orange-to-yellow lead chromate coating indicates that the anodes are not passing current properly. Periodic cleaning of the anodes and their hooks is mandatory for efficient operation.

Insoluble antimonial lead (93Pb, bal Sb + Sn) and lead-tin alloy (93Pb-7Sn) are the most widely used anode materials in chromium plating solutions. These alloys minimize corrosion of the anode; the antimony in the first composition stiffens the anode against shape changes. Each anode must have sufficient cross-sectional area to pass the requisite current without overheating. If high current densities are to be used with mixed-catalyst or fluoride-free solutions, it may be necessary to use larger anode cross sections than would be the case in the low-current-density conventional solutions. In any case the bottom of each anode should be at least 150 mm (6 in.) above the bottom of the plating tank to avoid possible electrical shorts.

Conductivity of the chromium solution is based on chromic acid concentration. Concentrations higher than 250 g/L (33 oz/gal) require lower operating voltage; however, current efficiency decreases with increasing chromic acid concentration. Concentrations below about 180 g/L are usually impractical unless high-voltage rectifiers are available.

Current Density and Efficiency. Cathode current efficiency varies with current density and temperature of the plating solution. Efficiency increases significantly with increasing current density and slightly with decreasing temperature. These two variables have a definite effect on the appearance and hardness of the deposit. A high solution temperature results in a milky, dull, and softer deposit at lower current efficiencies, unless the current density is increased substantially. Raising current density causes the deposit to change successively at specific temperatures (Table 6). Because tank time is an important economic factor, the highest rates of deposition that are produced by the highest available currents may determine which plating solution temperature is most useful.

Table 6 Effect of bath temperature and current density on appearance and hardness of chromium deposits plated from a conventional sulfate solution

Bath contained 406 g/L CrO_3; ratio of CrO_3 to SO_4 ranged from 90-to-1 to 100-to-1

Current density		Appearance of deposit	Hardness[(a)], DPH
A/dm^2	A/in.^{2}		
Plating bath at 43 °C (110 °F)			
Below 8.53	Below 0.55	Dull matte	[(b)]
8.53	0.55	Semibright	695
17.1	1.10	Bright	900
25.6	1.65	Bright, pebbly	Over 940
34.1	2.20	Dull, nodular[(c)]	Over 940
Plating bath at 49 °C (120 °F)			
Below 10.9	Below 0.70	Dull matte	510-595
10.9	0.70	Semibright	695
21.7	1.40[(d)]	Bright	900
32.6	2.10	Bright, pebbly	Over 940
43.4	2.80	Dull, nodular[(c)]	Over 940
Plating bath at 54 °C (130 °F)			
Below 14.0	Below 0.90	Dull matte	510-595
14.0	0.90	Semibright	695

27.9	1.80[d]	Bright	900
41.9	2.70	Bright, pebbly	Over 940
55.8	3.60	Dull, nodular[c]	Over 940

(a) Hardness of mounted and unmounted specimens was determined with a tester employing a Vickers diamond, a load of 200 g, and a magnifaction of 200×. Mounted specimens were mounted flat (not cross section).

(b) Current density too low to plate a sufficient amount of chromium for hardness test.

(c) Specimens polished lightly to smooth out nodules.

(d) Optimum current density

Deposition Rates. Times required to plate hard chromium deposits of various thicknesses are shown as a function of current density in Table 7 (for low-concentration solutions) and Table 8 (for high-concentration solutions).

Table 7 Rates of deposition of hard chromium from low-concentration baths

Thickness of plate		**Plating time, h:min, at current density, A/dm^2 (A/in.^{2}), of:**		
μm	**mils**	**31 (2.0)**	**47 (3.0)**	**62 (4.0)**
Conventional sulfate bath[a]				
25	1	1:05	0:40	0:25
50	2	2:05	1:20	0:55
125	5	5:20	3:20	2:20
Mixed catalyst bath[b]				
25	1	0:50	0:30	0:20
50	2	1:40	1:00	0:40
125	5	4:05	2:25	1:45

Fluoride-free bath[c]				
25	1	0:40	0:27	0:17
50	2	1:25	0:53	0:37
125	5	3:35	2:15	1:30

(a) Bath containing 250 g/L (33 oz/gal) of chromic acid with 100-to-1 ratio of chromic acid to sulfate, operated at 54 °C (130 °F).

(b) Proprietary bath containing 250 g/L (33 oz/gal) of chromic acid, operated at 54 °C (130 °F).

(c) Proprietary bath containing 250 g/L (33 oz/gal) of chromic acid, operated at 54 °C (130 °F)

Table 8 Rates of deposition of hard chromium from high-concentration baths

Thickness of plate		**Plating time, h:min, at current density of:**				
µm	**mils**	**23 A/dm^2 (1.5 A/in.^{2})**	**31 A/dm^2 (2.0 A/in.^{2})**	**39 A/dm^2 (2.5 A/in.^{2})**	**47 A/dm^2 (3.0 A/in.^{2})**	**54 A/dm^2 (3.5 A/in.^{2})**
Conventional sulfate bath[a]						
25	1	2:20	1:35	1:15	0:55	0:45
50	2	4:35	3:10	2:30	1:55	1:30
125	5	11:30	8:00	6:15	4:40	3:50
255	10	23:00	16:00	12:30	9:25	7:35
380	15	34:30	24:00	18:45	14:05	11:25
510	20	46:00	32:00	25:00	18:50	15:10
Mixed catalyst bath[b]						
25	1	2:00	1:10	0:55	0:40	0:30
50	2	4:00	2:20	1:50	1:20	1:00

125	5	10:00	5:50	4:30	3:20	2:30
255	10	20:00	12:00	9:00	6:40	5:00
380	15	30:00	18:00	13:00	10:00	7:30
510	20	40:00	24:00	18:00	16:40	12:30
Fluoride-free solution[(c)]						
25	1	1:50	1:05	0:50	0:37	0:27
50	2	3:40	2:10	1:40	1:15	0:55
125	5	9:10	5:30	4:10	3:10	2:15
255	10	18:20	11:00	8:20	6:20	4:30
380	15	27:30	16:30	12:30	9:30	6:45
510	20	36:40	22:00	16:40	12:40	9:00

(a) Chromic acid content, 400 g/L (53 oz/gal); ratio of chromic acid to sulfate, 100:1; operating temperature, 55 °C (130 °F).

(b) Chromic acid content, 400 g/L (53 oz/gal); sulfate content, 1.5 g/L (0.20 oz/gal); contains sufficient fluoride catalyst to give 100-to-1 ratio results.

(c) Chromic acid content, 400 g/L (53 oz/gal); contains appropriate amount of proprietary catalyst; operating temperature, 55 °C (130 °F)

Solution temperature affects both the conductivity and the current required. If limited power is available, satisfactory hard chromium plating deposits can be obtained at lower temperatures (43 to 49 °C, or 110 to 120 °F), but if power supply is adequate, it is advantageous to work at higher temperatures (up to 60 °C, or 140 °F) because of the faster deposition rate and the improved durability of the deposit. At 43 to 49 °C (110 to 120 °F), current densities of 8 to 30 A/dm^2 ($\frac{1}{2}$ to 2 A/in.^{2}) are satisfactory; at 60 to 66 °C (140 to 150 °F), 45 to 60 A/dm^2 (3 to 4 A/in.^{2}) may be required, and as high as 80 to 90 A/dm^2 (5 to 6 A/in.^{2}) can sometimes be needed. At all temperatures, increased agitation will allow higher current densities.

Control of solution temperature to within a narrow range is necessary because of the marked influence of temperature on deposition rate and deposit quality. An increase of 2 °C (5 °F) in mean solution temperature, for example, can cause a reduction of 5% or more in mean chromium thickness, thus necessitating a sizable adjustment in either plating time or current density. The solution temperature should be maintained within 1 °C (2 °F). Solution temperature is usually controlled automatically. Manual control is impractical for a production operation.

For automatic control, it is important that the thermostat be placed in the plating solution in a location where it can readily sense any significant change in solution temperature. Obviously, the thermostat must not be in close proximity to a heating or cooling pipe or to an electric heating element. Location of the thermostat is greatly simplified when an external heat exchanger is used and the solution is pumped from the heat exchanger to the solution. Rapid movement of the solution or air agitation helps to promote temperature uniformity.

Problems and Corrective Procedures

Faulty operation of a chromium-plating solution can result in slow plating speed or deposits with undesirable characteristics. The problems encountered in hard chromium plating are similar for all three chemistries. Possible causes and suggested corrective procedures include:

Poor coverage

- Low chromic acid content
- Low ratio of chromic acid content to total catalyst content. Correct by adding chromic acid or by precipitating sulfate, if too high, with barium carbonate.
- Temperature too high
- Current density too low
- Passive or scaled anodes. Correct by cleaning and reactivating anodes, using high current density until uniform gassing is obtained, and checking for good anode contact.
- Rack contacts too heavily built up with metal, causing rack to rob plate
- Thieves too large or too close
- Open holes preventing uniform plate in adjacent areas. Correct by using nonconducting plugs in holes.
- Gas entrapment preventing plating solution from reaching some areas. Correct by positioning parts in solution so that all gases can escape or by agitating parts while they are plating.

Burnt deposits

- Ratio of chromic acid to total catalysts too high. Correct by adding necessary catalyst or by lowering chromic acid content.
- Current density too high
- Temperature too low
- Large parts were colder than solution temperature when plating began.
- Some parts, in a load of different parts, receive too much current. Correct by adjusting anodes and contacts to ensure that each part receives correct current density.
- Excessive amount of anode within a given area for the part being plated. Correct by eliminating all excess anodes in the tank, designing the shape of conforming anodes to minimize current density at high-density areas, and, if necessary, using nonconducting shields at these areas.

Slow plating speed

- Chromic acid content too high
- Ratio of chromic acid to total catalyst too high
- Temperature too high
- Current density too low
- Scaled anodes
- Insufficient or inadequate sizes of conductors in anode or cathode circuits
- Thief obtains too much current. Correct by redesigning thief or by removing nodules from thief.
- Single phasing of rectifier caused by partial burnout. Correct by repairing rectifier.
- High contact resistance on busbars, racks, or jigs. Correct by cleaning contacts to lower contact resistance. Do not always rely on voltage for control, because it does not indicate the conditions present on the part; instead, control by amperage.

- Large variety of parts in same tank prohibiting proper current density for each part
- Tank overcrowded with parts
- High content of metallic impurities. Correct by discarding a portion of solution; readjust after dilution.

Nodular deposits

- Insufficient etching before plating in relation to thickness of deposit. Correct by increasing etching time.
- Rough surface before plating
- Chromic acid content too high. Correct by removing portion of solution; dilute the remainder and adjust.
- Low temperature
- Low sulfate content
- Current density too high

Pitted deposits

- Marking dye not completely removed
- Material suspended in solution. Correct by filtering out suspended material.
- Surface-activating agents caused deep pits when plating thick deposits. Correct by discarding as much of the solution as necessary to eliminate pits and replace with fresh solution. Prevent by discontinuing use of mist suppressors. Plastic parts that decompose, such as floats, can form decomposition products that also create pits.
- Gas bubbles adhering to part. Correct by improving surface finish before plating and by agitating part occasionally during plating.
- Part is magnetized. Correct by demagnetizing.
- Magnetic particles in the solution. Correct by removing particles with magnet.
- Insufficient cleaning prior to plating
- Particles falling on work from anodes or thieves. Correct by improving design of anodes and thieves and by cleaning both regularly to remove loose particles.
- Carbon smut on surface. Correct by scrubbing before plating.
- Excessively etched surface during reverse-etch or stripping operation

Poor adhesion

- Insufficient or no etching before plating
- Contaminants not completely removed from surfaces during cleaning
- Excessive grinding rate at edges or sharp projections, where base metal fractures and it may appear that plated material did not adhere
- Single phasing of rectifier caused by partial burnout. Correct by repairing rectifier.
- Current interruption during plating
- Cold solution

Macrocracks

- Highly stressed base metal; cracks are visible during grinding or when heat is applied. Correct by relieving stresses in base metal.
- Grinding at too fast a rate (heat checks)

Equipment

The discussion of equipment that follows is confined largely to considerations that are specific to chromic acid plating processes. Mixed-catalyst and fluoride-free solutions have essentially the same equipment requirements as conventional

sulfate solutions, except that all parts of the electrical system may need to be heavier to accommodate the increased current used. Equipment requirements for plating three specific parts are given in Table 9.

Table 9 Process and equipment requirements for hard chromium plating using conventional solutions

Item	Area of part		Area of load		No. of pieces/ 8 h	Thickness of plate		Current density		Plating time, min	Temperature of bath		No. of work rods	Tank dimensions	
	mm^2	$in.^2$	mm^2	$in.^2$		μm	mil	A/dm^2	$A/in.^2$		°C	°F		mm	in.
Small cutting tools	4,800	7.5	967,000	1500	10,000	1.3	0.05	30	2	5	50	120	1	1500 × 760 × 910	60 × 30 × 36
Shafts	20,000	30	600,000	930	200	25	1	30	2	63	50	120	2	1800 × 910 × 910	72 × 36 × 36
Gun barrels[(a)]	15,000	23	543,000	828	180	25	1	45	3	40	54	130	2	2400 × 910 × 610	96 × 36 × 24

(a) Plating of inside diameter 30-caliber gun barrels

Tanks and Linings. Figure 1 illustrates a hard chromium plating tank arrangement. Most tanks for chromium plating are made of steel and lined with an acid-resisting material. Because of their excellent resistance to corrosion by chromic acid, lead alloys containing antimony or tin may be used as tank linings.

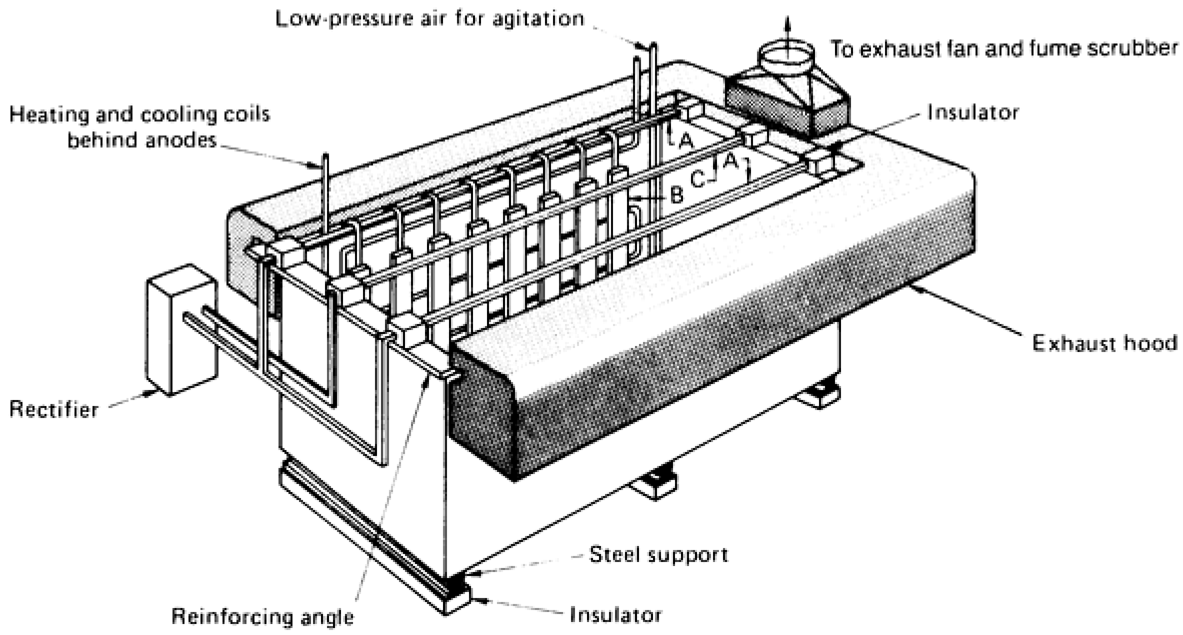


Fig. 1 Tank and accessory equipment used for hard chromium plating. A, anode rods; B, lead or lead-tin anodes; C, cathode rod

Acid-resistant brick has been used as a lining material. Because of its electrical insulating characteristics, acid-resistant brick lining has the advantage over metal linings of reducing possible current losses or stray currents. Some installations combine a lead lining or plastic sheet lining with an acid-resistant brick facing. With fluoride-containing solutions, a brick lining is suitable only for temporary use.

Almost invariably, plasticized polyvinyl chloride is used for all three types of chromium plating solutions, provided that the solution temperature does not exceed 66 °C (150 °F). Sheets of this plastic are cemented to tank walls and welded at joints and corners. Other plastic materials are equally resistant to chemical attack but are more likely to fail at the welds when exposed to an oxidizing acid. Fiberglass utilizing either polyester or epoxy is unsatisfactory for use in mixed-catalyst solutions, because exposed fiberglass will be attacked by the secondary fluoride catalyst.

Design specifications for low-carbon steel tanks for chromium plating are given in Table 10. Lining materials for low-carbon steel tanks are given in Table 11. Steel tanks should be supported at least 100 mm (4 in.) from the floor; steel I-beams are used to provide this support and are mandatory when side bracing is required. To provide insulation, reinforced strips of resin-bonded glass fiber can be placed between the floor and the I-beams. Glass brick can be used as insulation between electrodes and the plating tank.

Table 10 Design specifications for low-carbon steel tanks for hard chromium plating

Size of tank				**Thickness of low-carbon steel**		**Width of rim**		**Tank reinforcing**
Length		**Depth**						
m	**ft**	**m**	**ft**	**mm**	**in.**	**mm**	**in.**	
Up to 1	Up to 4	Under 0.9	Under 3	5	$\frac{3}{16}$	50	2	No
Up to 1	Up to 4	Over 0.9	Over 3	5	$\frac{3}{16}$	50	2	Yes
1-4	4-12	All	All	6	$\frac{1}{4}$	75	3	Yes
Over 4	Over 12	All	All	10	$\frac{3}{8}$	75	3	Yes

Table 11 Lining materials for low-carbon steel tanks for hard chromium plating

Tank length		**Lining material**					
		Lead alloy[(a)]		**PVC**[(b)]		**Brick**[(c)]	
m	**ft**	**kg/m^2**	**lb/ft^2**	**mm**	**in.**	**mm**	**in.**

Up to 2	Up to 6	40	8	5[d]	$\frac{3}{16}$ [d]	100	4
2-4	6-12	50	10	5[d]	$\frac{3}{16}$ [d]	100	4
Over 4	Over 12	60	12	5[d]	$\frac{3}{16}$ [d]	100	4

(a) Antimonial lead, or lead-tin alloy.

(b) Plasticized polyvinyl chloride.

(c) Acid-resistant brick. For further protection, brick may be backed up with 39 kg/m^2 (8 lb/ft^2) of antimonial lead or lead-tin alloy, or with plasticized polyvinyl chloride sheet.

(d) Lining should be 10 mm ($\frac{3}{8}$ in.) thick at top to 0.3 m (1 ft) below top of tank.

Heating and Cooling. Steam heating coils and cooling coils can be made of antimonial lead or silver-bearing lead. Titanium coils are preferred for conventional and fluoride-free plating solutions because of their relatively low cost and long life. Tantalum or niobium-clad coils should be used for mixed-catalyst solutions due to the fluoride attack on titanium. These coils are mounted on tank walls behind the anodes. Steel pipes carrying steam and cooling water to the tank must have a nonconducting section in each leg, so that the coils cannot become an electrical ground back through the power plant system.

Electric immersion heaters sheathed in fused quartz are suitable for heating chromic acid solutions. The quartz is fragile and must be handled with care. Similar immersion heaters are sheathed in either tantalum, titanium, or lead alloy. It is sometimes feasible to heat and cool a chromic acid solution by piping the liquid to a tube bundle, concentric, or tube heat exchanger located outside the plating tank. Preferably, heat exchanger tubes should be made of tantalum or titanium. This method has the disadvantage of requiring pumping of the solution.

Temperature-control planning should begin with selection of the volume of solution required in the plating solution. An ideal volume consists of 1 L or more of solution for each 13 W of plating power (1 gal or more of solution for each 50 W of plating power). About 60% of this plating power (30 W) produces heat and maintains the solution at temperature in an uninsulated tank of standard design. Power applications in excess of 13 W/L (50 W/gal) require cooling of the plating solution and cause relatively rapid changes in solution composition.

Agitation. A chromium-plating solution should be agitated periodically, particularly when the solution is being started, to prevent temperature stratification. Air agitation is effective, but oil from an air pump must not be permitted to leak into the air system. Preferably, the air should come from an oil-free low-pressure blower. A perforated pipe of rigid polyvinyl chloride may be used to distribute air in the solution.

Busbars. Anode and cathode busbars are usually made of round or rectangular copper bar stock. These rods should be adequately supported to prevent them from sagging under the weight of anodes and work. Generally, selection of bar size is determined by allowing 1 cm^2 of cross-sectional area for each 150 A (1 in^2 of cross-sectional area for each 1000 A), although mechanical strength for load support is also a factor in determining rod size. Anode and cathode rods are supported above the tank rim by insulators, which may be made of brick, porcelain, or plastic. Even metallic supports can be used if a strip of electrical insulating material is placed between the plating tank and the busbar.

Power Sources. Although dynamos or motor-generator sets were once the usual sources of power for low-voltage direct current for plating, rectifiers are now regularly used. In general, use of motor-generator sets is now restricted to larger and more permanent installations. Originally, plating rectifiers were made of copper oxide or magnesium-copper sulfide, but these have been largely replaced by silicon rectifiers. Silicon is favored for plating rectifiers because of its high resistance to thermal overload and small space requirement. Hard chromium platers often start plating on a piece by sweeping up applied voltage and current from very low values to the high values used for plating. Because silicon-controlled rectifiers have high ripple at low output, the output should be filtered. Tap-switch controls, however, produce relatively low ripple over the entire output range.

A 6 V power source can be used for chromium plating, but it is generally desirable or necessary to operate with 9 to 12 V available. Chromium plating requires full-wave rectification with a three-phase input and full control, giving a ripple less than 5% and no current interruptions. If a rectifier becomes partially burned out, it may single phase to some degree, and this can cause dull or laminated, peeling deposits.

Fume Exhaust. A chromium-plating process produces a chromic acid mist, which is toxic. The maximum allowable concentration for 8 h continuous exposure is 0.1 mg of chromic acid mist per cubic meter of air. This concentration value is in accordance with recommendations by the American Conference of Governmental Industrial Hygienists. Because of the extreme toxicity of this mist, it is mandatory to provide adequate facilities for removing it. The minimum ventilation rate should be 60 m^3/min per square meter (200 ft^3/min per square foot) of solution surface area. (It should be noted that these regulations are presently under revision and are subject to changes.)

Generally, fumes are exhausted from a chromium plating tank by means of lateral exhaust vents along both long sides of the tank. For narrow tanks, up to 600 mm (24 in.) wide, a lateral exhaust on one side of the tank should be adequate unless strong cross-drafts exist. Velocity of the air at the lateral exhaust hood slots should be 600 m/min (2000 ft/min) or more.

In the design of ductwork, condensate duct traps should be included to capture chromic acid solution. Drains from these traps should be directed to a special container and not to the sewer. In this way, chromic acid solutions can be returned to the tank or recovery system or be safely destroyed. A fume scrubber or a demister should also be included in the system to remove most of the chromic acid fumes before exhausted air is emitted to the atmosphere. Many communities have air pollution regulations requiring fume scrubbers. Fume exhaust ductwork may be made of carbon steel and coated with acid-resistant paint. Modern construction uses chlorinated polyvinyl chloride.

Rinse Facilities. Rinsing the work after chromium plating prevents it from becoming stained or discolored. Insufficient rinsing can result in contamination of cleaning solutions during subsequent cycling of racks. Multiple rinsing facilities are recommended. After being plated, parts should be rinsed in a nonrunning reclaim tank, which can be used to recover part of the chromium solution dragout. After they are rinsed in the reclaim tank, plated parts should be rinsed in counterflowing cold water and hot water tanks. Water should cascade from the hot water tank to the cold water tank. A multiple counterflowing arrangement requires much less water than two separate rinsing tanks.

If rinse water is being returned to a chromic acid waste disposal unit, the flow of water into the hot water tank should be controlled automatically by a conductivity-sensing element in the cold water tank. At a predetermined concentration of chromic acid in the cold water, the water inlet to the hot water tank should flow, causing an overflow of cold water to the waste disposal unit. This arrangement decreases the amount of water consumed and minimizes the required capacity of the waste disposal unit.

Cold water rinse tanks may be coated, sprayed, or otherwise lined with plasticized polyvinyl chloride. Hot water rinse tanks may be constructed of types 347, 304, or 316 stainless steel, or they may be made of carbon steel and lined with lead. Reinforced polyester glass fiber also may be used for either hot water or cold water rinse tanks.

Spray rinsing also effectively removes residual chromic acid. Because spraying does not always reach recessed areas, sprays should be positioned above a dip rinse. As parts are removed from the dip rinse, they may be sprayed with clean water, which, in turn, is returned to the dip tank.

Maintenance. Following is a maintenance schedule for a still tank installation for hard chromium plating:

- *Daily:* Check temperature. Check concentration of solution by density measurements. Clean busbars and electrical connections. Remove any parts that fall from racks.

- *Weekly:* Analyze for chromic acid and sulfate contents.
- *Monthly:* Remove all sludge and parts from tank, using a hoe and dragging the bottom. If tank is used for plating inside diameters, analyze for trivalent chromium.
- *Semiannually:* Check tanks for leaks and condition of lining. Clean and inspect rectifiers or motor-generating units. Check ammeter calibration.
- *As necessary:* Analyze for trivalent chromium, iron, nickel, copper, and zinc. Check condition of anodes.

This schedule is intended only as a guide; local conditions determine exact requirements. The rate of variation of solution constituents depends on the volume of solution, the method of operation for the solution, and the type and amount of work.

Racks and Fixtures

The following recommendations are offered regarding the design and use of plating racks:

- Racks should be designed to hold workpieces in a favorable position for plating uniformly on significant surfaces and to facilitate racking and unracking.
- Workpieces with protruding sections should be racked so that parts shield each other. If this is not possible, a current thief should be used to reduce current density at the protruding points.
- Electrical contact with the part should be made on an insignificant surface.
- The contact or rack tip should be rigid enough to hold workpieces securely and maintain positive contact. When the work is heavy enough to ensure positive contact, a hook often suffices.
- To minimize solution losses due to dragout, the work should be hung as nearly vertical as possible, with the lower edge of the work tilted from the horizontal to permit runoff at a corner rather than a whole edge. When recessed areas cannot be racked to allow proper runoff, provision should be made for drain holes or perhaps tilting of the rack when it is being withdrawn from the solution.

Although the design of racks and the methods of racking vary greatly, two basic types of racks are generally used. The first type consists of a single high-conductivity bar on which suitable supports have been mounted for holding the work to be plated; this rack is the cathode side of the plating circuit. The second type consists of two elements, the cathode and the anode; the work is held by the cathode and the cathode is attached to, but insulated from, the anode. Both types of racks are illustrated in Fig. 2. To prevent deposition of chromium or attack by the plating solution on parts of the rack that are immersed in the solution, these parts are covered with nonconducting material such as water-resistant tape, special insulating lacquer, or plastisol coatings.

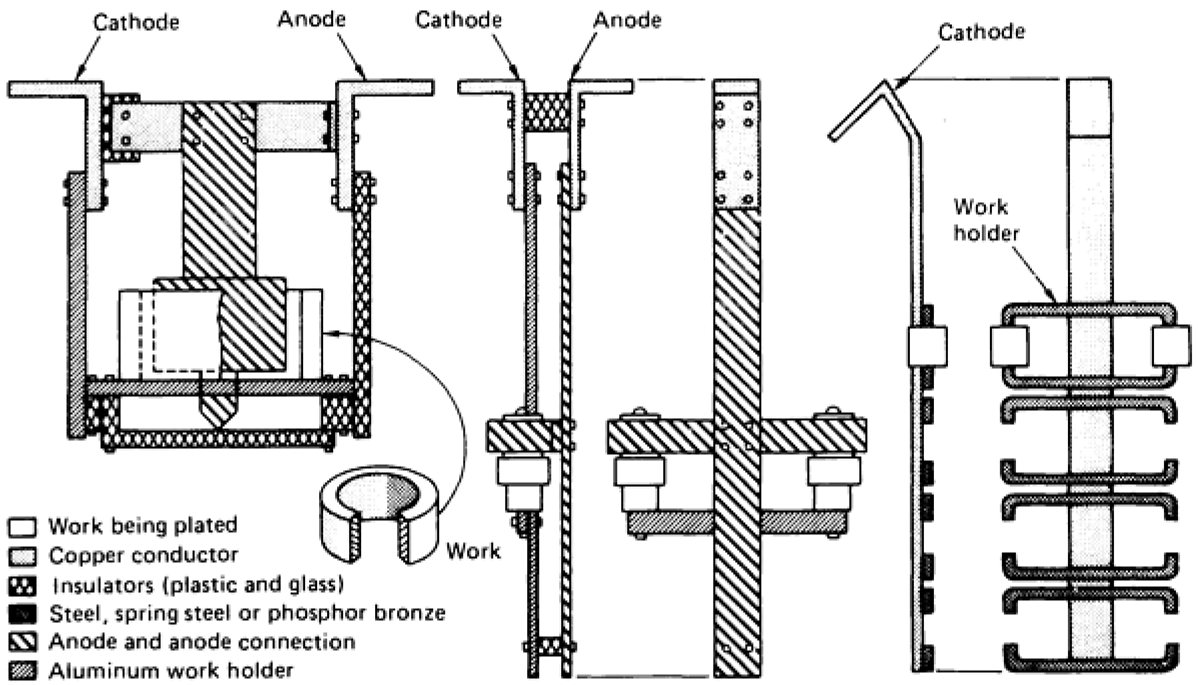


Fig. 2 Racks used in hard chromium plating

Surface Preparation

All soils and passive films must be removed from surfaces of ferrous and nonferrous metals before they are hard chromium plated. In addition to cleaning, certain surface-activating processes are often important in preparing the base metal for hard chromium plating. The processes include etching of steel, preplate machining, and nonferrous metals preparation.

Etching of steel before plating is needed to ensure adherence of the chromium deposit. Anodic etching is preferred for this purpose. Slight etching by acid immersion may be used for highly finished surfaces, but with possible sacrifice of maximum adherence.

Steel can be etched anodically in the chromium plating solution at its operating temperature for plating. A reversing switch is used so that the steel to be plated can serve as the anode for 10 s to 1 min (usually 30 s to 1 min) at a current density of about 15 to 45 A/dm^2 (1 to 3 A/in^2). Tank voltage should ordinarily be 4 to 6 V. Because mixed-catalyst solutions chemically attack the steel, causing etching of the surface, shorter electrochemical etching time frequently is required than is the case with conventional or fluoride-free chemistries. This process has the disadvantage of causing the solution to become contaminated with iron from the work and with copper from the conductors.

As an alternative, steel may be anodically etched in a separate chromic acid solution without sulfate additions and containing 120 to 450 g/L (16 to 60 oz/gal) of chromic acid. Solution temperature may range from room temperature to that of the chromic acid plating solution, or even higher, provided that current density and time of treatment are adjusted to suit the type of work being processed.

A sulfuric acid solution (specific gravity 1.53 to 1.71) may be used for anodic etching, provided that the solution temperature is held below 30 °C (86 °F), and preferably below 25 °C (77 °F). The time of treatment may vary from 30 to 60 s and the current density may vary from about 15 to 45 A/dm^2 (1 to 3 A/in^2) at tank voltages ordinarily between 4 and 6 V. A lead-lined tank with lead cathodes should be used. With the use of a sulfuric acid solution, however, two difficulties may be encountered. First, if the rinsing following etching is incomplete, the drag-in of sulfuric acid throws the chromium plating solution out of balance with respect to the ratio of chromic acid to sulfate. Second, in handling parts that are difficult to manipulate, there is danger that surfaces exposed to air more than a very short time will rust and that finely finished surfaces will be overetched.

For high-carbon steel, a sulfuric acid solution of 250 to 1000 g/L (33 to 133 oz/gal), used at a temperature of not more than 30 °C (86 °F) and preferably below 25 °C (77 °F), is effective for anodic etching. The addition of 125 g/L (16.6 oz/gal) of sodium sulfate, based on the anhydrous salt, is of benefit for many grades of steel. Anodic treatment in this solution usually does not exceed 1 min at a current density of about 15 A/dm^2 (1 A/in^2) (range of 15 to 45 A/dm^2, or 1 to 3 A/in^2). High acid content, high current density, and low temperature (within the ranges specified) minimize the attack on the base metal and produce a smoother surface. This sulfuric acid solution is stable and not appreciably affected by iron buildup.

Preplate Machining. Metal debris on the surface should be removed before etching (an activation procedure). The use of abrasive-coated papers is common, as is the use of successively finer grit stones in honing and grinding. To prepare a sound surface in superfinishing, 600-grit stones may be used. Electropolishing is sometimes used to remove highly stressed metal and metal debris from the surface of cold-worked steel. This process improves bond strength and corrosion resistance of electroplated coatings. It accomplishes this function without formation of smut, which may result from anodic etching. This treatment is not recommended for parts that are subjected to critical fatigue stresses and that are expensive to manufacture.

Preparation of Nonferrous Metals. Aluminum, in common with certain other metals, quickly develops a natural, passive oxide film after exposure to preplating cleaning cycles. This film must be removed before aluminum is plated. The most widely used method of preparing aluminum for plating involves a zincating treatment, which may be followed by a thin 5 μm (0.2 mil) copper electrodeposit. However, it is possible to plate chromium directly over the zincate.

Aluminum parts used in hydraulic systems require a nickel undercoat before being plated, to provide corrosion protection to all plated surfaces that are not completely and constantly immersed in hydraulic fluid or similarly protective fluids. A minimum thickness of 10 to 15 μm (0.4 to 0.6 mil) of nickel is usually specified. This undercoat may also be required for steel parts in similar applications.

Titanium and titanium alloys, as well as magnesium, also form a tight, stable oxide coating and are therefore difficult to plate. These metals can be pretreated with an electroless nickel plate or a coating deposited from a high-chloride nickel strike solution.

Variations in Plate Thickness

Variations in the thickness of hard chromium plate depend primarily on the potential field distribution. Potential field is controlled by the placement of anodes, shields, thieves, and other parts, as well as the relative position of the sides and surface of the tank. Variations in plate thickness also depend on surface preparation, control of solution conditions, and uniformity of the power source.

Methods of Measuring Plate Thickness. Several methods and types of instruments are available for determining the thickness of plate. These include electrolytic stripping, microscopic measurements of cross sections, torsion dynamometer measurements made with magnets of various strengths, measurement by eddy current instruments, and accurate measurement of the dimensions of the part before and after plating to determine thickness by difference.

Electrolytic stripping and microscopic measurements of cross sections are destructive methods that are most frequently used for purposes of verification, calibration, and sampling of production runs. When calibrating instruments with prototype plated parts, using microscopic measurements of cross sections as umpire checks, several calibration reference curves may be required, depending on the parts being plated.

Measurements by properly calibrated eddy current or torsion dynamometer instruments are affected by the surface finish of the deposit, width and thickness of the piece, surface contour, and composition of the base material. With a properly calibrated instrument, thickness measurements are usually within 10% of the actual thickness. Individual thickness measurements should not be used as the basis for acceptance or rejection; however, an average of several determinations from a well-calibrated instrument is an acceptable measure of the mean thickness from a controlled process.

The normal variation in plate thickness that can be expected when plating the outside diameter of cylinders, rods, or round parts racked as cylinders is ±0.2μm/μm (±0.2 mil/mil) of plate intended. This has been determined over a period of several years by average quality level thickness measurements on piston rings racked as cylinders.

This normal variation of 20% was confirmed in an actual production situation. In plating identical parts to a consistent thickness requirement, sample checks from 74 loads (110,000 parts) representing 27 days of operation were made to determine the plating tolerances that could be expected. The plating cycle was set to provide a plate thickness of 200 to 230 μm (8 to 9 mils) to meet a final requirement for a minimum plate thickness of 150 μm (6 mils) after light stock removal during the subsequent finishing operation. Results of this analysis are shown in Fig. 3.

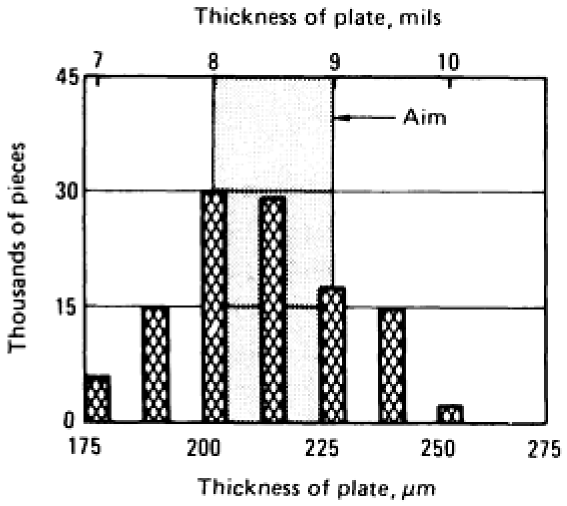


Fig. 3 Variations in hard chromium plate thickness for 74 loads, representing 110,000 parts of the same design plated over a period of 27 days of operation. Target thickness was 200 to 230 μm (8 to 9 mils) of hard chromium. Average thickness for the 74 loads was 215 μm (8.4 mils).

The throwing power of chromium-plating solutions is related to the ratio of chromic acid concentration to the catalyst concentration. Higher ratios give better throwing power at a given temperature and current density. This is evidenced by the fact that when a very low current density is present on certain areas of irregularly shaped parts, the cathode efficiency at that low current density is less for a solution high in sulfate than for a solution with lower sulfate content. Therefore, less metal is deposited on the areas of low current density from a solution of high catalyst content.

The current density at which no metal deposits is greater for high catalyst solutions than for lower catalyst solutions. Also, metal deposits from a solution of low catalyst concentration at a current density that would be too low for depositing from a solution with high catalyst concentration. Thus, the following factors must be considered to ensure successful plating of complex shapes: chemical balance, operating variables, type of anode, and design of fixtures or racks.

Chromium plating requires far more attention to the variables that affect current distribution than cadmium, zinc, copper, or nickel plating. It is theoretically impossible to obtain the same current density at an inside corner as on the flat adjacent to it. An outside corner without shielding or thieving always has the highest current density and hence the greatest plate thickness. Conforming anodes, shields, and thieves may be used to minimize thickness variation, but except on the simplest shapes, they do not eliminate it.

Some metal is deposited at low current densities in most other plating solutions, but in chromic acid solutions there is a minimum current density for a given solution at a given temperature below which no metal is deposited. If an area of an internal or irregular shape receives less than this minimum current density, no deposition of metal occurs in this area. This explains why it is so difficult to chromium plate recesses and internal shapes without special anodes. Special hardware, in the form of thieves or shields, is required for lowering the current density on areas such as edges to prevent excessive buildup of deposit.

In most electroplating solutions, the primary current distribution on an irregular object can be improved by increasing the tank anode-to-cathode distance. However, beyond a minimum distance, which depends on the shape of the part, no further improvement can be attained.

Because of the low throwing power of hard chromium plating solutions, an increase in the anode-to-cathode distance does not result in even plating of sharp reentrant surfaces such as those formed by internal angles. For plating parts containing shapes of this type, conforming anodes and/or current shields must be used.

Figure 4 illustrates the relation between thickness of deposit and distance of the anode from the part being plated. In this instance, an alternative to an increase in the anode distance is the use of an anode contoured to the curvature of the part.

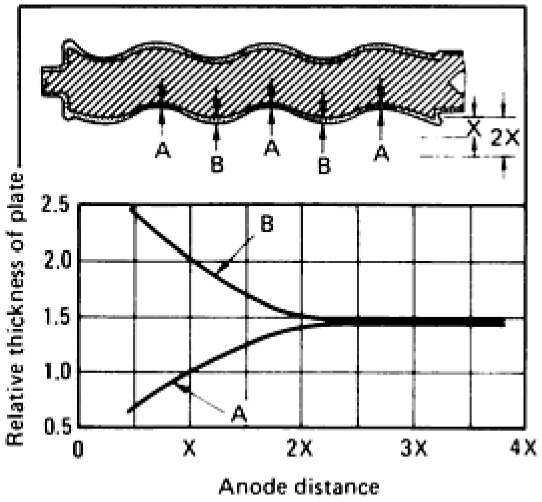


Fig. 4 Variation in thickness of chromium plate on feedworm as a function of the distance of the anode from the part. Values of *x* are about 25 mm (1 in.) or more.

Special Anodes. When the part contains sharp, narrow recesses, such as grooves, a reduction of the anode distance may help to increase the thickness of the deposit at the bottom of the grooves. However, some parts with sharp-cornered grooves, bosses, and undercuts cannot be uniformly covered even when contoured anodes are used. Examples of parts in this category and the areas of heavy deposits are illustrated in Fig. 5.

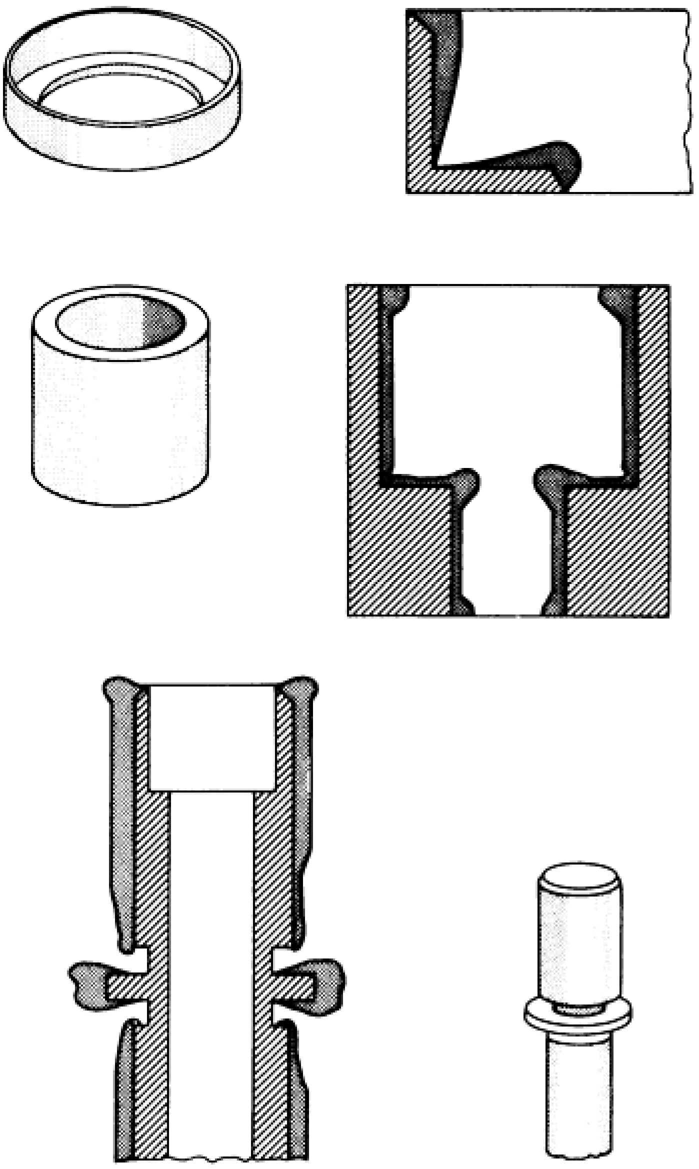


Fig. 5 Parts difficult to plate uniformly with hard chromium, even with the use of specially contoured anodes. Variations in plate thickness shown are approximately to scale.

Anodes used for plating recesses can be directly connected to the power supply, or they can be bipolar in nature. The bipolar anode has no direct electrical connection and takes advantage of the fact that current follows the path of least resistance. Bipolar anodes are an interesting curiosity that may have application in rare instances; however, direct connection of the anode to the positive direct current through a rheostat and ammeter, if required, is far more controllable.

The deposit on internal shapes can also be affected by the evolution of gas that occurs during plating. Gas can cause streaked deposits or produce a taper in a long bore. To minimize this effect, the parts should be positioned in a manner that permits the gas to move rapidly away from the part.

Because of fabrication problems encountered with lead alloys, complex-shaped anodes are made of steel, then coated with lead to produce the effect of solid lead anodes. These composite anodes are more economical and lighter in weight. However, the base metal can be destroyed if there are pores or throughholes in the lead alloy coatings. Brass or copper should never be used on the anode side, as they dissolve rapidly and seriously contaminate the solution. Low-carbon steel may be used alone for short runs, and lead-coated steel may be used for longer service.

Crack Patterns and Other Characteristics of Hard Chromium Plate

The quality of hard chromium plate is evaluated chiefly from the standpoint of thickness and thickness distribution, appearance, crack pattern, crack size, porosity, roughness, and adhesion of the plate to the base metal.

Surface Cracks. During the deposition of chromium deposits, microcracks form to relieve the internal stress. These cracks subsequently fill in with plated chromium. The chromium in these former cracks is more easily etched and has a different refractive index than the surrounding deposits. For this reason, with the use of a microscope one can determine where and how many microcracks were present at one time on the surface of the deposit. The pattern usually consists of crack-free areas and plateaus completely surrounded by crack boundaries. The plateaus from an average conventional sulfate solution are 2 to 3 times larger than those from a mixed-catalyst solution; that is, there are more cracks per inch in a deposit from the average mixed-catalyst solution. The fluoride-free chemistry gives yet an additional factor of 2 to 3 times more microcracks.

Interestingly, the more microcracks present, the shorter the penetration into the deposit of each one (i.e., with the conventional solution, a microcrack can extend all the way through a 1 mil thick deposit, while in the fluoride-free solution deposit they extend very short distances). Since these (former) cracks provide the pathway for corrosion, it is desirable to have as many discontinuities as possible as one progresses through the deposit to the substrate. It is for this reason that in corrosion applications, the solution that provides the greatest amount of microcracking possible is used.

Crack-Free Deposits. It is possible to plate chromium with virtually no microcracks. This is done by altering the current density and temperature, altering the catalyst concentrations, or using pulsed-current or periodic-reverse plating. Crack-free deposits are gray and have very poor wear properties. The corrosion resistance is also very poor due to residual stresses in the deposit, which eventually (in a few days or months) cause large cracks that extend through the entire deposit.

Some specialized applications for this type of deposit include broaches, cams, dies for metal forming, metalworking rolls, and stamping dies for embossing silverware. Complicated shapes create a large range of current densities and are difficult to plate with a crack-free surface. Corners, edges, or other high-current-density areas are most likely to crack during plating.

Porous Chromium. Although the cracks or porosity that characterize chromium deposits are not desirable for resistance to corrosion, a porous structure can be advantageous in wear applications in which lubrication is required, because it promotes wetting action and provides oil retention after initial lubrication. Engine cylinders are the outstanding application.

Most chromium-plated cylinder surfaces consist of some form of interrupted surface, generally porous chromium. An interrupted surface may be obtained by electrolytic or chemical etching of chromium after it is plated on a smoothly honed bore, as with porous chromium, or by preroughening the bore by shot blasting, knurling, or tooling and then reproducing this roughness in the final chromium plate or by machining in roughness after plating.

Two distinct types of porous chromium are produced. One has pinpoint porosity with many microscopic depressions in a honed chromium surface. This has been used in all types of engine cylinders except aircraft. The other type is also finish honed but is broken by randomly connected channels, leaving isolated bearing plateaus. For both types, the percentage of porosity is generally controlled between 20 and 50% of the total area. Average plateau diameter is further controlled between 0.25 to 0.75 mm (0.010 to 0.030 in.) with the channel type of porosity. Porosity as low as 5% approaches dense chromium and is susceptible to scoring because of sparse oil distribution. High porosity, such as 75%, may cause high initial ring wear and high oil consumption. In normal engine service, cylinders coated with chromium of optimum porosity give wear rates one-third to one-tenth better than those of uncoated cast iron or steel, hardened or unhardened.

Several methods--electrochemical, mechanical, and combinations of both--have been developed to provide controlled porosity in heavy chromium deposits. Mechanical methods entail either severe grit blasting of the surface to be plated or roughening of the surface with a fine knurling tool. The roughened surface is reproduced by the deposit. Using a patterned mask, the surface can also be roughened by chemical or electrochemical means before plating The most widely used techniques, however, involve chemical or electrochemical etching of the chromium deposit after plating. Note that the pattern or crack density and the size of the plateaus are largely determined by the composition (ratio) of the solution, and the plating temperature.

Etching is performed on plated thicknesses ranging from 120 to 180 μm (5 to 7 mils). Porosity is developed after plating by electrochemically etching anodically in chromic acid solution. The etched surface is finished by honing, polishing, or

lapping. Metal removal that exceeds the depth of porosity must be avoided. To avoid accelerated wear in service, finished surfaces must be thoroughly cleaned of abrasive and chromium particles.

Quality Control Tests. Usually, visual examination is sufficient for determining appearances and roughness of the surface of hard chromium plate. Magnetic particle inspection can be used to examine chromium plate up to 100 μm (4 mils) thick for cracks after grinding. The as-plated deposit prior to postfinishing should be as smooth as the base metal before plating and should be free of pits and nodules. The deposit should not exhibit excessive thickness variation. Particularly, deposits with dendritic growths (trees) should be rejected. Adequate plating control requires that such dendritic deposits occur on thieves rather than in functional areas.

For process development and quality verification, destructive testing may be used to determine the crack pattern and bond between the plate and base metal. The crack pattern can be developed by etchants such as a hot 50 vol% hydrochloric acid aqueous solution, or by short etching in a chromium plating solution.

The quality of the bond can be determined by punch testing, bend testing, examining the bond line metallographically, or judging of ground or hammered samples. Well-bonded chromium, because of its low ductility, does not fail by pulling away from the bond line; however, it fails by cracking and spalling if it is subjected to excessive stress or distortion in 45° diagonal tension.

Excessive porosity of thin (less than 25 μm, or 1 mil, thick) chromium plate on steel can be determined by applying an acidified copper sulfate solution to the plated areas. The pores permit the solution to copper coat steel by displacement, and the degree of copper coating thus indicates the degree of porosity. Porosity can also be determined by the ferroxyl test described in *Metal Finishing Guidebook,* 1982.

The mandrel test can also be used in quality control. If a portion of the chromium plate is made anodic for 3 min at 15 A/dm^2 (1 A/in^2) in a solution containing 250 g/L (33 oz/gal) chromic acid at 60 °C (140 °F), the crack pattern is developed. Counting the crack density under the microscope is an excellent procedure for noting the constancy of the composition (mainly ratio) and the temperature of the solution.

Hardness of Plate

Valid hardness measurements of chromium deposits are difficult to make, and values are dependent on test conditions, so hardness values should not ordinarily be used as quality control specifications and routine criteria. Rather, the as-plated brightness can serve as an indication of hardness.

The hardness of chromium plate cannot be accurately determined by the common hardness testers, such as Brinell and Rockwell, because hard chrome is generally too thin for these tests. The indentation produced in these tests distorts the base metal and is influenced by it, which usually results in low hardness readings.

The most reliable and most widely accepted hardness values are those obtained with the Vickers 136 diamond pyramid indenter or the Knoop indenter. With these, the hardness test must be made on a carefully prepared and polished surface, preferably on a cross section of the plate, to eliminate any possible influence of the base metal on the hardness values obtained.

Cracks in the chromium plate influence the hardness values, depending on the type of indenter used and the load applied. In general, lighter loads are more sensitive to hardness variations and result in higher hardness values. Cracks influence values obtained with heavy loads more than values obtained with light loads. Also, because of the smaller area covered by the Vickers 136 diamond pyramid indenter, hardness values determined with this indenter are influenced less by underlying cracks than values obtained with the Knoop indenter.

When conducting microhardness tests, it is important to make sharp and accurate impressions, particularly when using light loads. Also, when hardness values are reported, the load, type of indenter, and optical system used should be indicated. The importance of stating the load and type of indenter is shown by the following data obtained on chromium plate from one plating cycle (each range or average represents 25 tests):

Load, g	Hardness value	
	136° diamond pyramid	Knoop indenter
100	950-1110 (1040 avg)	940-1090 (1025 avg)

In an investigation of the scratch hardness of chromium deposits of all types, it was observed that bright or semibright deposits had the best combination of hardness and wear resistance, regardless of plating conditions. In this investigation, the wear resistance was measured by means of a specially constructed abrasion hardness machine. The machine contained a small grinding wheel that revolved at 18 rpm. The number of revolutions required to grind through a 25 μm (1 mil) deposit on steel was an indication of the abrasion hardness. Results are summarized in Table 12, which shows the relation between the appearance of deposits and their hardness and resistance to abrasive wear.

Table 12 Relation between appearance and hardness of hard chromium plate deposited from conventional solutions

Average appearance	Average scratch hardness[(a)], HB	Average relative abrasive hardness
Matte (cold bath)	640	25
Milky	830	100
Slightly milky	990	290
Bright	1000	300
Slighty frosty	1005	300
Frosty (smooth)	1020	235
Frosty (rough)	1060	125
Burnt	1165	110

(a) Converted to Brinell scale from values obtained with a Bierbaum microcharacter using a 9 g (0.3 oz) load

The effect of temperature on the hardness of electrodeposited chromium is often a significant factor in applications involving wear resistance. The electrodeposited metal begins to decrease in hardness when it is exposed to temperatures above about 205 °C (400 °F). Hardness decreases progressively with an increase in temperature (Fig. 6). As the hardness of chromium plate decreases, its resistance to wear may be affected adversely. Chromium plate should not be used for wear resistance in applications where service temperature exceeds 420 °C (790 °F).

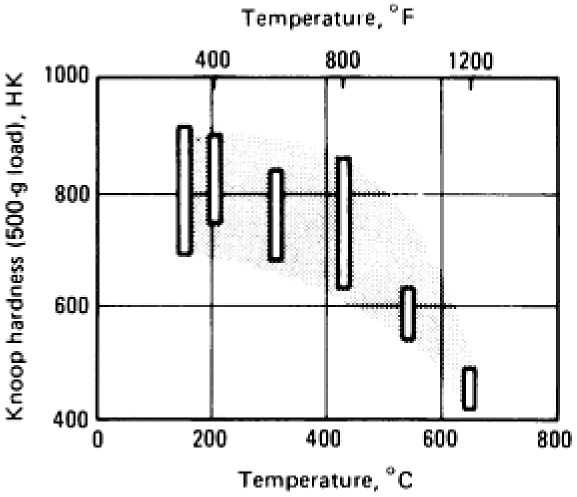


Fig. 6 Effect of annealing temperature on the hardness of chromium plate deposited during a single cycle in a mixed-catalyst solution. All data represent 25 measurements of each condition; every readable impression was accepted as valid. Heating cycles of 1 h were used.

Cost

The electroplating of hard chromium is very cost-effective, giving a high throughput with reliable, reproducible quality deposits that are unattainable by any alternative technology. The important cost factors are capital and labor expenses, followed by electricity, and, lastly, chemicals, which are relatively inexpensive. Almost always the fluoride-free solution is the least expensive chemistry to operate, followed by mixed-catalyst and then conventional sulfate solutions. Although the chemical costs increase going from conventional to mixed-catalyst to fluoride-free solutions, this increase is offset by savings in electrical costs, capacity improvements, and deposit quality improvements.

Factors that affect the relative cost of plating, regardless of the solution used, include the shape of the part, the design and arrangement of anodes, and special finishing techniques. Labor charges for hard chromium plating may be higher than for other plating processes, largely because many chromium plating operations are performed manually. Also, more labor is required to prepare some parts for plating or for finishing after plating.

The cost of plating increases with the complexity of the part design. Parts containing sharp notches, section changes, and unplated areas of cross-holes necessitate more handling during preparation and finishing than parts of simple shape. Also, anodes must more precisely conform to the shape of such parts for accurate control of plating thickness. Defects associated with chrome plate, such as dendritic growths and excessive buildups on external corners, can be minimized with tooling and special techniques. Depending on the nature of the part, these may increase costs. Special finishing techniques, primarily grinding and lapping, are required. Often a heat treatment of plated parts is necessary before they are ground or lapped.

For surfaces that are difficult to finish mechanically, even greater care must be taken in design and construction of anodes to approximate desired results closely. The cost of anode design and construction must be amortized over the number of parts plated. If sufficient production is required, refinement of masking and anodizing generally pays with decreased postplate finishing. Costs are affected also by the quality of the plate. Hard, high-quality plating finished to a bright luster is very expensive because of the rigid controls required in its production. As with other plating processes, costs vary because of local utility charges and ordinances pertaining to disposal of wastes. The availability of power and water, and the quality of the water available, can significantly affect cost. Safety requirements and waste disposal methods can be responsible for at least a 20% difference in plating costs among different plants.

Removal of Chromium Plate

Most manufacturers require salvage of misplated parts because of their high value. Further, in the aircraft industry, business machine industry, and plastic mold industry, significant numbers of parts are run for the life of the deposit and then overhauled by stripping worn deposits and replating.

Methods of Stripping. Chemical, electrochemical, or mechanical methods are used to remove hard chromium deposits. When the base material is steel, brass, copper, or nickel, hydrochloric acid at any concentration over 10 vol% and at room temperature or above removes chromium. In some operations, inhibitors are added to the acid solution to minimize attack on the steel substrate.

Chromium is removed electrochemically from steel or nickel by the use of any convenient heavy-duty alkaline cleaner at room temperature or above, at 5 to 6 V with anodic current. This method is unsatisfactory for nickel-base alloys, which should be stripped chemically in hydrochloric acid. Chromium may be stripped from aluminum by making the part the anode in a cold chromium (nonfluoride) plating solution or in conventional chromic acid or sulfuric acid anodizing solutions. Aluminum alloys with a high alloy content and alloys subjected to various heat treatments all react differently in stripping solutions, so precautions must be taken to prevent attack on the base metal. Anodic stripping operations result in formation of oxide films on the base metal. These films should be removed by one of the conventional deoxidizing processes prior to replating.

Stripping of chromium deposits from high-strength steel must be performed electrochemically in an alkaline solution. The parts are then stress relieved at 190 °C (375 °F) for a minimum of 3 h. The following solutions and operating conditions are recommended for removing chromium deposits from the materials indicated. Proprietary formulations having a longer operational life are also available.

Removal from steel or nickel-plated steel

- Sodium hydroxide, 45 to 320 g/L (6 to 30 oz/gal); anodic treatment at 3 to 8 A/dm^2) (0.2 to 0.5 A/in^2); solution temperature, 21 to 71 °C (70 to 160 °F)
- Anhydrous sodium carbonate, 45 to 60 g/L (6 to 8 oz/gal); anodic treatment at 2.5 to 5.5 A/dm^2 (0.15 to 0.35 A/in^2); solution temperature, 21 to 66 °C (70 to 150 °F). Use 2.3 A/dm^2 (0.15 A/in^2) with solution temperature of 66 °C (150 °F) to reduce possibility of pitting alloy steel.
- Sodium hydroxide, 52 g/L (7 oz/gal); sodium carbonate, 30 g/L (4 oz/gal); anodic treatment at 8 A/dm^2 (0.5 $A/in.^2$)
- Concentrated hydrochloric acid at room temperature
- Hydrochloric acid, 50 vol%, at room temperature

Removal from aluminum and aluminum alloys

- Sulfuric acid, 67 vol%; glycerin, 5 vol%; anodic treatment at 1 to 3 A/dm^2 (0.1 to 0.2 A/in^2); solution temperature, 21 to 27 °C (70 to 80 °F)

Removal from magnesium and magnesium alloys

- Anhydrous sodium carbonate, 50 g/L (6.5 oz/gal); anodic treatment at 2 to 5 A/dm^2 (0.15 to 0.30 A/in^2); solution temperature, 21 to 27 °C (70 to 80 °F)

Grinding is used occasionally to remove heavy chromium deposits. Most defective chromium deposits are observed during subsequent grinding for finishing, so it is sometimes expedient to continue grinding to remove all of the plate and then replate. In the grinding of heavy deposits for the removal of several thousandths of an inch of chromium to attain required dimensions or surface finish, the most important requisites for successful results are:

- A soft grinding wheel
- A sufficient amount of coolant
- A light cut
- Correct peripheral speed
- Freedom from vibration
- Frequent wheel dressing

Because chromium is hard and brittle, a soft grinding wheel is essential. A hard wheel forms a glazed surface, which results in a temperature rise that causes the chromium to crack. A soft wheel breaks down rapidly enough to prevent formation of a glaze; however, too soft a wheel is not economical because of rapid wheel wear. Good performance can be obtained with an aluminum oxide resin-bonded wheel of about 60 grit and H-grade (hardness).

To prevent or minimize glazing, the contact area should be flooded with a coolant. Usually, the coolant is water with a small amount of soluble oil. Because of its hardness, excess chromium cannot be removed as rapidly as when grinding most other materials. The maximum thickness of metal removed should not exceed 5 μm (0.2 mil) per pass, and this amount should be reduced if there is any evidence of cracking. The optimum grinding speed is about 20.4 m/s (4000 sfm).

Effective grinding requires a rigid machine. Any appreciable vibration can cause cracking of chromium because of uneven contact pressure, and it also results in a wavy surface. Factors essential for a rigid machine include a well-fitting spindle bearing, a balanced wheel, a heavy bed, and a well-supported workpiece. Whenever there is the least indication of glazing or nonuniform wheel surface, the wheel should be dressed with a diamond point. Adherence to the preceding recommendations will result in a good surface with a finish of 0.35 to 0.5 μm (14 to 20 μin.). Subsequent lapping (240 grit) will produce a finish of 0.1 to 0.3 μm (5 to 10 μin.).

Special care should be taken when grinding chromium-plated parts made from high-strength steel (steel with an ultimate tensile strength of 1240 MPa, or 180 ksi, and above) that are to be used in stressed applications. Numerous failures have occurred due to formation of untempered martensite caused by the heat of the grinding operation. For information and guidelines on grinding chromium-plated high-strength steel parts, see military specification MIL-STD-866B.

Hydrogen Embrittlement

The susceptibility of chromium-plated parts to hydrogen embrittlement is affected by hardening of the steel, grinding, surface defects, pickling, cathodic cleaning, and the depth of plate relative to the thickness and hardness of the part being plated. (It should be noted that the chemistry of the chromium plating solution is not a factor.) Unless the hydrogen absorbed during pickling and cathodic cleaning is removed, subsequent plating further embrittles the part to such an extent that breakage can occur during plating. This effect becomes more prevalent with increasing hardness of steel and on parts of thin cross section.

The thickness of plate on thin steel sections is of importance from the standpoint of notch effect. This was illustrated in an actual production setting. Thin sections of steel, 2.5 by 0.5 mm (0.10 by 0.020 in.) and 25 to 38 mm (1 to $1\frac{1}{2}$ in.) long, were plated with chromium to a thickness of 8 to 13 μm (0.3 to 0.5 mil). The hardness of the steel was 57 to 59 HRC. These parts were aligned by being bent until permanently set. When the thickness of the chromium plate was increased to range from 15 to 23 μm (0.6 to 0.9 mil), the parts would break before taking a set. Baking them at 205 °C (400 °F) for 4 days did not relieve this condition. It was necessary to decrease the hardness of the steel to 53 to 55 HRC to prevent breakage of parts with heavier plate.

Stress Relieving before Plating. Surfaces to be chromium plated must be free from stresses induced during machining, grinding, or hardening. Stresses from the hardening operation may be further increased during grinding and result in microcracks. If the hardness of the steel is less than 40 HRC, it is unlikely that any damaging effect will occur as a result of residual stress. Steel with a hardness exceeding 40 HRC should be stress relieved before it is plated by heating at 150 to 230 °C (300 to 450 °F).

Baking after Plating. Steel parts with a hardness above 40 HRC should be baked at a temperature of at least 190 °C (375 °F) for 4 h after plating to ameliorate the effects of hydrogen embrittlement. This treatment should be started as soon as possible, preferably within 15 min after plating. The fatigue strength of parts subjected to alternating stresses is reduced by the baking treatment, so such parts should be shot peened before plating.

The use of shot peening and baking, as related to the hardness of steel to be chromium plated, is described in federal specification QQ-C-320B, amendment 1, as follows:

- Plated parts below 40 HRC and subject to static loads or designed for limited life under dynamic loads, or combination thereof, shall not require shot peening prior to plating or baking after plating.
- Plated parts below 40 HRC that are designed for unlimited life under dynamic loads shall be shot

peened in accordance with military specification MIL-S-13165 before plating. Unless otherwise specified, the shot peening shall be accomplished on all surfaces for which the coating is required and on all immediately adjacent surfaces when they contain notched fillets, or other abrupt changes of section size where stresses will be concentrated.

- Plated parts with a hardness of 40 HRC, or above, and subject to static loads or designed for limited life under dynamic loads, or combinations thereof, shall be baked after plating at 190 ± 14 °C (375 ± 25 °F) for not less than 3 h.
- Plated parts with a hardness of 40 HRC, or above, and designed for unlimited life under dynamic loads, shall be shot peened in accordance with military specification MIL-S-13165 before plating. Unless otherwise specified, the shot peening shall be accomplished on all surfaces for which the coating is required and on all immediately adjacent surfaces when they contain notched fillets, or other abrupt changes of section size where stresses will be concentrated. After plating, parts shall be baked at 190 °C (375 °F) for not less than 3 h.

Safety Precautions

All applicable OSHA, EPA, and local regulations pertaining to electroplating in general and specifically to chromium plating should be carefully reviewed and strictly followed. Material Safety Data Sheet forms should always be available, and precautions should be carefully noted, especially with respect to the incapability of mixing certain chemicals.

Personnel should wear rubber gloves, rubber aprons, and face shields when making additions to any plating or cleaning solution. Tank operators should wear proper protective clothing and eye protection at all times.

Health and safety concerns related to the use of chromium and possible alternative plating technologies are discussed in the article "Chromium Elimination" in this Volume.

Recovery and Disposal of Wastes

Chromic acid wastes may be either recovered or destroyed, and the choice of process should be based on a comparison of initial costs, labor costs for operation and maintenance, chemical costs, space requirements, and utility costs. The volume of wastes and the value of the chromic acid and rinse water saved can greatly influence the choice.

Local, state, and federal authorities are constantly increasing their attention to antipollution programs. Strict regulations are being enforced regarding the allowable limits for chromic acid wastes that leave the plating plant in any form. The prevailing limits for chromic acid contamination of waste water range from about 0.05 to 5 ppm. These limits vary for each locality, depending on the uses of the receiving body of water, supplementary water flows that affect dilution, and the ability of sewage plants to handle wastes. A new plater must check with federal, state, and local authorities to determine what limits are applicable at that time.

Preventive Measures. The problem of waste disposal can be greatly minimized if suitable measures are taken to minimize the amount of wastes produced. The following practices contribute to minimizing wastes:

- Extend drainage periods to permit more solution to return to the tank. In hand operations, this is made possible by providing a drainage bar over the tank to hold racks.
- Provide drip boards to return solution lost when going from tank to tank.
- If possible, rack parts in such a way as to eliminate cupping action.
- Use reclaim rinse tanks. The rinse solution can be used to maintain the level of liquid in the processing tank. Sometimes concentration methods may be profitable to facilitate use of rinse waters.
- Control drag-in of water to permit use of reclaim rinse tanks.
- Complete recovery should be used only in conjunction with technologies for the removal of metallic impurities.

Disposal of chromic acid wastes is most commonly based on reduction of hexavalent chromium to the trivalent form and, in either a batch or a continuous operation, precipitating the trivalent metal hydroxide by means of an alkali. The

actual chemicals used vary from locality to locality, depending on cost and availability. Chromic acid is first neutralized to a suitable pH and is then reduced with one of the sulfite compounds (sodium sulfite, sodium metabisulfite), sulfur dioxide, ferrous sulfate, iron, copper, or brass. After completion of reduction, trivalent chromium is precipitated as hydroxide with alkali. The amount of chemicals required to complete reduction can be governed by laboratory analysis, or, because the reaction is solely one of oxidation-reduction, it may be controlled automatically by use of electrodes.

The most commonly used reducing agent for large plants is sulfur dioxide gas. It can be obtained in liquid form in cylinders of various sizes, is comparatively inexpensive, and can be fed directly into the treatment tank. The rate of addition is easily controlled and gas is delivered from the cylinder under its own pressure. A lower initial acidity is required because the gas forms sulfurous acid when dissolved in water. The operating pH is 2 to 3, and the ratio of sulfur dioxide to chromic acid used commercially is slightly under 3 to 1. The sulfur dioxide method lends itself readily to an automatic system because the gas feed can be controlled by a flowmeter, and the reaction can be controlled by oxidation-reduction potentials.

Ferrous sulfate also is a widely used reducing chemical, especially in localities where large quantities are available from pickling plants. The quantity required can be easily determined by titration. The ratio of ferrous sulfate to chromic acid varies between 5 and 16 to 1. Reduction of chromium is followed by neutralization with lime or caustic. Above a pH of 7, the metals precipitate as hydroxides, together with calcium sulfate. The main disadvantage of the ferrous sulfate method is the large volumes of sludge that have to be handled.

The sulfite-containing compounds generally are slightly more expensive than sulfur dioxide or ferrous sulfate. In addition, several difficulties are involved in sulfite treatment, such as solubility, loss of hydrogen sulfide through hydrolysis, slightly lower pH, and, occasionally, the need for additional treatment to complete the process.

Regardless of the chemical treatment selected, all chromic acid disposal systems require collection, treatment, and settling tanks. The operating procedure consists of chemical additions, mixing, separation of precipitated metal, clarification, and sludge disposal. Variations in equipment design affect economy, time and labor requirements, and equipment costs.

In recent years several new companies have been formed that recycle chromium plating wastes into new products, thereby avoiding the long-term potential liabilities of landfill operations. No matter what method of waste disposal is selected, the plater is well advised to know what happens to the wastes and what the liability could be.

Stopoff Media for Selective Plating

During plating, part surfaces that are not to be plated may need to be protected from the solution by stopoff media, such as lacquers, foils, tapes, waxes, and machined reusable fixtures. Stopoff media must adhere well to the metal surface, not become soft at the temperature of the solution or brittle at room temperatures, be resistant to solutions used for cleaning, etching, and plating, and be easy to remove after plating.

Lacquers used to prevent surfaces from being plated can be easily applied by brushing, spraying, or dipping. After plating, the lacquer can be stripped off or dissolved in an appropriate solvent.

Lead sheet, foil, and wire not only provide a positive stopoff but also act as thieves to aid in current distribution. Lead can be pounded into holes, keyways, or slots and trimmed with a sharp knife.

Tapes of several kinds are used as stopoff media. They vary from adhesive tapes backed with lead foil to tapes made of vinyl and other plastics. Lead foil tapes combine a specially compounded lead foil with a highly pressure-sensitive adhesive to provide a quick and convenient stopoff for short runs. The lead backing is useful as a thief in areas of high current density, or it can be lacquered when used in areas of low current density for equalizing current distribution. It is soft enough to conform to various configurations. Vinyl and other plastic tapes are soft and pliable and have extruded edges for providing a lead-free seal on almost any contour.

Sheet Materials. For large production runs, it is convenient to make stop-off forms that can be reused many times. Plastic sheet, generally 0.1 to 0.15 mm (0.004 to 0.006 in.) thick, is excellent for masking simple plates, cylinders, or other configurations. Steel sheet is sometimes substituted for plastic if it is desirable to equalize current distribution. To prevent plating or corrosion of the base metal, the plastic or steel stopoff must adhere firmly to the area being masked. Snug-fitting cylinders can be made to fit inside or outside diameters. To mask areas that are flat or of irregular shape, lacquer may be used to glue the stop-off material to the part; the lacquer may be removed with a thinner after plating.

Waxes. Several waxes designed for use as stopoffs are obtainable commercially. The use of a dip tank, thermostatically controlled to maintain the temperature at 15 to 20 °C (30 to 40 °F) above the melting point of the wax, makes the use of these materials comparatively fast and simple. The portion of the part to be plated can be covered with masking tape to prevent wax from adhering, or, if desired, the whole part can be coated and the wax stripped with a knife from areas to be plated. The wax mixture should have a melting point low enough to allow removal of the bulk with boiling water. Because they evolve poisonous fumes when heated, waxes containing chlorinated naphthalene must be used with exhaust equipment. High-melting-point mineral and vegetable waxes are not dangerous to use.

Decorative Chromium Plating

Revised by: James H. Lindsay, General Motors; Donald L. Snyder, Atotech USA Inc.

Introduction

DECORATIVE CHROMIUM PLATING is different from hard chromium plating in terms of thickness and the type of undercoating used. The average thickness of decorative plating is actually very thin, usually not more than 1.25 μm (50 μin.). A decorative chromium deposit is used primarily for its pleasing blue-white color. Its highly reflective appearance is maintained in service because chromium can resist tarnish, chemicals, scratches, and wear. If the deposit is defect-free, then a level of corrosion resistance also is provided, because the deposit acts as a physical barrier to the environment. Decorative chromium is applied over undercoatings, such as nickel or copper and nickel, which give the chromium bright, semibright, or satin cosmetic appearances. Corrosion protection depends on the choice of undercoating, as well as the type of chromium being applied. Parts made from steel, copper and its alloys, zinc, stainless steel, and aluminum are typically plated with nickel-chromium or copper-nickel-chromium.

Most decorative chromium coatings have been applied using hexavalent chromium processes that are based on chromic anhydride. However, since 1975, trivalent chromium processes have become available commercially. They are increasing in importance because of their increased throwing and covering powers and because they offer environmental advantages. Both systems are considered in detail in this article.

Chromium Electrodeposits

Decorative chromium plating baths generally produce deposits that range from 0.13 to 1.25 μm (5 to 50 μin.) in thickness. These deposits generally reproduce the finish of the substrate, or, in a multilayer system, the undercoating that is applied prior to the chromium layer. Optimum luster of the final chromium deposit is obtained by plating the substrate coating to a uniformly bright condition. If the substrate is nonuniform, grainy, hazy, or dull, then it should be polished and buffed to a uniformly high luster before being plated with chromium. When a final chromium coating over a uniformly bright substrate is hazy in certain areas, these areas can be buffed on a wheel or the coating can be stripped and the substrate replated. Buffing of chromium is not allowed when corrosive service conditions will be encountered.

In addition to being lustrous, the final chromium deposit should cover all significant areas. When there is not adequate coverage, because of an improperly operated chromium bath, the chromium should be stripped, the substrate reactivated, if necessary, and the part replated.

Decorative chromium that has been applied over nickel, the typical undercoating, is readily stripped by immersion in a 1:1 solution of hydrochloric acid. An alternate method involves treating the part anodically in an alkaline cleaning solution. However, this method requires reactivation of the nickel surface prior to replating, which is typically accomplished by immersion in dilute sulfuric or hydrochloric acid. Cathodic, but never anodic, alkaline cleaning can also be used for activation.

Excessively high current densities, improper temperatures, and passivated substrates can produce hazy, nonuniform chromium deposits. Operating conditions for chromium plating should be in the specified ranges. Properly operated nickel baths and other similar precautions also are necessary to ensure uniformly lustrous chromium deposits.

The adhesion of chromium to an active or properly prepared substrate is usually not a problem. However, if chromium is plated on an undercoating that has been improperly applied and has questionable adhesion, then blistering or exfoliation can occur, either immediately after chromium plating or during storage or service. Organizations that generate standards,

such as ASTM, can provide procedures for checking adhesion if a related method has not been specified in the purchase agreement for the part being plated.

Microporosity and Microcracking. The key to the corrosion durability offered by decorative chromium deposits lies in controlling the type, size, and distribution of microdiscontinuities that form in the deposit. These can occur as either pores or cracks. In an outdoor corrosive environment, as well as in accelerated corrosion tests, corrosion has been observed to proceed by galvanic cell action between the nickel and the chromium, with the nickel acting anodically. Microcracks or micropores in the chromium expose the underlying nickel through a uniform, diffuse network of discontinuities. Because the rate of corrosion penetration through the nickel layer is a function of the anodic current density of the corrosion cell, the reduction of current density that is obtained by the increase in exposed nickel area prolongs the time required to penetrate a given thickness of nickel. The advantage of such a system lies in its ability to provide long-term corrosion protection without developing easily visible fine surface pits in the nickel, which eventually become corrosion sites. The use of microdiscontinuous chromium makes the surface pits much smaller, which means that the substrate will be protected from corrosion for a longer time. However, after excessive corrosion, these fine pits will become visible as a haze on the corroded surface.

Chromium deposits, up to a thickness of 0.13 μm (5 μin.), that are obtained from hexavalent processes are somewhat porous. Because porosity decreases with increasing thickness, at approximately 0.5 μm (20 μin.), the deposits become nearly pore-free when plated (Fig. 1). However, because of the hard, brittle nature of the highly stressed chromium deposits, they quickly become cracked during storage or service. These cracks do not improve the corrosion resistance, as do deposits with intentionally developed micropores or microcracks.

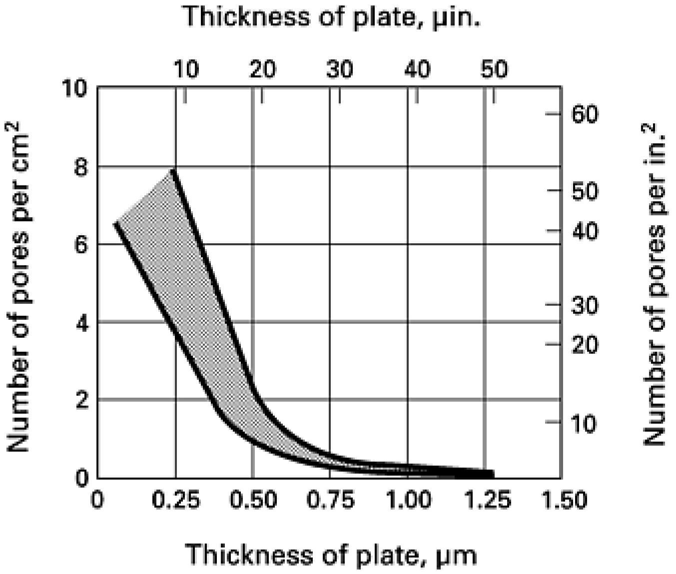


Fig. 1 Porosity in chromium plate as a function of plate thickness. Chromium deposited in low-temperature baths begins to crack at 75 μm (3000 μin.).

Except when special hexavalent chromium processes and conditions are used, hexavalent chromium deposits that are more than 0.5 μm (20 μin.) thick will have visible nondecorative microcracks. In contrast, chromium deposits from trivalent processes are microporous up to thicknesses of 0.5 to 0.6 μm (20 to 25 μin.), above which they become microcracked. Both features enhance the corrosion resistance of the part.

When hexavalent chromium is deposited from solutions operated below 50 °C (120 °F), the deposit will begin to craze when it exceeds 0.5 μm (20 μin.) in thickness, and a macrocrack pattern visible to the unaided eye will appear. This pattern generally has 5 to 10 cracks/cm (12.5 to 25 cracks/in.).

Either microcracked or microporous chromium deposits can be produced by altering the nature of the nickel undercoating. Microporous chromium can be obtained by plating over a thin layer of nickel deposited from a solution containing very fine, nonconductive particles. Chromium will not plate over these particles, which creates a microporous deposit with pore densities proportional to the amount of inert particles and additives in the nickel solution. An average pore density of

10,000 pores/cm^2 (60,000 pores/in^2) is the typical minimum specified for enhanced corrosion resistance. A disadvantage of this process is the addition of an extra nickel plating tank between the bright nickel and the chromium tanks. The pore count is also current-density dependent, and chromium deposits of 0.3 to 0.4 μm (12 to 16 μin.) in thickness have a tendency to bridge over the inert particles and reduce the pore count.

Trivalent chromium deposits provide pore counts of more than 16,000 pores/cm^2 (100,000 pores/in^2), without any special procedures. The pore count also is rather current-density independent.

Another very common method for obtaining microporous chromium deposits is to mildly blast the chromium deposit with an abrasive, such as sand or aluminum oxide. The brittle chromium fractures where it is hit by the particles, thus causing a microporous deposit to form. This method permits the pore count to be varied, based on the amount of particles used, and is independent of current density.

Microporous chromium is the most common microdiscontinuous chromium deposit used in North America to enhance the corrosion resistance of the decorative nickel-chromium type of electrodeposit. Microcracked chromium is somewhat more popular in the rest of the world.

Microcracking can be produced by using a thin layer, approximately 1.25 μm (50 μin.), of a highly stressed nickel deposit between the bright nickel and chromium deposits. Approximately 0.25 μm (10 μin.) of chromium is typically used with this procedure. A crack density of 275 to 790 cracks/cm (700 to 2000 cracks/in.) is typically produced. Thicker chromium deposits are required with other microcracking methods.

Microcracked chromium deposits can be obtained from systems using either a single or a dual specially formulated chromium solution. An example of the latter is duplex chromium. Although single-deposit systems are easier to operate, conditions that favor the formation of microcracks, such as high solution temperature, low chromic-acid concentration, and high fluoride content, usually have an adverse effect on the covering power of the chromium deposit. Duplex chromium systems have resolved this problem by using two successive chromium baths. The first obtains coverage and the second creates the microcrack pattern.

Satisfactory coatings are not too difficult to obtain on parts with relatively simple shapes, but complex parts can present a serious problem because it is difficult to obtain adequately thick chromium in areas of low current density. Auxiliary anodes can be used to increase the thickness in these areas.

Influence of Design on Quality and Cost

The cost of electroplating is often greatly influenced by the complexity of the workpiece. Simple shapes can be processed through all cleaning and plating sequences, with a minimum of approximately 33 μm (1300 μin.) of copper and nickel and 0.25 μm (10 μin.) of chromium, in approximately 50 min. Providing these minimum thicknesses on complex shapes requires longer plating periods, special fixturing, special anodes, and current shields. Plating costs are increased by each of these factors, although buffing and cleaning costs may be unchanged. Equipment and overhead costs per workpiece also increase in direct proportion to the plating time. In addition, the cost of materials is increased, because more metal is plated unnecessarily on projections and other areas of high current density. Figure 2 indicates the approximate increase of plating costs with plating time at a fixed current density.

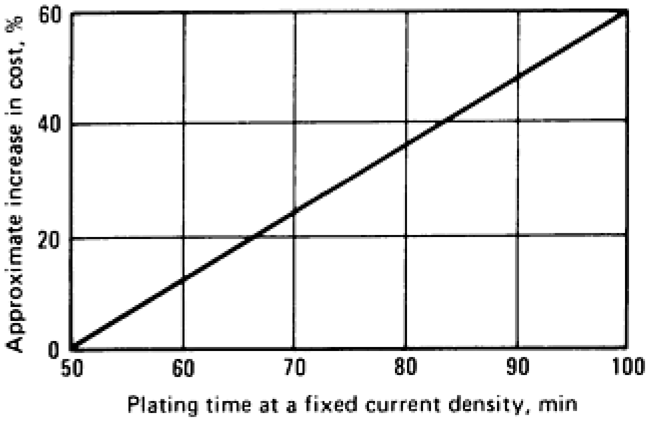
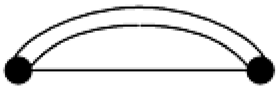
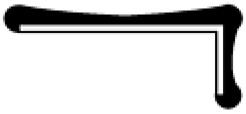
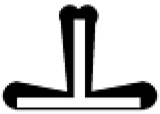
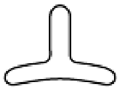
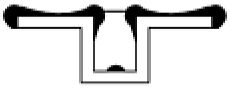
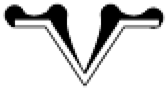
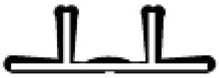
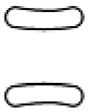
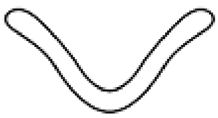
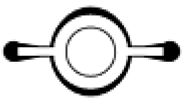


Fig. 2 Plating cost-time relationship

Extreme workpiece complexity can preclude the application of a truly corrosion-protective deposit by conventional plating procedures. The influence of some design features on platability and plating cost are described in Table 1.

Table 1 Influence of design on platability of zinc-base die castings

Design feature	Influence on platability	Better design
	**Convex surface.** Ideal shape. Easy to plate to uniform thickness, especially where edges are rounded.	
	Flat surface. Not as desirable as crowned surface. Use 0.015 mm/mm (0.015 in./in.) crown to hide undulations caused by uneven buffing.	
	**Sharply angled edge.** Undesirable. Reduced thickness of plate at center areas. Requires increased plating time for depositing minimum thickness of durable plate. All edges should be rounded. Edges that contact painted surfaces should have a 0.8 mm ($\frac{1}{32}$ in.) min radius.	
	**Flange.** Large flange with sharp inside angles should be avoided to minimize plating costs. Use generous radius on inside angles and taper abutment.	
	Slots. Narrow, closely spaced slots and holes cannot be plated properly with some metals (e.g., nickel and chromium) unless corners are rounded.	
	**Blind hole.** Must usually be exempted from minimum thickness requirements.	
	Sharply angled indentation. Increases plating time and cost for attaining a specified minimum thickness and reduces the durability of the plated part.	
	Flat-bottom groove. Inside and outside angles should be rounded generously to minimize plating costs.	
	**V-shaped groove.** Deep grooves cannot be plated satisfactorily; should be avoided. Shallow, rounded grooves are better.	
	**Fins.** Increase plating time and costs for attaining a specified minimum thickness and reduce the durability of the plated part.	

	Ribs. Narrow ribs with sharp angles usually reduce platability; wide ribs with rounded edges impose no problem. Taper each rib from its center to both sides and round off edges. Increase spacing, if possible.	
	Deep scoop. Increases time and cost for plating specified minimum thickness.	
	Spearlike jut. Buildup on jut robs corners of electroplate. Crown base and round all corners.	
	**Ring.** Platability depends on dimensions. Round corners; crown from center line, sloping toward both sides.	

Note: Distribution of electroplate on design shapes is intentionally exaggerated by solid black outline. Cross-hatched areas indicate part before plating.

Hexavalent Chromium Plating

The first hexavalent chromium plating bath used for decorative plating, sometimes referred to as the conventional bath, consisted of an aqueous solution of chromic anhydride (CrO_3) and a small amount of soluble sulfate ($SO_4^{=}$), referred to as the catalyst. The latter was added as sulfuric acid or as a soluble sulfate salt, such as sodium sulfate. When dissolved in water, the chromic anhydride forms chromic acid, which is believed to exist in the following equilibrium:

$$H_2Cr_2O_7 + H_2O \rightleftharpoons 2H_2CrO_4$$

The ratio of chromic acid to sulfate, generally given as the weight ratio of chromic anhydride to sulfate, governs the current efficiency for chromium metal deposition. The cathode current efficiency also is affected by solution variables, such as concentration of chromic acid, temperature, and content of metallic impurities. The latter variable is an important consideration for commercial operations, because an excessively high content of impurities such as copper, iron, zinc, and nickel seriously affects bath conductivity, cathode current efficiency, and both throwing and covering power, even if the ratio of chromic anhydride to sulfate is within optimum limits for the application.

Most decorative chromium is deposited within these operating limits:

- Chromic anhydride, 200 to 400 g/L (27 to 54 oz/gal)
- Chromic anhydride-to-sulfate ratio, 80:1 to 125:1
- Cathode current density, 810 to 1880 A/m^2 (75 to 175 A/ft^2)

These wide limits encompass a broad variety of decorative applications. As of 1994, the trend is toward using chromic-anhydride concentrations of 250 to 300 g/L (33 to 40 oz/gal) and avoiding more highly concentrated baths and their attendant environmental and recovery concerns. The ratio of chromic acid to sulfate ion is usually maintained at levels near 100:1.

With the development of duplex, microcracked, and crack-free applications, specialized bath compositions and operating conditions have come into use. However, many of these are either proprietary or are not subjects of general agreement. The compositions and operating conditions for a general, additive-free, decorative chromium plating bath and a bright, crack-free bath are given in Table 2.

Table 2 Compositions and operating conditions for two chromium plating baths

Constituent or condition	General decorative bath	Bright, crack-free bath
Chromic acid	250 g/L (33.0 oz/gal)	260-300 g/L (35-40 oz/gal)
Ratio of chromic acid to sulfate	100:1 to 125:1	150:1
Operating temperature	38-49 °C (100-120 °F)	52-54 °C (125-130 °F)
Cathode current density	810 - 1885 A/m^2 (75 - 175 A/ft^2)	2690 - 3230 A/m^2 (250 - 300 A/ft^2)

To meet specific requirements for plating speed, nickel activation, and crack pattern, the chromium anhydride and sulfate concentrations should be properly correlated with temperature and cathode current-density limits. In preparing a bath and establishing operating conditions, these relationships should be considered:

- An increase in the temperature of the bath, except for mixed-catalyst baths, will decrease the cathode efficiency, decrease the number of cracks per unit length, decrease coverage at low current density, increase the limiting current density at which burning occurs, and increase passivating action on nickel.
- An increase in the weight ratio of chromic anhydride to sulfate will decrease the crack density and increase the nickel passivity. The chromium will whitewash (have a milky appearance) when plated over passive nickel.
- An increase in sulfate, at a constant chromic-acid concentration, temperature, and cathode current density, will increase the cathode current efficiency to an upper limit; beyond this point, any further increase in sulfate concentration can cause a decrease in cathode current efficiency.

In dilute chromic-acid solutions containing as low as 150 g/L (20 oz/gal) of sulfate, any small carryover of soluble sulfates from earlier solutions can quickly upset the balance of the solution. However, dilute solutions do have a higher cathode efficiency and a slightly wider bright range, although they require higher tank voltages to maintain desired current density. Even when other plating conditions (such as temperature and current density) are held constant, the plating operation can be seriously disrupted by any change in the ratio of chromic acid to sulfate.

Because there are advantages and disadvantages to using either high or low chromic-acid contents, some compromise is necessary. The size and shape of the article to be plated and the available equipment and power often determine exactly which solution should be used. In decorative chromium plating, all variables must be kept in the proper relationship. Frequent bath analysis and prompt adjustments are essential to maintain balanced conditions.

Mixed-Catalyst Baths. Since the mid-1950s, a number of mixed-catalyst proprietary chromium plating baths have been developed. The advantages of these baths are increased cathode current efficiencies, increased activating action on nickel and stainless steel, improved coverage at low current density, broader bright plating ranges, and improved decorative chromium applications, including dual, microcracked, and bright or dull crack-free.

Mixed-catalyst compositions contain chromic acid, sulfate, and fluorine compounds (frequently, fluosilicate ions) as active ingredients. Proprietary baths, formulated to regulate the concentration of catalyst ions, contain strontium, calcium, or potassium salts, to control the solubility of fluosilicate ions. Details on mixed-catalyst compositions are provided in several U.S. patents and at least one British patent (see "Selected References" at the end of this article). Most control requirements applicable to standard baths also apply to proprietary baths.

With the exception of ratio control, the problems associated with low, medium, or high chromic-acid concentrations in mixed-catalyst baths are the same as those for conventional chromium baths. After optimum conditions are found, the same close control must be maintained to prevent mischromes (absence of plate) in areas of low current density and blue,

matte, or burnt deposits in areas of high current density. Because supplies for mixed-catalyst solutions are more expensive than chromic acid alone, using less-concentrated solutions can provide a cost advantage.

Baths for Microcracked Chromium. Typically, two chromium solutions are used successively to produce microcracked chromium plate. The first chromium solution can either be conventional or proprietary and is operated in a normal manner. A plating time of 8 min is preferred when recessed areas are involved, although plating times of 5 to 6 min are often used. Surging of the current can be used to increase coverage. Composition ranges and operating conditions for nonproprietary, first-plating solutions that are used to plate steel and zinc parts are given in Table 3.

Table 3 Bath compositions and conditions for plating microcracked chromium

Substrate material	Constituents				Chromic anhydride to sulfate ratio	Temperature		Current density	
	Chromic acid		Fluoride						
	g/L	oz/gal	g/L	oz/gal		°C	°F	A/m^2	A/ft^2
First plating bath									
Steel	338-375	45-50	. . .	. . .	100:1	46-52	115-125	1075-1615	100-150
Zinc	375-413	50-55	. . .	. . .	140:1	46-52	115-125	1290-1720	120-160
Second plating bath									
Steel	165-195	22-26	1.5-2.25	0.20-0.30	180:1	43-54	120-130	970-1345	90-125

The second chromium solution is similar to the first and can be either proprietary or nonproprietary. The chromic-acid concentration is lower and fluosilicate ions must be present in the bath to promote cracking. The plating time is approximately the same as in the first solution, 5 to 8 min, and current surging can be used, if desired. Composition ranges and operating conditions for the second chromium bath also are given in Table 3. The plating conditions are governed by the nature of the parts being plated. Solutions for parts having deep recesses should have a higher chromic acid and fluoride content and a lower sulfate content. However, thickness must be weighed against other influences on microcrack formation. For this reason, operating conditions can be established on a firm basis only by actual operation with the parts to be processed. On simple shapes, the second plating bath formulation can be used alone.

The use of a rinse or rinses between the two chromium solutions is not essential to the process, but it may help to avoid control problems, because of drag-out from the first chromium solution into the low-concentration second solution. When used, these rinses can be operated as reclaim tanks to minimize drag-out losses.

Solution Control. Regardless of which chromium bath is used, periodic analyses are required. Information on control procedures is provided in the article "Industrial (Hard) Chromium Plating" in this Volume.

Temperature. All chromium plating solutions require the control of temperature, current density, and solution composition. The exact temperature at which bright, milky, frosty, or burnt deposits occur depends on solution composition and current density. Chromium plating is usually performed within the range of 38 to 60 °C (100 to 140 °F), but the most common operating range is from 46 to 52 °C (115 to 125 °F). At room temperature, the bright plating range is impractically narrow. In a process set up to plate at 50 °C (120 °F) with all variables properly controlled, the temperature need vary only 1.5 or 2 °C (3 or 4 °F) to move the electrodeposit out of the clear, bright range. Consequently,

an accurate temperature controller and facilities for rapid cooling and heating of the bath are essential. Temperature variation outside the bright operating range can either cause an unacceptably high rejection rate or necessitate costly stripping and replating operations. The preheating of heavy parts is necessary to avoid plating solution cooling and temperature fluctuation.

Current Density. The standard sulfate bath is usually operated at 1075 to 1720 A/m^2 (100 to 160 A/ft^2). A current density of about 1075 A/m^2 (100 A/ft^2) is used for solutions maintained at 38 °C (100 °F). A higher current density, sometimes as high as 3230 A/m^2 (300 A/ft^2), is required for solutions operated at 55 °C (130 °F). The choice for a specific use depends on such variables as the complexity of the articles being plated and the equipment available. After the current density has been established, close control must be maintained.

Changes in the ratio of chromic acid to sulfate require compensating adjustments in current density. If the sulfate content is increased (lower ratio), then current density must be increased to maintain full coverage in areas of low current density. If the sulfate content is decreased (higher ratio), then current density must be decreased to prevent burning in areas of high current density.

An increase in temperature may require an increase in current density to ensure full coverage in areas of low current density. A decrease in temperature may require a decrease in current density to prevent gray (burnt) deposits in areas of high current density.

As chromic-acid content increases, higher current densities can be used. The average cathode efficiency of most conventional chromium solutions is about 13% over a wide range of concentration, making it possible to plate for shorter times when using the most concentrated solution. Rectifiers with low ripple, not exceeding 5%, must be used to maintain trouble-free, uniform deposition.

Anodes. In chromium plating, insoluble lead or lead-alloy anodes are almost always used. Chromium metal is supplied by the chromic acid in the electrolyte.

Pure lead anodes are often attacked excessively by idle baths, which causes the formation of a heavy sludge of lead chromate on the bottom of the tank, making pure lead anodes impractical for all but continuous operations. During plating, a coating of lead peroxide forms on the anode. The coating favors oxidation of trivalent chromium at the anode. However, when the bath is idle, the coating dissolves to some extent in the solution, making attack on the anode possible.

To reduce the attack of the chromic-acid bath on the anode, several lead alloys are used. For conventional sulfate baths, 6 to 8% antimonial (Sb) lead is preferred, whereas for solutions containing fluoride, lead alloys with 4 to 7% Sn are used.

For an anode to provide optimum throwing power and coverage, it must be positioned properly in relation to the workpiece and have a continuous, uniform film of lead peroxide on the entire surface. Anodes with crusty surfaces have low conductivity and should be cleaned periodically by wire brushing or alkaline cleaning to ensure proper current distribution. The function of the anode is not only to conduct the plating current, but to oxidize trivalent chromium, which forms at the cathode, back to hexavalent chromium. To accomplish this, the anode area should be adjusted to provide the optimum anode current density for the oxidation necessary to keep the trivalent chromium at the desired level, usually 0.25 to 1.0 g/L (0.033 to 0.13 oz/gal). In decorative chromium plating, an anode-to-cathode area ratio of 2:1 is common for proper reoxidation and balance. If trivalent chromium continues to increase above the desired level, then the anode area should be increased to the point where the trivalent chromium concentration remains stable. Overheating of the bath can occur if the anode area is so small that resistive heating becomes a factor.

Anodes with round cross sections are most commonly used. When maximum anode area is desired, corrugated, ribbed, ridged, and multi-edged anodes are used. The round anode is preferred, because its surface is active on its entire circumference, enabling it to carry higher amperage at lower voltage. The absence of inactive areas on this anode minimizes the formation of lead chromate film, reducing maintenance requirements. If the weight of the anode presents a problem, then hollow, round anodes can be used. Although such anodes provide a 25 to 40% reduction in weight, their current-carrying capacity is less than that of solid anodes.

Anodes are manufactured by extrusion. Contact with the bus bar can be provided by a copper hook homogeneously burned to the extruded anode. Pure nickel, nickel-plated copper, and lead-coated copper are also used for hooks. Several hook styles are used, but the knife-edge hook is preferred. The hook and the top of the anode are covered with plastisol for protection against corrosion by fumes and drag-out drip. Bags typically used to cover the anodes in nickel- and

copper-plating processes should not be used in chromium-plating processes. Roughness that is due to nonuniform anode corrosion is not a problem in chromium-plating operations. Therefore, the resulting particles do not have to be captured by the bags.

Control of Current Distribution. Chromium plating baths have poorer throwing and covering power than most other plating baths. To obtain thickness and coverage in areas of low current density, special auxiliary anodes are sometimes used.

Any workpiece of complex shape constitutes a problem of proper current distribution when nonconforming anodes are used. The current density and the thickness on a workpiece varies from highest on corners, edges, and areas closest to the anode to lowest on recesses and areas distant from the anode. Variations in current density result in differences of cathode efficiency, which accentuate the problems of uneven plate, burning, or complete absence of plate. These problems can be overcome, to some extent, by special racking and shielding techniques, such as:

- Wide spacing of concave parts on rack
- Increasing the distance between workpiece and anode
- Intentional shielding of a projection on one piece with a depression on an adjacent one
- Orienting areas of low current density toward the periphery of the fixture
- Moving the parts in the center of the rack closer to the anodes than those on the periphery of the rack

Improved coverage on areas of low current density can be achieved with striking, that is, plating at high current density for a short period of time. The striking time duration is kept to a minimum, usually 5 to 20 s, to avoid burning. Plating is continued at normal current density after the strike.

Current Shields. A nonconducting plate or panel (current shield) can be mounted on the plating rack to direct current away from areas of high current density or to direct additional current into areas of low current density. Figure 3 illustrates the use of a device to divert some of the current that would otherwise cause excessive current density and possible burning at the work areas closest to the anodes. The position and size of current shields are extremely important for their effective use and can be established best by trial and error. The use of shields, however, is always accompanied by some increase in drag-out.

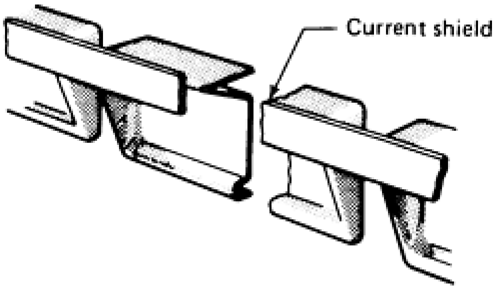


Fig. 3 Current shield

Thieves or robbers made of metal conductors can be positioned near edges and points to shunt away current from these areas. Rods with a diameter of 9.5 to 16 mm ($\frac{3}{8}$ to $\frac{5}{8}$ in.) are sometimes suspended vertically on both ends of a plating rack to prevent burning or rough plate on the edges of the cathodes. Maintenance of robbers is of utmost importance, because they can be the source of large drag-out losses if metal is allowed to build up excessively.

Auxiliary Anodes. Special racks and auxiliary anodes are used only when conventional techniques fail to produce satisfactory coatings. Parts with deep recesses, such as coffeepots and small appliance housings, require auxiliary anodes. Auxiliary anodes are also used for parts with concave surfaces that are difficult to plate uniformly (Fig. 4). Auxiliary anodes also offer potential cost reductions by directing the plate into areas of minimum plate thickness without the penalty of overplating areas of high current density. The use of such devices should be considered even for some parts

that do not present serious problems in meeting specifications for plate thickness. The shapes of many die castings make the use of auxiliary anodes particularly applicable. The current supply for auxiliary anodes can be the same as the major plating circuit with a separate current control, such as a rheostat. Greater flexibility is obtained if a separate current source is used for the auxiliary anodes.

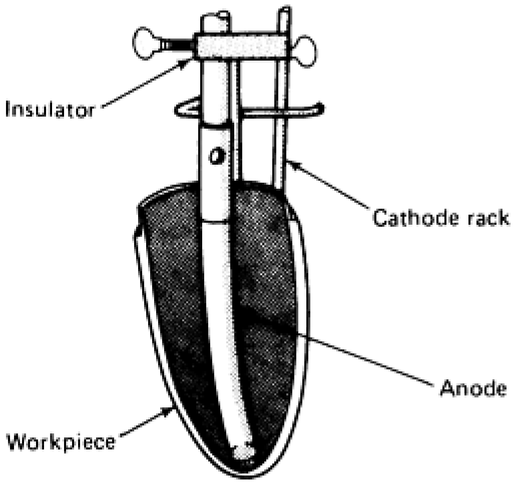


Fig. 4 Use of auxiliary anode for a part difficult to plate to uniform thickness because of concave surface

Auxiliary anodes are mounted on the plating rack, insulated from cathode current-carrying members, and provided with means of direct connection to the anodic side of the electrical circuit (Fig. 5). In still tanks, the connection can simply be a flexible cable equipped with battery clamps. In fully automatic machines, cables are permanently mounted on the carriers, and contact brushes riding on an anode rail are provided to pick up the current. Connections must be positive. An interruption or drastic reduction of current could cause the auxiliary anode to function as a robber or shield, resulting in local interruption of plate, with consequent darkening and loss of adhesion.

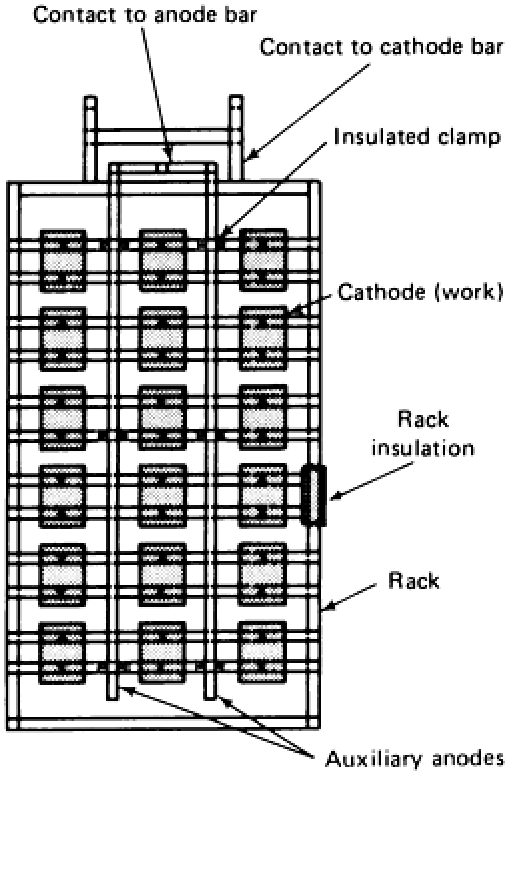


Fig. 5 Rack assembly for decorative chromium plating

The auxiliary anode need not follow the contour of the part closely. An anode-to-work spacing of 13 mm ($\frac{1}{2}$ in.) or slightly more is usually effective. The auxiliary anode mounting must be designed carefully to prevent the anode from interfering with efficient racking and unracking of parts. The anode can be designed for removal while parts are being loaded on the rack, but good contact must be preserved. The auxiliary anode should be held rigidly to prevent it from short circuiting against the cathode.

Some platers connect auxiliary anodes electrically only during chromium plating, a practice that is usually satisfactory for still tank operation, where an anode can be physically mounted immediately before chromium plating. In an automatic plating machine, however, the auxiliary anode should be connected in the acid-copper bath, the nickel bath (at least, in the last half of the tank), and the chromium bath to avoid low thicknesses and low current density effects that could detract from appearance and cause difficulty in chromium plating.

Unless they are made of insoluble material, auxiliary anodes are consumed in plating. Their design should therefore permit easy replacement. Plastisol-coated steel bushings with locking screw heads protected by stop-off lacquer are satisfactory. As anodes become thin, they must be carefully inspected for replacement to avoid shorting out. The diameter of rod used should be as large as is compatible with the size of the part and with construction requirements to minimize the need for frequent replacement. A diameter of 13 mm ($\frac{1}{2}$ in.) is suitable for a variety of parts, ranging from small brackets to instrument panels and moldings. On larger parts, diameters as large as 25 mm (1 in.) or specially cast sections can be useful.

Bags should not be used on auxiliary anodes, because of the resulting solution contamination from drag-in. Avoiding roughness from bare anodes requires serious consideration if the anodes are to be immersed in copper and nickel undercoating baths. Roughness is not a problem when the anode is to be immersed only in the chromium solution. Lead-alloy or steel anode material has been used satisfactorily for this purpose. Graphite rods also have been used to a limited extent. Auxiliary anodes are most frequently made of platinized titanium.

Bipolar anodes are a special variation of auxiliary anodes, in which current is not supplied by external connection. In use, collector plates are mounted at the cathodic end (the end closest to the tank anodes) of the bipolar anode to draw current from a larger section of the bath. Bipolar anodes can be used on conveyorized systems when a special bus bar is unavailable. Although adequate for some purposes, bipolar anodes are usually less effective than other auxiliary anodes and must be carefully maintained to avoid the problems of roughness from loosely adherent deposits of nickel and chromium on the collector plates. The metal deposited on the collector plates is often not reusable.

Stop-offs are not widely used in decorative chromium plating. However, when selective plating is required, a number of materials have the necessary qualifications, including ease of application and removal, resistance to hot cleaners and plating solutions, and excellent adherence and electrical insulation characteristics during use.

Special racks are sometimes used to prevent plating solution from entering tapped holes and areas where plate is not wanted. Figure 6 shows a plated lever with a 7.92 mm (0.312 in.) diameter hole that had to be free of plate. If conventional racking had been used, then the hole would have had to be reamed to remove the plate.

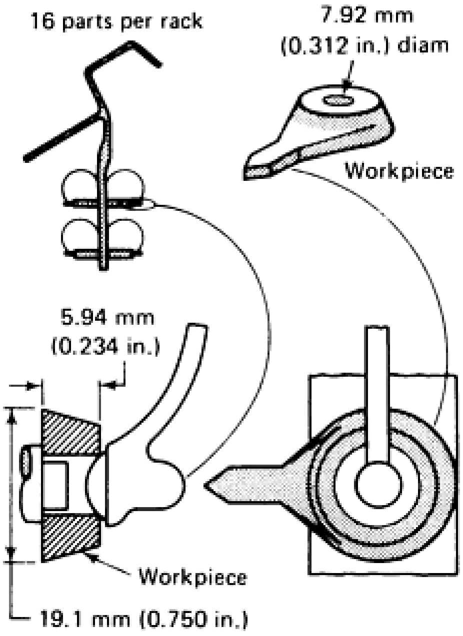


Fig. 6 Racking arrangement to prevent plating of chromium in the hole of a shift lever

Tanks. Chromium plating tanks can be constructed of steel and lined with flexible plastic-type materials, such as fiberglass or polyvinyl chloride (sheet form or sprayed) or lead alloy (6% Sb). Lead-alloy linings should be approximately 3.2 mm ($\frac{1}{8}$ in.) thick. Plastic liners should range in thickness from 2.4 to 4.8 mm ($\frac{3}{32}$ to $\frac{3}{16}$ in.). Plastic linings are preferred, particularly for proprietary baths with fluoride-containing anions, which may have a greater rate of attack on lead linings. Rubber mats or plastisol-coated metal ribs are often used to protect the sides or bottoms of lead-lined tanks from shorts that are due to either accidental contact or being punctured by dropped anodes or workpieces. Lead linings can cause serious bipolarity problems, because of their electrical conductivity.

Heating. Chromium plating tanks can be heated internally or externally. Internal heating, by steam coils or electric immersion heaters, is usually used for small tanks. External heating by heat exchangers is used for large tanks. Coils for internal heating can be made of lead, a lead alloy such as 4% Sn or 6% Sb, or tantalum. Titanium can be used for baths that do not contain fluoride ions. Immersion heaters should be quartz-covered. Heat exchangers can be made of tantalum, lead alloy (4% Sn or 6% Sb), high-silicon cast iron, or heat-resistant glass. Tantalum is preferred for heating coils or heat exchangers when proprietary solutions containing fluoride ions are used, because titanium is attacked by the fluoride. Consultation with vendors on specific material/process compatibility is suggested.

Plating Cycles. Typical system cycles for the application of six decorative chromium plating systems to identical workloads are given in Table 4. Each system is identified by the specific combination of metals successively deposited, the total thickness of plate, and the total plating time. The plating times and power requirements listed in Table 4 are theoretical values for perfect coverage. In practice, these values would be considerably higher to ensure adequate plate thickness in all areas. Table 5 provides the requirements for the design of several installed machines for the continuous plating of zinc die castings of average complexity. The higher-than-normal designed current density is related to potential future needs that exceed present requirements.

Table 4 Typical system cycles

System	Cycles	Total plate		Total time, min[(a)]
		μm	μin.	

Cu + Ni + Cr	A, B, D, F	50	1970	48
Cu + Cr	A, B, F	20	790	14
Ni + Cr	D, F	30	1180	36
Ni + Cr + Cr	D, G	32	1260	41.5
Ni + Ni + Cr	C, E, F	30	1180	36
Ni + Ni + Cr + Cr	C, E, G	32	1260	41.5

Operating parameters	
A: Copper strike	
Current density	325 A/m^2 (30 A/ft^2)
Plating time	2 min
Heat[(b)]	49-65 °C (120-150 °F)
Filtration	Yes
Agitation	Optional
B: Acid copper plate, high speed, bright (20 µm, or 790 µin.)	
Current density	430 A/m^2 (40 A/ft^2)
Plating time (100% efficiency)	10 min
Heat[(b)]	21-27 °C (70-80 °F)
Filtration and agitation	Yes
C: Nickel plate, semibright (23 µm, or 900 µin.)	
Current density	430 A/m^2 (40 A/ft^2)
Plating time(100% efficiency)	26 min

Heat(b)	55-65 °C (130-150 °F)
Filtration	Yes
Agitation	Usually
D: Nickel plate, bright (30 µm or 1180 µin.)	
Current density	430 A/m^2 (40 A/ft^2)
Plating time (100% efficiency)	34 min
Heat(b)	55-65 °C (130-150 °F)
Filtration	Yes
Agitation	Usually
E: Nickel plate, bright (8 µm, or 315 µin.)	
Current density	430 A/m^2 (40 A/ft^2)
Plating time (100% efficiency)	34 min
Heat(b)	55-65 °C (130-150 °F)
Filtration	Yes
Agitation	Usually
F: Chromium plate (0.3 µm, or µin.)	
Current density	1550 A/m^2 (144 A/ft^2)
Plating time	
Conventional (10% efficiency)	2 min
High speed (25% efficiency)	54 s
Heat(b)(c)	46-65 °C (115-150 °F)

Filtration and agitation	No
Ventilation[(d)]	Yes
G: Chromium plate, microcracked (0.64 μm, or 25 μin.)	
Current density	1550 A/m^2 (144 A/ft^2)
Plating time (25% efficiency)	2.5 min
Heat[(b)(c)]	45-65 °C (115-150 °F)
Filtration and agitation	No
Ventilation[(d)]	Yes

(a) Power requirements and plating times given are theoretical values for perfect coverage. In practice, these values would be approximately doubled to ensure adequate thickness of plate in all areas. Table 5 has data for practical conditions.

(b) For operating temperature indicated.

(c) Cooling as well as heating may be required.

(d) Chemical suppressant (mist or spray) may be used in addition to ventilation.

Table 5 Design basis of equipment for continuous chromium plating of zinc-base die castings

Metal deposited	**Designed current density**		**Minimum thickness of plate**		**Nominal thickness of plate**		**Plating time, min**
	A/m^2	**A/ft^2**	**μm**	**μin.[(a)]**	**μm**	**μin.**	
Copper cyanide strike	1075	100	. . .	. . .	0.25	10	3-4
Bright copper	320	30	15	590	20	790	25-30
Semibright nickel	810	75	15	590	20	790	30
Bright nickel	1075	100	5	197	7.5	295	17
First chromium	2150	200	0.3	12	0.5	20	6.5

Second chromium	1615	150	0.25	10	0.5	20	6.5

(a) On parts of moderate complexity

Maintenance. The importance of proper solution maintenance and electrical, mechanical, and other equipment used in plating processes cannot be overemphasized. Table 6 identifies the daily, weekly, monthly, and annual inspection and correction operations that should enable the setup of an adequate maintenance program for chromium plating.

Table 6 Chromium plating maintenance schedule

Frequency	Action
Daily	Fill plating tank with solution from save-rinse and boil-down tanks.
	Stir solution thoroughly, using low-pressure air agitation.
	Check solution for chromic acid, sulfate, and anti-spray additives; make corrective additions.
	Check temperature controls for satisfactory operation; adjust temperature to proper range.
	Inspect plating racks; repair as necessary.
	Check ground lights to see that plating circuits are clear; do not start plating until grounds are clear.
	Put dummy cathodes in tanks and electrolyze solutions at maximum voltage for 15 to 30 min at start of each day.
	Check hull cell.
Weekly	Boil down the save-rinse solution.
	Check auxiliary catalyst; make additions as necessary.
Monthly	Check solution for metallic impurity content (iron, zinc, copper, nickel).
	Clean and straighten anodes.
	Check solution for trivalent chromium content.
Annually	Check all ammeters and ampere-hour meters.
	Inspect and adjust all temperature controllers.

	Clean and repair outside of all tanks; clean and repair all ventilation hoods and ducts.
	Pump out solution, remove sludge. Clean and inspect tank and heating coil; repair as needed. Disconnect all bus bar connections; clean, draw-file and reconnect, including all anode and cathode joints. Inspect anodes; clean, straighten or replace as required.

Troubleshooting. Plating problems can still develop, even when proper maintenance is used. Some typical plating problems and solutions are given in Table 7. Examples of actual problems and solutions used with a variety of chromium-plated parts are given in Table 8.

Table 7 Chromium plating problems and corrections

Defect	Possible cause	Possible remedy
Poor covering power or low deposit thickness	Temperature too high	Adjust temperature to standard range.
	Current density too low	Increase current density.
	Low chromic acid	Adjust chromic acid to standard range.
	Fluoride catalyst too high	Reduce concentration (by dilution).
	Low chromic acid to sulfate ratio	Adjust ratio.
	Poor electrical contact	Correct electrical contact.
	Bath contamination	Remove impurities.
Burning in high current density areas	Temperature too low	Adjust temperature to standard range.
	Current density too high	Reduce current density.
	Chromic acid low	Raise chromic acid.
	High chromic acid/sulfate ratio	Adjust ratio.
	Fluoride catalyst too low	Adjust concentration of fluoride catalyst.
Deposit color nonuniform	Underlying surface not clean or active	Remove any interfering films and provide active surface.
	Bipolarity during entrance to chromium	Enter bath with precontact (live entry).

	Bath contamination by metallic impurities	Analyze bath, remove impurities.

Table 8 Case histories of plating problems

Condition	Cause and correction
Passivation	Nickel-plated business machine parts were stored submerged in cold water to await barrel chromium plating. Although these parts were acid activated before chromium plating, chromium coverage was poor to nil on parts that had been stored for only a few hours. To remedy the problem, parts were stored submerged in a 10% solution of potassium bitartrate (cream of tartar). After several days of storage, the parts could be electrolytically reactivated and barrel chromium plated satisfactorily.
Burning	Although bath composition and temperature were carefully controlled, burnt chromium deposits occurred on die castings plated at moderate amperage. This resulted from nonuniform distribution of current caused by the corrosion of mounting blocks attaching the bus bar to the anode bar. The situation was corrected by welding the bus bar to the anode rail, eliminating mounting blocks.
Poor electrical contact	L-shaped die-cast frames approximately 0.09 m^2 (1 ft^2) in area, although plated in identical racks in an automatic plating machine,exhibited nonuniformity of plate and, in some racks, burnt deposits. This was found to be caused by variations in current from rack to rack in the plating machine. To correct this, mechanical joints were eliminated from the electrical circuit. The mechanical joints were replaced by welding cables from the carrier contact brushes to the rack mounting bar.
Mischromes	Mischromes (absence of chromium on certain areas) occurred on die-cast window frames that occupied the lower portions of racks during plating in a full-return-type automatic plating machine. These defects were caused by the presence of short anodes at the exit end of the nickel plating tank. Replacement with anodes of the correct length solved the problem.
Inadequate rinsing	Inadequate rinsing after chromium plating, which failed to remove small amounts of bath impurities,resulted in nonuniform appearance of the plate on zinc die castings. The parts were given a hot rinse at 93 °C (200 °F) before customary room-temperature rinses to remove bath impurities.

Trivalent Chromium Plating

The use of the trivalent chromium ion, instead of the hexavalent ion, in solution to deposit chromium has been of interest for many years. The first commercially successful decorative trivalent chromium process began in England in 1975 and in the United States in 1976. Environmental, safety, and productivity advantages have been the driving forces for the commercialization of trivalent chromium processes.

Hexavalent chromium ions are also considered carcinogenic and can cause skin ulcerations. The trivalent chromium ion is estimated to be about 100 times less toxic than hexavalent chromium ions.

Trivalent chromium processes have reduced misting to the extent that scrubbers, such as those used with hexavalent chromium processes, are presently not required to meet federal and state air-quality discharge standards. Waste-treatment costs are reduced by a factor of 10, because less than one-tenth of the chromium contained in hexavalent processes is used in the trivalent process (8 to 23 g/L, or 1 to 3 oz/gal, versus 115 to 300 g/L, or 15 to 40 oz/gal). In addition, the solution drains faster, so that less solution is removed with the parts. Finally, the chromium in the rinse water is already in the trivalent state, which eliminates the expensive and sludge-volume-building reduction step required with hexavalent chromium ions.

Some of the trivalent chromium processes plate up to three times faster than hexavalent chromium processes. This increases productivity in some shops. Increased throwing and covering powers, lack of burning, and tolerance to current interruptions and ripple also reduce rejects and can increase the allowable number of parts on a rack.

One of the main difficulties with the development of trivalent chromium baths was the formation of hexavalent chromium at the insoluble anodes during plating. Hexavalent chromium ions are a contaminant in trivalent chromium processes. They initially cause a poor deposit appearance and eventually result in the cessation of plating.

Two well-known proprietary approaches were developed to address the problem of hexavalent chromium formation during plating. The oldest and most frequently used technique incorporates several lines of defense against hexavalent chromium ions. Under normal operating conditions, hexavalent chromium cannot form. If it does manage to get into the plating solution, then it is reduced to the trivalent state, which eliminates it as a contaminant. This technique is referred to as the single-cell process, in contrast to the second technique, which isolates the insoluble graphite anodes from the trivalent-chromium-containing plating solution to restrict the formation of hexavalent chromium.

This second technique, commonly referred to as the double-cell, or shielded anode, method, uses an ion-selective membrane to create a barrier around the anode. Conventional lead anodes are used in a 10% sulfuric-acid electrolyte. The membrane keeps the trivalent chromium from contacting the anode, thereby preventing the formation of hexavalent chromium.

Solution Compositions. Depending on the process used and its operating conditions, the trivalent chromium ion content typically ranges from 5 to 20 g/L (0.67 to 2.67 oz/gal). It is introduced as a water-soluble salt and forms a stable specie upon combining with the stabilizing agents/catalysts. These agents permit the trivalent chromium ion to be stable in solution until it is plated out at the cathode. However, the stability process is not strong enough to interfere with the normal precipitation sequence used with chromium during waste treatment.

In comparison to hexavalent chromium solutions, which have good conductivity, the conductivity of the relatively high-pH and low-metal-content trivalent plating solution is increased by the addition of conductivity salts/buffers. Lower amperes but higher volts are required for trivalent chromium processes, compared with hexavalent chromium process requirements. Surfactants are added to reduce the surface tension of the solution for mist suppression, as well as to act as additives in the plating operation.

Solution Operation. The typical operating conditions for trivalent chromium processes are summarized in Table 9. High current density spiking at the onset of plating increases the already excellent covering and throwing powers of trivalent chromium processes, when compared with those of hexavalent processes. In general, wherever nickel can be plated, trivalent chromium can be plated. Hexavalent chromium processes fall short, particularly around holes and slots and in low current density areas. Process control, while plating at high current densities, is not a serious concern for trivalent processes, because they have less tendency to produce burnt deposits, compared with hexavalent processes. However, some earlier trivalent processes did produce thick deposits, over 1.3 μm (50 μin.). This thickness is sufficient to produce macrocracking. The cathode efficiency decreases with increasing current density. Therefore, the plating speed does not increase proportionally with an increase in current density.

Table 9 Typical operating conditions for trivalent chromium processes

Parameter	**Value**
pH	2.3-4.0
Temperature	27-50 °C (80-122 °F)
Current density	
Cathode	430-1400 A/m^2 (40-130 A/ft^2)
Anode	540 A/m^2 (50 A/ft^2)

Agitation	Mild air
Rectifier voltage	6-15 V
Deposition rate	
Single-cell process	0.20-0.25 μm/min (8-10 μin./min)
Double-cell process	0.08-0.10μm/min (3-4 μin./min)

Once the operating range has been established for a particular plating installation, the pH and temperature must be controlled well, because they influence plating speed, covering power, and color. The buffering ability of the solution is strong enough that large pH fluctuations do not occur. As the pH increases, the plating rate decreases, but the covering power increases. In general, trivalent chromium deposits do not have the blue-white color of hexavalent chromium deposits. Generally, they have a deeper, slightly darker appearance. However, the newer trivalent processes can produce deposits very close in appearance to hexavalent chromium deposits. In most cases, the color difference is noticeable only when the part is placed next to a hexavalent chromium-plated part.

Temperature. Depending on the process selected, either cooling or heating might be required for temperature control to maintain a bath at desired operating parameters. When lower operating temperatures are desired, some degree of cooling might be required to offset the power used for deposition. Cooler operating temperatures increase the covering power of the process, but slightly darken the color.

Anodes and Agitation. Anode current density should be maintained below 540 A/m^2 (50 A/ft^2) to promote anode life and consistent bath operation. The insoluble graphite anode used in the single-cell process should last indefinitely, if it is not physically damaged. Lead anodes will form protective insoluble films as long as the anodic current density is properly maintained in the double-cell process, resulting in a limited production of lead salts. Mild and uniform air agitation is used around the parts to assist in obtaining metal distribution and appearance.

Contamination Control. The major contributor to a change in appearance of the trivalent chromium deposits is solution contamination. Trivalent chromium solutions are much more sensitive to bath contamination, but are much more easily purified than are hexavalent chromium solutions. Organic contaminants, a minor problem, are typically removed by filtration through carbon. Organic contamination appears in the chromium deposit as white smears that resemble a pattern typically associated with poor cleaning.

Inorganic contaminants, such as iron, nickel, copper, and zinc, cause the deposit to have dark streaks and/or to lose covering power. The newest and easiest method for removing inorganic impurities is to continuously purify the plating solution by passing it through a specially designed resin. Using this technique, the inorganic impurity levels can be maintained much below the level that will cause any operational or appearance problems.

Three other general methods can be used to remove these contaminants. The slowest approach is to plate them out whenever the bath is not being used for production. An alternative method is to set a small plating unit, connected by a recirculating pump, to the main plating tank. Dummy sheets are used in the small unit to continuously plate out impurities without interrupting production.

A third method that is available for some processes is to use chemical purifiers that can remove large quantities of inorganic contaminants during one or two hours of downtime. Although this method is very fast, it has two disadvantages. The chemical precipitates the impurities within the plating bath. The precipitation itself does not cause any plating problems, but the precipitates could adhere to the parts as they leave the tank, causing them to have an objectionable white film. If chemical purifiers are improperly used, then the solution chemistry can be affected, resulting in a darker deposit and poorcoverage.

Plating Problems and Corrections. Some of the plating problems experienced with trivalent chromium baths can be ascribed to common operational problems. Poor coverage is typically due to low pH, high temperature, low current density, or lead or zinc contamination. Dark clouds or smudges on the work can arise from metallic contamination or low complexant or surfactant concentrations. White patches on the work can be caused by high concentrations of surfactants or other organics, lead contamination, or high wetting agent concentration in the nickel bath used prior to chromium plating.

Trivalent and Hexavalent Deposit Comparisons. The choice of chromium plating solution, whether hexavalent or trivalent, depends on the individual application under consideration. The characteristics of these processes are compared in Table 10.

Table 10 Trivalent and hexavalent chromium comparison

Parameter	Trivalent chromium	Hexavalent chromium
Throwing power	Good	Poor
Covering power	Good	Poor
Current interruptions	Completely tolerant	Intolerant
Rectifier ripple	Completely tolerant	Intolerant
Deposit structure (microdiscontinuous):		
Single cell	Microporous and microcracked	Special processes required
Double cell	Microporous	. . .
Ease of burning	Very difficult	Easy
Ease of rinsing	Easy	Moderate
Color buffing requirement	Never	Occasional
Filtering requirement:		
Single cell	Only after purification	Never
Double cell	Daily with carbon	. . .
Conditioning/dummying:		
Single cell	Never	Start up to each day

Double cell	Start up and routinely	. . .
Passivity of nonplated surfaces	Needs post dip	"Chromate" surfaces
Color of deposit:		
Single cell:		
Ambient temperature	Pewter or stainless steel	Blue-white
Elevated temperature	Metallic white	. . .
Double cell:		
Elevated temperature	Metallic white	. . .
Waste treatment	Easy	Moderate
Relative safety	Similar to nickel	Similar to cyanide
Misting	Almost eliminated	Heavy
Odor	Almost eliminated	Strong and dangerous

Nickel Plating

Revised by George A. Di Bari, International Nickel Inc.

Introduction

THE NICKEL PLATING PROCESS is used extensively for decorative, engineering, and electroforming purposes because the appearance and other properties of electrodeposited nickel can be varied over wide ranges by controlling the composition and the operating parameters of the plating solution. Decorative applications account for about 80% of the nickel consumed in plating; 20% is consumed for engineering and electroforming purposes. Autocatalytic (electroless) nickel plating processes are commercially important but are outside the scope of this section. The annual worldwide consumption of nickel for electroplating is approximately 180 million pounds (81,700 metric tons) and accounts for 11 to 12% of world nickel consumption. Some basic information about nickel and common nickel salts for plating is given in the following table:

Nickel	Atomic weight 58.69. Valency 2. Specific gravity 8.90. Plating rate, at 100% cathode efficiency, 1.095 g/A · h (0.039 oz/A · h)

Nickel salts	
Nickel chloride	Formula is $NiCl_2 \cdot 6H_2O$. Contains 24.7% Ni.
Nickel sulfate	Formula is $NiSO_4 \cdot 6H_2O$. Contains 22.3% Ni.
Nickel sulfamate	Formula is $Ni(NH_2SO_3)_2$. Contains 23.2% Ni.
Nickel carbonate	Formula is $NiCO_3$. Contains about 46% Ni.

Decorative Plating. Modern decorative nickel plating solutions contain organic additives that modify the electrocrystallization process so that mirror-bright, highly-leveled nickel coatings are deposited directly from solution. Prior to the introduction of "organic" baths, decorative nickel coatings were produced by polishing nickel-plated parts mechanically, a practice that continued from 1870 to about 1945. Thin layers of chromium were electrodeposited over polished nickel coatings for the first time in 1927 to prevent the "yellowing" or tarnishing of nickel in outdoor atmospheres, and that practice continues with the "as-deposited" bright nickel coatings now available. An effort to develop improved decorative, electroplated nickel coatings began in the late 1940s and led to the development of multilayer nickel coatings (early 1950s) and microdiscontinuous chromium coatings (mid- to late 1960s). Modern multilayer nickel coatings in combination with microdiscontinuous chromium are capable of protecting and enhancing the appearance of most metals and alloys, plateable plastics, and other materials for extended periods of time.

Engineering Plating. The engineering applications of nickel plating include those where a fully bright appearance is not required. Engineering nickel deposits are usually sulfur-free and matte in appearance. These deposits may be specified to improve corrosion and wear resistance, to salvage or build up worn or undersized parts, to modify magnetic properties, to prepare surfaces for enameling or for organic coating, to function as diffusion barriers in electronic applications and for other purposes. Engineering applications exist in the chemical, nuclear, telecommunications, consumer electronics, and computer industries.

Electroforming. Nickel electroforming is electrodeposition applied to the manufacture of nickel products of various kinds, and it differs from electroplating in one major respect. In electroplating, the coating is metallurgically bonded to the substrate and is an integral part of the surface. In electroforming, nickel is deposited onto a mandrel or mold nonadherently so that the nickel can be separated from the mandrel when it is removed from the plating solution. Electroforming applications include the fabrication of molds and dies, mesh, and other products that are indispensable to operations in the textile, aerospace, communication, electronics, automotive, photocopying, and entertainment industries. Additional information is available in the article "Electroforming" in this Volume.

Basic Process Considerations

Before describing decorative, engineering, and electroforming plating processes, some basic facts are reviewed that make it possible to control the nickel plating process, predict the amount of nickel deposited, and estimate nickel coating thickness.

The Basic Process. Nickel plating is similar to other electroplating processes that employ soluble metal anodes. It requires the passage of direct current between two electrodes that are immersed in a conductive, aqueous solution of nickel salts. The flow of direct current causes one of the electrodes (the anode) to dissolve and the other electrode (the cathode) to become covered with nickel. The nickel in solution is present in the form of divalent positively charged ions (Ni^{++}). When current flows, the positive ions react with two electrons ($2e^-$) and are converted to metallic nickel (Ni^0) at the cathode surface. The reverse occurs at the anode, where metallic nickel is dissolved to form divalent positively charged ions, which enter the solution. The nickel ions discharged at the cathode are replenished by those formed at the anode.

Hydrogen Evolution and Cathode Efficiency. The discharge of nickel ions is not the only reaction that can occur at the cathode; a small percentage of the current is consumed in the discharge of hydrogen ions from water. This reduces the cathode efficiency for nickel deposition from 100% to 92 to 97%, depending on the nature of the electrolyte. The discharged hydrogen atoms form bubbles of hydrogen gas at the cathode surface.

Anode Efficiency. Under normal conditions the efficiency of dissolution at the anode is 100% and no hydroxyl ions are discharged from the water. If the pH of the solution is too high, however, hydroxyl ions may be discharged in preference to the dissolution of nickel, and oxygen will be evolved. Under those conditions, the nickel anode becomes passive and ceases to dissolve nickel. Activated nickel anode materials are available commercially that resist the onset of passivity and replenish the solution with nickel ions over a wide range of plating conditions.

Nickel Ion and pH Changes. Under normal operating conditions, the nickel ion concentration and the pH of the solution will slowly increase as plating proceeds. The rate of increase in nickel ion concentration depends on the difference between cathode and anode efficiencies. Because cathode efficiencies may vary from 92 to 97%, whereas anode efficiency is always 100%, the rate of increase in nickel ion concentration depends on the nature of the plating solution and not on the type of soluble nickel anode material that is used.

Faraday's Law for Nickel. The amount of nickel deposited at the cathode and the amount dissolved at the anode are directly proportional to the product of the current and time (Faraday's Law). The proportionality constant is equal to M divided by nF, where M is the molecular weight, n is the number of electrons involved in the electrochemical reaction, and F is Faraday's constant, equal to 96,500 coulombs (ampere-seconds). For nickel, the constant is 1.095 g/A · h. The constant for nickel deposition is calculated assuming that cathode efficiency is 100%; because a small part of the current goes to discharge hydrogen, the constant must be adjusted by multiplying by the cathode efficiency (for example, $1.095 \times 0.955 = 1.046$).

Faraday's Law for nickel may be expressed as $m = 1.095\ (a)\ (l)\ (t)$, where m is the amount of nickel deposited at the cathode (or dissolved at the anode), in grams; l is the current that flows through the plating tank, in amperes; t is the time that the current flows, in hours; and a is the current efficiency ratio for the reaction of interest. In almost all cases, the anode efficiency is 100% ($a = 1$). The cathode efficiency may vary from 92 to 97% and accordingly, a will vary from 0.92 to 0.97.

Average Nickel Thickness. The nickel electrodeposition data compiled in Table 1 have been calculated on the assumption that cathode efficiency is 95.5%, which approximates the case for most nickel plating solutions. From the table, one can estimate the time required to deposit a specified thickness of nickel at a specified current density. If the plating process is operated at 5 A/dm^2, for example, it takes about 20 min to deposit a nickel coating with an average thickness of 20 μm.

Table 1 Nickel electrodeposition data

Deposit thickness, μm	Weight per unit area, g/dm^2	Amp hours per unit, A · h/dm^2	Time (min) required to obtain deposit at current density (A/dm^2) of:									
			0.5	**1**	**1.5**	**2**	**3**	**4**	**5**	**6**	**8**	**10**
2	0.18	0.17	20	10	6.8	5.1	3.4	2.6	2.0	1.7	1.3	1
4	0.36	0.34	41	20	14	10	6.8	5.1	4.1	3.4	2.6	2
6	0.53	0.51	61	31	20	15	10	7.7	6.1	5.1	3.8	3.1
8	0.71	0.68	82	41	27	20	13	10	8.2	6.8	5.1	4.1
10	0.89	0.85	100	51	34	26	17	13	10	8.5	6.4	5.1

12	1.1	1.0	120	61	41	31	20	15	12	10	7.7	6.1
14	1.2	1.2	140	71	48	36	24	18	14	12	8.9	7.1
16	1.4	1.4	160	82	54	41	27	20	16	14	10	8.2
18	1.6	1.5	180	92	61	46	31	23	18	15	11	9.2
20	1.8	1.7	200	100	68	51	34	26	20	17	13	10
40	3.6	3.4	410	200	140	100	68	51	41	34	26	20

Note: Values are based on 95.5% cathode efficiency.

The data in Table 1 provide a means of estimating the average coating thickness. The actual thickness on an individual part depends on the uniformity of current density distribution. Under practical plating conditions, the thickness of the nickel on a batch of parts is measured in one or more trials, and adjustments are made, if necessary, as to how the parts are placed in the tank relative to the anode and how they are positioned on the plating racks. In some cases, shields and auxiliary anodes may be required to obtain acceptable thickness uniformity. Shields are made of nonconductive materials and may be placed on the anode, on the cathode, or between electrodes to block or control current flow. Auxiliary anodes may be either soluble or insoluble, and they are placed closer to the cathode than principal anodes so as to direct current to a recessed or relatively small area on the cathode. With care, current density distribution and coating thickness can be made reasonably uniform and predictable.

The Watts Solution and Deposit Properties

The nickel plating solution described by Watts in 1916 was a major milestone in the development of nickel plating technology. The solution eventually replaced all others in use up to that time. It remains the basis of most decorative nickel plating processes, and it is used for engineering applications and for electroforming. It is operated at elevated temperatures and is capable of being used with high current densities.

The composition of the modern Watts bath is included in Table 2. The constituents of the Watts bath have several functions.

- *Nickel sulfate* is available in commercially pure forms, is relatively inexpensive, and is the major source of the nickel ions in solution. A high nickel sulfate concentration is used when high current densities are required.
- *Nickel chloride* serves primarily to improve anode corrosion, but it also increases conductivity and uniformity of coating thickness distribution. Excessive amounts of chloride increase the corrosivity of the solution and the internal stress of the deposits. (*Internal stress* refers to forces created within the deposit as a result of the electrocrystallization process and/or the codeposition of impurities such as hydrogen, sulfur, and other elements. Internal stress is either tensile [contractile] or compressive [expansive] and may cause plating problems if excessively high.)
- *Boric acid* is used in nickel plating solutions for buffering purposes; its concentration may affect the appearance of the deposits. The deposit may first become frosty in high current density areas at 30 g/L (4 oz/gal) of boric acid, and then as the boric acid concentration approaches 15 to 23 g/L (2 to 3 oz/gal), the deposit may be burnt and cracked. No effect on appearance is observed at high boric acid concentrations up to saturation (45 g/L, or 6 oz/gal).
- *Wetting agents or surfactants,* formulated specifically for nickel plating solutions, are almost always added to control pitting. Their function is to lower the surface tension of the plating solution so that air

and hydrogen bubbles do not cling to the parts being plated.

Table 2 Nickel electroplating solutions

Electrolyte composition, [a] g/L	**Watts nickel**	**Nickel sulfamate**	**Typical semibright bath[b]**
Nickel sulfate, $NiSO_4 \cdot 6H_2O$	225 to 400	. . .	300
Nickel sulfamate, Ni $(SO_3NH_2)_2$	. . .	300 to 450	. . .
Nickel chloride, $NiCl_2 \cdot 6H_2O$	30 to 60	0 to 30	35
Boric acid, H_3BO_3	30 to 45	30 to 45	45
Operating conditions			
Temperature, °C	44 to 66	32 to 60	54
Agitation	Air or mechanical	Air or mechanical	Air or mechanical
Cathode current density, A/dm^2	3 to 11	0.5 to 30	3 to 10
Anodes	Nickel	Nickel	Nickel
pH	2 to 4.5	3.5 to 5.0	3.5 to 4.5
Mechanical properties[c]			
Tensile strength, MPa	345 to 485	415 to 610	. . .
Elongation, %	10 to 30	5 to 30	8 to 20
Vickers hardness, 100 gram load	130 to 200	170 to 230	300 to 400
Internal stress, MPa	125 to 210 (tensile)	0 to 55 (tensile)	35 to 200 (tensile)

(a) Antipitting agents formulated for nickel plating are often added to control pitting.

(b) Organic additives available from plating supply houses are required for semibright nickel plating.

(c) Typical properties of *bright* nickel deposits are as follows: elongation, 2 to 5%; Vickers hardness, 100 gram load, 600 to 800; internal stress,

12 to 25 MPa (compressive).

Good-quality nickel deposits can be produced within the ranges of solution pH, temperature, and current density given in Table 2. Although the maximum current density given in the table is 11 A/dm^2, higher rates of plating are possible with increased solution agitation and flow rates.

The physical and mechanical properties of nickel deposited from Watts solutions are affected by the operating conditions and chloride content of the solution as shown in Fig. 1, 2, 3, and 4. Figures 1, 2, and 3 show how pH, current density, and temperature affect properties such as internal stress, hardness, percent elongation, and tensile strength. Figure 4 shows how the chloride content affects those properties; the maximum ductility and softest deposits are produced when 25% of the nickel in solution is present as nickel chloride. Reference 2 is a comprehensive source of mechanical property data for electrodeposited nickel, nickel alloys, and nickel composite coatings.

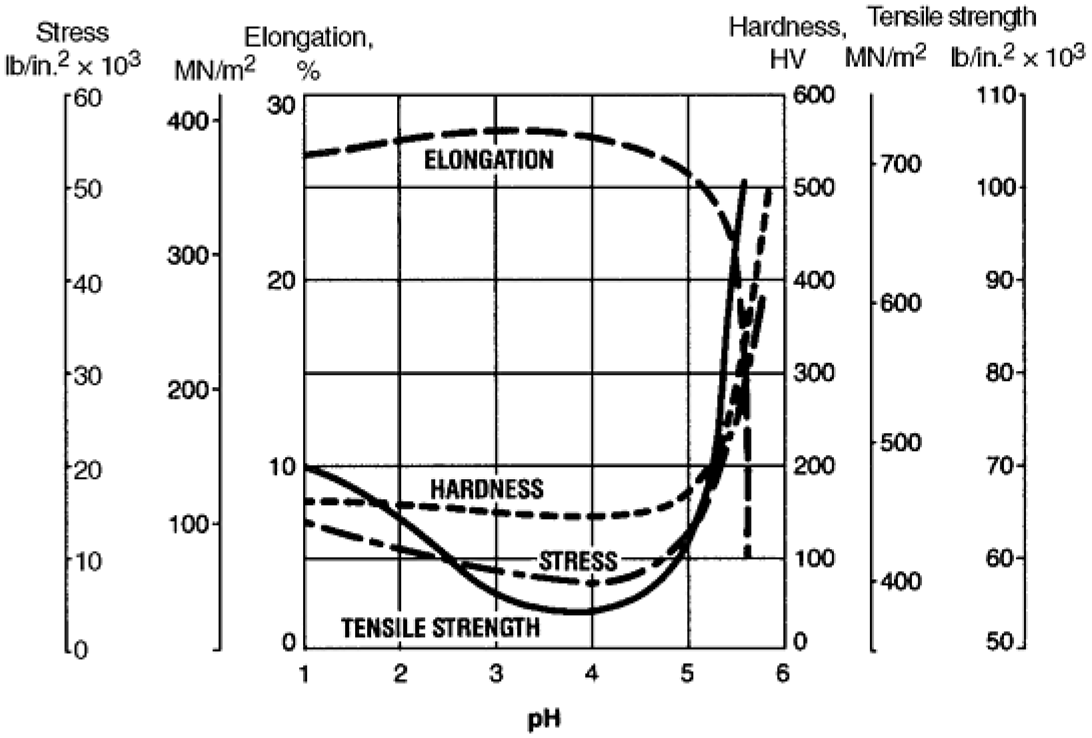


Fig. 1 Variation in internal stress, tensile strength, ductility, and hardness with pH. Watts bath operated at 54 °C and 5 A/dm^2. Internal stress is tensile (indicated by a positive number). Source: Ref 1

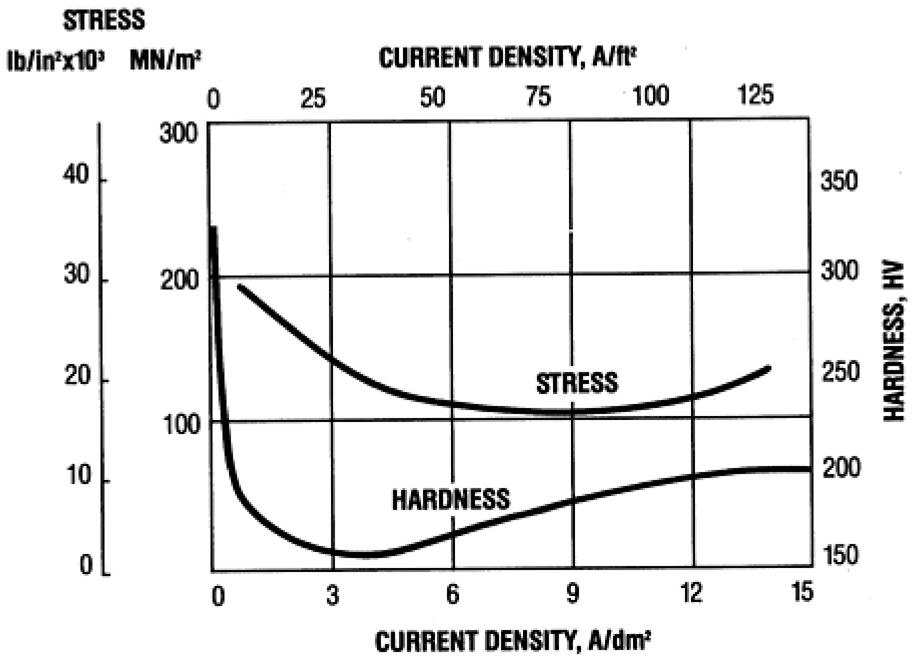


Fig. 2 Variation in internal stress and hardness with current density. Watts bath operated at 54 °C and pH 3.0. Internal stress is tensile (indicated by a positive number). Source: Ref 1

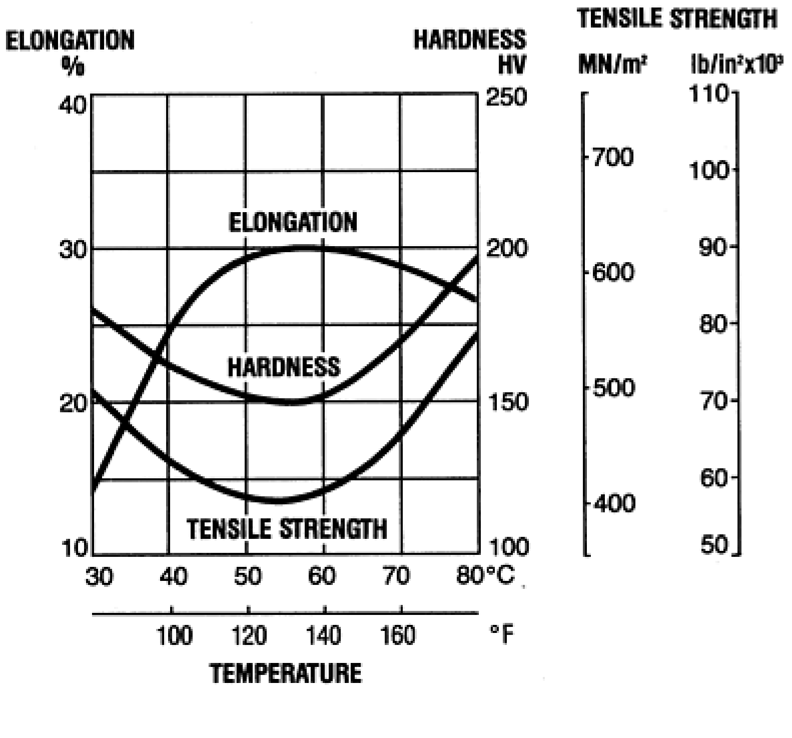


Fig. 3 Variation in elongation, tensile strength, and hardness with temperature. Watts bath operated at 54 °C and 5 A/dm^2. Source: Ref 1

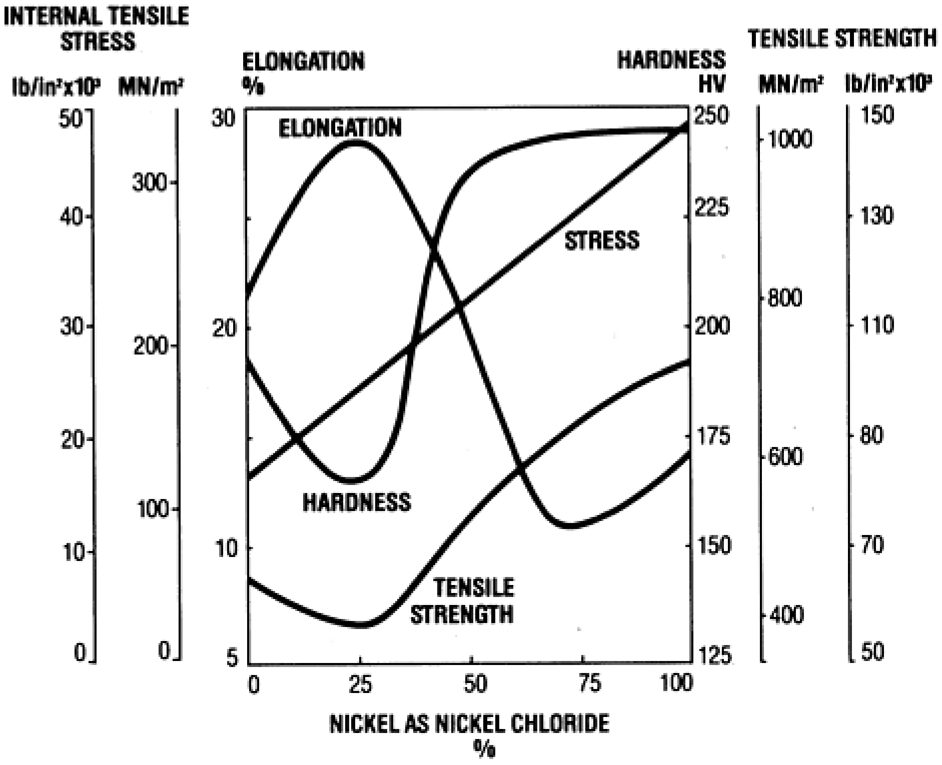


Fig. 4 Variation in internal stress, elongation, tensile strength, and hardness with chloride content in deposits from Watts solutions operated at 55 °C, pH 3.0, and 5 A/dm^2. Internal stress is tensile (indicated by a positive number). Source: Ref 1

The nickel plating processes used for decorative, engineering, and electroforming purposes are discussed in the following sections.

References cited in this section

1. *Plating,* Vol 39 (No. 365), 1952, p 1229
2. W.H. Safranek, *The Properties of Electrodeposited Alloys--A Handbook,* 2nd ed., American Electroplaters and Surface Finishers Society 1986

Decorative Nickel Plating Processes and Multilayer Coatings

The technology of decorative nickel plating has been improved continuously over the years. Prime examples include development of the organic bright nickel solutions, introduction of semibright nickel plating processes, development of multilayer nickel coatings, and the use of microdiscontinuous chromium in combination with multilayer nickel. The major result of these developments has been a remarkable improvement in the corrosion performance of decorative nickel plus chromium coatings without the need to increase deposit thickness.

Bright nickel plating solutions are modifications of the Watts formulation given in Table 2, but they contain organic and other additives that act to produce a fully bright finish suitable for immediate chromium plating without mechanical finishing. Portions of the addition agent molecules may be incorporated into the deposit, resulting in a hard, fine-grain coating that contains incorporated sulfur. The sulfur causes the deposit to be electrochemically more reactive than sulfur-free matte, polished, or semibright nickel deposits. Decomposition products of the additives accumulate in solution with time and are removed by purification with activated carbon. In modern solutions, continuous filtration through active carbon removes deleterious decomposition products without significant removal of the addition agents themselves.

Several substances--organic and inorganic--are used at appropriate concentrations to achieve brightness, leveling, and control of internal stress. (Leveling is the ability of the deposit to become smoother than the surface on which it is deposited as the thickness of the nickel is increased.) The substances used as additives in bright nickel plating solutions may be described by the following three terms: *carriers, auxiliary brighteners,* and *brighteners.* The terminology is not standardized, however, and alternative terms mentioned in the literature are shown in parentheses.

Carriers (brighteners of the first class, secondary brighteners, control agents, ductilizers) are usually aromatic organic compounds. They are the principal source of the sulfur codeposited with the nickel. Their main function is to refine grain structure and provide deposits with increased luster compared with matte or full deposits from baths without additives. Some of these additives can be used in Watts solution or high-chloride versions of the Watts solution (for example, solutions with 115 g/L nickel chloride). This class of brightener widens the bright range when used in combination with the auxiliary brighteners and brighteners discussed below. Some examples of carriers are saccharin (o-sulfobenzoic imide), paratoluene sulfonamide, benzene sulfonamide, benzene monosulfonate (sodium salt), ortho sulfobenzaldehyde (sodium salt), and naphthalene 1,3,6-trisulfonate (sodium salt). Carriers are used in concentrations of about 1 to 25 g/L (0.1 to 3 oz/gal), either singly or in combination. They are not consumed rapidly by electrolysis, and consumption is primarily by dragout and by losses during batch carbon treatment. (Batch treatment involves interrupting production and transferring the plating solution to a separate treatment tank where it is treated with activated carbon, filtered, and returned to the main tank.) The stress-reducing property of carriers is increased if they contain amido or imido nitrogen. For example, saccharin is a most effective stress reducer and often helps to decrease or eliminate hazes. It is generally used as sodium saccharin at a concentration of 0.5 to 4.0 g/L (0.07 to 0.5 oz/gal).

Auxiliary brighteners may be either organic or inorganic. Their functions are to augment the luster attainable with the carriers and brighteners and to increase the rate of brightening and leveling. Some examples are sodium allyl sulfonate; zinc, cobalt, cadmium (for rack and barrel plating); and 1,4-butyne 2-diol. The concentration of these additives may vary from about 0.1 to 4 g/L (0.01 to 0.5 oz/gal). The rate of consumption depends on the type of compound and may vary widely. These compounds may be of aromatic or aliphatic types and usually are heterocyclic or unsaturated. The inorganic metallic ions--zinc, cobalt, cadmium--are not often used anymore as auxiliary brighteners.

Brighteners (brighteners of the second class, primary brighteners, leveling agents), when used in combination with carriers and auxiliary brighteners, produce bright to brilliant deposits having good ductility and leveling characteristics over a wide range of current densities. Some of the compounds used as brighteners include reduced fuchsin, phenosafranin, thiourea, 1,4-butyne diol, n-allylquinolinium bromide) and 5-aminobenzimidazolethiol-2. Materials of this type generally are used in concentrations of 0.005 to 0.2 g/L (0.0006 to 0.02 oz/gal); an excess of brighteners may cause serious embrittlement. The rates of consumption of these materials may vary within wide limits.

Modern bright nickel plating solutions employ combinations of additives similar to those described and are formulated to produce bright deposits over a wide range of current densities. The deposits have excellent leveling or scratch-filling characteristics, produce deposits with fair ductility and low internal stress, produce bright deposits in areas of low current density, permit use of high average current densities and bath temperatures, are less sensitive to metallic contaminants than some of the solutions first commercialized, permit continuous purification of the plating solution by use of activated carbon on filters, produce breakdown products that can be removed by activated carbon, and are not overly sensitive to anode effects.

Multilayer Decorative Plating. The single-layer bright nickel coatings produced from solutions containing organic additives are less resistant to corrosion than polished nickel coatings. The lower corrosion resistance is due to the presence of small amounts of sulfur that originate from the organic additives present in solution. The amount of sulfur that is incorporated depends on exactly how the process is formulated and controlled. Single-layer bright nickel coatings are suitable for use in mildly corrosive service using a nickel thickness of 10 to 20 μm (0.39 to 0.79 mil). For severe and very severe conditions of exposure, especially where longtime resistance to corrosion is required, multilayer nickel coatings with microdiscontinuous chromium are used. The principal types are double- and triple- layer coatings.

Double-layer coatings involve the electrodeposition of two layers of nickel, one semibright and one bright, before the application of chromium. The first layer (semibright) is deposited from a Watts-type formulation containing one or more sulfur-free organic additives. Semibright nickel deposits contain less than 0.005 wt% S and are semilustrous, smooth, and fine-grain over a wide current density range. The deposits have a columnar structure and good ductility. The typical composition and operating conditions for a semibright nickel plating bath are given in Table 2. Deposit internal stress increases with increasing nickel chloride content; deposits also tend to be nonuniform in color and leveling at high chloride levels. The concentrations of the organic additives for semibright nickel solutions are usually fairly low, from 0.05 to 0.5 g/L (0.006 to 0.06 oz/gal). Examples of these additives are 1,4-butyne diol (or other aliphatic compounds with

olefinic or acetylenic unsaturation), formaldehyde, coumarin, and ethylene cyanohydrin. There are two families of semibright nickel plating processes that are usually referred to as *coumarin* and *noncoumarin* types. The latter were introduced more recently and offer advantages. Semibright nickel plating solutions usually contain anionic surfactants and antipitting agents, singly or in combination.

The bright nickel layer deposited on top of the semibright one may range in thickness from 5 to 8 μm (0.2 to 0.3 mil), or about 20 to 35% of the total nickel thickness. Ideally, it should be plated from a bath that is compatible with the semibright additive, or additives, because in most double-layer systems the semibright additive functions as either a brightener or an auxiliary brightener in the bright nickel bath.

Triple-layer coatings are similar to double-layer coatings except that a thin, high-sulfur-containing layer is deposited between the semibright and bright layers. The thin layer must contain greater than 0.15 wt% S. Some of the requirements for double- and triple-layer nickel coatings are summarized in Table 3. Why multilayer coatings improve corrosion performance is discussed in the section "Corrosion Performance" in this article.

Table 3 Requirements for double- or triple-layer nickel coatings

Type of nickel coating[(a)]	Specific elongation, %	Sulfur content, wt%	Thickness as a percentage of total nickel thickness	
			Double-layer	Triple-layer
Bottom (s--semibright)	Greater than 8	Less than 0.005	Greater than 60 (but at least 75 for steel)	Greater than 50 (but not more than 70)
Middle (b--high-sulfur bright)	. . .	Greater than 0.15	. . .	10 max
Top (b--bright)	. . .	Between 0.04 and	Greater than 10, but less than 40	Equal to or greater than 30

(a) s,semibright nickel layer applied prior to bright nickel; b, fully bright nickel layer that contains the amount of sulfur specified

Microdiscontinuous Chromium. Decorative, electrodeposited nickel coatings, whether single- or multilayer, are most often used in combination with electrodeposited chromium. The thin layer of chromium, initially applied over nickel to prevent tarnishing, now provides added resistance to corrosion because of the developments discussed in this and the next section.

Conventional or regular chromium deposits are low-porosity coatings, whereas microdiscontinuous chromium deposits have a high, controlled degree of microporosity or microcracking. Controlled microporosity or microcracking in the chromium is achieved by depositing a special nickel strike on top of the bright nickel layer just prior to chromium plating. When it is plated over with chromium, the thin layer of nickel, usually about 1 to 2 μm (0.04 to 0.08 mil), helps create microcracks or micropores in the chromium. Microporosity may also be achieved without the use of a special nickel layer by means of the Pixie process, a patented process that involves postplating treatment of the chromium to increase porosity on a microscopic scale. Traditionally, the chromium is deposited from conventional hexavalent processes, but within the last ten years, trivalent chromium plating processes have grown in popularity.

Microcracked chromium is produced by depositing the thin layer of nickel from a special bath formulated to produce nickel with a high internal tensile stress. When the chromium deposit is chromium plated, the thin nickel and the chromium then crack. Varying the conditions under which the nickel layer is deposited can provide variations in the crack density over a range of from 30 cracks/mm (750 cracks/in.) to 80 cracks/mm (2000 cracks/in.). The nickel bath usually consists of a basic nickel chloride electrolyte with additives that provide additional stress, such as the ammonium ion. Boric acid is not used, but other buffers such as the acetate ion may be added. Proprietary organic additives are also used to enhance the brightness and the ability of the deposit to crack, especially in the low-current-density areas. Temperature

and pH are controlled to vary the crack density; low temperature (23 °C, or 73 °F) and high pH (4.5) favor higher crack densities; high temperature (36 °C, or 97 °F) and low pH (3.5) favor lower crack densities. Cracking of the chromium deposit must occur subsequent to chromium plating. Aging or the use of a hot water dip may be necessary to promote the formation of all microcracks.

Microporous chromium is produced from Watts-type nickel baths using air agitation and containing very fine inert particles, usually inorganic, and the normal additives used for bright nickel plating. Chromium, plated over the resulting nickel-particle matrix, deposits around the particles, creating pores. The nickel baths are operated much like bright nickel solutions, with the exception that filtration cannot be performed. In some instances, auxiliary additives permit reduction of the particle concentration in the plating bath and still provide high pore densities. Pore densities can vary according to the concentration of particles, agitation rates, and additives. Generally, a minimum pore density of 100 pores/mm^2 (64,000 pores/in.^{2}) is specified. In either case, chromium thicknesses should not be allowed to exceed about 0.5 μm (0.02 mil) or the cracks and pores will start to heal.

Microcracked chromium deposits can also be produced directly from chromium baths by increasing thickness, or by depositing chromium over chromium. The latter, dual-layer chromium technique is no longer popular.

Corrosion Performance. The remarkable corrosion resistance of modern decorative nickel-plus-chromium coatings depends on the use of multilayer nickel in combination with microdiscontinuous chromium. The improved performance of multilayer nickel coatings is due to the fact that the combination of layers of nickel have different electrochemical reactivities. If one measures the corrosion potentials of various nickel deposits in the same electrolyte, one finds that the bright nickel deposits display more active dissolution potentials than do the semibright nickels. If bright and semibright nickel deposits (for example, in the form of foils separated from the substrate) are electrically connected in the electrolyte, electrons will flow from the bright nickel to the semibright nickel. The result is that the rate of corrosion of the bright nickel is increased, whereas the rate of corrosion of the semibright nickel is decreased. In a composite coating consisting of bright nickel over semibright nickel, this is manifested by enhanced lateral corrosion of the bright nickel layer and delayed penetration of the semibright nickel layer.

The extent to which bright nickel protects the underlying semibright nickel layer by sacrificial action is dependent on the difference between the corrosion potentials of the semibright and bright nickel. The difference should be at least 100 mV (as measured by the simultaneous thickness and electrochemical potential, or STEP test, described in the section "Quality Control of Nickel Plating" in this article), differences in potential are beneficial, especially in low-current-density areas of complicated parts. If the difference becomes too great, appearance suffers because of the accelerated corrosion of the bright nickel layer; that is, there is an optimum value that represents a compromise between preventing basis metal attack and controlling superficial corrosion. The result is that penetration of the coating and exposure of the underlying substrate occur slowly. Multilayer nickel coatings are thus more protective than single-layer bright nickel coatings of equal thickness.

The rate of pit penetration through the nickel layers varies inversely with the number of microdiscontinuities in the chromium layer. Pit penetration may occur rapidly with low-porosity, conventional chromium. When corrosion takes place at a pore in conventional chromium, the large cathodic area of chromium surrounding the pore accelerates the corrosion of the nickel, and pitting may occur rapidly. With microdiscontinuous chromium, a large number of microscopic pores or cracks are deliberately induced in the chromium deposit so that corrosion can start at many sites. The available corrosion current has to be spread over a myriad number of tiny corrosion cells, so that the rate of corrosion of the nickel is greatly reduced. For example, the approximate depth of pitting of nickel after 16 h of CASS testing (ASTM B 368, "Copper-Accelerated Acetic Acid Salt Spray [Fog] Testing") was 10 to 20 μm with conventional chromium and 1 to 6 μm with microdiscontinuous chromium.

Corrosion studies conducted by plating suppliers, nickel producers, and groups such as ASTM Committee B-8 have confirmed that multilayer nickel coatings are significantly more protective than single-layer bright nickel coatings, that microdiscontinuous chromium coatings provide more protection than conventional chromium coatings, and that the corrosion protection of decorative, electroplated nickel-plus-chromium coatings is directly proportional to nickel thickness and to the ratio of semibright and bright nickel in multilayer coatings. Table 4 is based on the results of a study conducted at the LaQue Center for Corrosion Technology, Wrightsville Beach, NC, and it summarizes the types of coatings that protected standard panels from corrosion for more than 15 years outdoors in a severe marine atmosphere.

Table 4 Coating systems on steel giving best performance after 15 years of outdoor marine exposure and 96 h of CASS testing

Type and thickness of coating, µm			ASTM performance ratings[(a)]	
Copper	Nickel[(b)]	Chromium[(c)]	Outdoor marine, 15 years	CASS, 96 h
. . .	38d	1.5 mc	10/8	10/8
12	26d	1.5 mc	10/9	10/8
. . .	38d	0.25 mp	10/7	10/7
12	26d	0.25 mp	10/9	10/7

Note: CASS testing ("Copper-Accelerated Acetic Salt Spray [Fog] Testing") is conducted according to ASTM B 368.

(a) A two-number system has been adopted by ASTM for rating panels after corrosion testing. The first, the protection number, is based on the percentage of the base metal that is defective due to corrosion. A rating of 10 on steel indicates that the panel did not rust. The second, the appearance number, is similarly based on percentage of defective area, but it rates the extent to which corrosion of the base metal as well as superficial corrosion, detract from the overall appearance. Appearance ratings of 7, 8, or 9 indicate that 0.25 to 0.5%, 0.1 to .25%, or 0 to 0.1% of the area, respectively, is defective due to superficial staining and corrosion.

(b) d, double layer. The double-layer nickel coatings in the program differed in reactivity. For details see G.A. DiBari and F.X. Carlin, Decorative Nickel/Chromium Electrodeposits on Steel--15 Years Corrosion Performance Data, *Plating and Surface Finishing,* May 1985, p 128.

(c) mc, microcracked; mp, microporous. The type of microcracked chromium used in this study is based on the addition of selenium compounds to a conventional chromium bath to obtain microcracking. Consistent crack patterns were obtained at the chromium thicknesses given in the table.

Standards and Recommended Thicknesses. ASTM B 456 provides information on specific requirements for decorative nickel-plus-chromium coatings to achieve acceptable performance under five different conditions of service. The standard defines several classes of coatings that differ in thickness and type, and it classifies the various coating systems according to their resistance to corrosion. The standard specifies the requirements for double- and triple-layer nickel coatings (Table 3), and it gives the classification numbers of coatings appropriate for each service condition number. For example, Table 5 specifies decorative nickel-plus-chromium coatings on steel.

Table 5 Decorative nickel-plus-chromium coatings on steel

Service condition number (typical applications)	Coating designation[(a)]	Minimum nickel thickness, µm
SC 5--Extended very severe (exterior automotive where long-time corrosion protection is a requirement)	Fe/Ni35d Cr mc	35
	Fe/Ni35d Cr mp	35
SC 4--Very severe (exterior automotive, boat fittings)	Fe/Ni40d Cr r	40

	Fe/Ni30d Cr mp	30
	Fe/Ni30d Cr mc	30
SC 3--Severe (patio and lawn furniture, bicycles, hospital furniture and cabinets)	Fe/Ni30d Cr r	30
	Fe/Ni25d Cr mp	25
	Fe/Ni25d Cr mc	25
	Fe/Ni40p; Cr r	40
	Fe/Ni30p Cr mp	30
	Fe/Ni30p Cr mc	30
SC 2--Moderate service (stove tops, oven liners, office furniture, golf club shafts, plumbing fixtures and bathroom accessories)	Fe/Ni20b Cr r	20
	Fe/Ni15b Cr mp	15
	Fe/Ni15b Cr mc	15
SC 1--Mild (toaster bodies, interior automotive accessories, trim for major appliances, fans, light fixtures)	Fe/Ni10b Cr r	10

(a) b, electrodeposited single-layer bright nickel; d, double-layer or multilayer nickel coating; r, regular or conventional chromium; mc, microcracked chromium; mp, microporous chromium. The numerals in the designations denote the thickness of the nickel coating in microns. The thickness of the chromium is assumed to be 0.3 μm unless otherwise specified. When permitted by the purchaser, copper may be used as an undercoat for nickel, but it cannot be substituted for any of the part of the nickel specified. Results of several test programs have raised doubt about whether coating systems involving regular chromium are satisfactory for SC 4 and SC 3.

The service condition number characterizes the severity of the corrosion environment, 5 being the most severe and 1 being the least severe. The classification number is a way to specify the details of the coating in an abbreviated fashion. For example, the classification number Fe/Ni30d Cr mp indicates that the coating is applied to steel (Fe) and consists of 30 μm of double-layer nickel (d) with a top layer of microporous (mp) chromium that is 0.3 μm thick. (The thickness value of the chromium is not included in the classification number unless its thickness is different from 0.3 μm.) The type of nickel is designated by the following symbols: "b" for electrodeposited single-layer bright nickel, "d" for double- or multilayer nickel coatings, "p" for dull, satin, or semibright nickel deposits, and "s" for polished dull or semibright electrodeposited nickel. The type of chromium is given by the following symbols: "r" for regular or conventional chromium, "mp" for microporous chromium, and "mc" for microcracked chromium.

Decorative nickel-iron alloy plating processes were introduced to conserve nickel and to lower anode material costs by substituting a portion of the nickel with iron. Decorative nickel-iron alloy deposits have full brightness, high leveling, excellent ductility, and good receptivity for chromium. Nickel-iron can be plated on steel, brass, aluminum, zinc die castings, or plastic substrates in either barrel or rack equipment. The operation and the proprietary additives used in commercially available processes are similar to those in conventional bright nickel plating. In addition, the bath requires special additives to stabilize the ferrous and ferric ions so that hydroxide compounds do not form and precipitate. The stabilizers are either complexers or reducing agents, depending on the nature of the proprietary process. The processes should be controlled within the limits recommended by plating supply houses. Deposits on steel or copper that is subsequently chromium plated have had good acceptance for interior applications as a substitute for bright nickel. Decorative nickel-iron alloy deposits are not often used for outdoor applications where corrosion conditions are severe, because the deposits tend to form a fine, superficial brown stain relatively quickly. The rate at which this occurs depends on the iron content of the deposits, and those with less than 15% Fe have been used in outdoor applications.

Engineering and Electroforming Processes

Electrodeposited nickel coatings are applied in engineering applications to modify or improve surface properties, such as corrosion resistance, hardness, wear, and magnetic properties. Although the appearance of the coating is important and the plated surface should be defect-free, the lustrous, mirror-like deposits described in previous sections are not usually required. Nickel electroforming is the specialized use of the nickel plating process to produce or reproduce articles by electroplating onto a mandrel that is subsequently separated from the deposit.

Watts and Nickel Sulfamate Processes. The two most popular solutions for depositing engineering nickel coatings and for electroforming, Watts nickel and nickel sulfamate, have been included in Table 2. The table summarizes the chemical composition, operating conditions, and typical mechanical property data for deposits from these solutions. The Watts solution is relatively inexpensive and easy to control; it has already been discussed.

Nickel sulfamate solutions are widely used for electroforming because of the low internal stress of the deposits, high rates of deposition, and superior throwing power. Throwing power is the relationship between current distribution and uniformity of coating thickness, as influenced by geometric factors (the shape and relative positioning of anode and cathode), and by the electrochemical characteristics of the solution (conductivity, cathode polarization, and cathode efficiency). Throwing power is a measure of the extent to which a solution will produce deposits that are more uniform than those that would be produced in the absence of cathode polarization and cathode efficiency effects. Because of the very high solubility of nickel sulfamate, a higher nickel metal concentration is possible than in other nickel electrolytes, permitting lower operating temperatures and higher plating rates.

A small amount of nickel chloride is usually added to nickel sulfamate solutions to minimize anode passivity, especially at high current densities. If nickel chloride is not added, sulfur-containing nickel anode materials with about 0.02% S are essential to avoid anodic oxidation of the sulfamate ion, which can result in the uncontrolled and unpredictable production of sulfur-containing compounds that act as stress reducers and that cannot easily be removed from solution. Bromide ions, instead of chloride, are sometimes added to nickel sulfamate solutions to promote anode dissolution.

Nickel sulfamate is so soluble that it cannot be readily recrystallized from solution. It is commercially available as a concentrated solution, usually prepared by reacting high-purity nickel powder with sulfamic acid under controlled conditions. Nickel sulfamate plating solutions are more expensive than those based on commercial grades of nickel sulfate and nickel chloride. The extra cost of using solutions that are as pure as possible is more than offset by savings in the preliminary purification procedures necessary otherwise.

Prolonged use of sulfamate solutions at temperatures above 60 °C (140 °F) or at a pH of less than 3.0 can hydrolyze the nickel sulfamate to the less soluble form of nickel ammonium sulfate. The ammonium and sulfate ions produced from the hydrolysis increase the internal tensile stress and hardness of the deposits.

Nickel electrodeposited from a well-purified sulfamate bath containing no stress-reducing agent and operated at 46 °C (115 °F), a pH of 4.0, and a current density of 2.0 A/dm^2 (20 A/ft^2) has a residual tensile stress varying from 15 to 40 MPa (2 to 6 ksi). The stress in a deposit produced from a similarly operated Watts bath would be about 170 MPa (25 ksi).

Sulfamate nickel plating baths are especially useful for applications requiring low residual stress in the electrodeposited nickel, such as in electroforming, and for coating objects that are susceptible to fatigue cracking. Steel crankshafts that are nickel plated for resistance to corrosion and wear should be coated with a low-stress nickel deposit, such as sulfamate

nickel, to minimize loss of fatigue strength. The fatigue limit of nickel-plated steel is reduced almost proportionally to the amount of residual tensile stress in the nickel plate, and the use of compressively stressed deposits provides additional benefits.

Other nickel plating solutions for engineering applications are listed in Table 6, along with available mechanical properties of the deposits. Many of these solutions were developed to meet specific engineering requirements; all are used to a lesser extent than Watts and nickel sulfamate solutions.

Table 6 Other nickel plating solutions and some properties of the deposits

Type	**Composition[(a)],g/L**	**pH**	**Temperature, °C**	**Cathode current density, A/dm^2**	**Vickers hardness, 100 g load**	**Tensile strength, MPa**	**Elongation, %**	**Internal stress, MPa**
Fluoborate	Nickel fluoborate, 225-300 Nickel chloride, 0-15 Boric acid, 15-30	2.5-4	38-70	3-30	125-300	380-600	5-30	90-200
Hard nickel	Nickel sulfate, 180 Ammonium chloride, 25 Boric acid, 30	5.6-5.9	43-60	2-10	350-500	990-1100	5-8	300
All-chloride	Nickel chloride, 225-300 Boric acid, 30-35	1-4	50-70	2.5-10	230-260	620-930	4-20	275-340
All-sulfate	Nickel sulfate, 225-410 Boric acid, 30-45	1.5-4	38-70	1-10	180-275	410-480	20	120
Sulfate chloride	Nickel sulfate, 150-225 Nickel chloride, 150-225 Boric acid, 30-45	1.5-2.5	43-52	2.5-15	150-280	480-720	5-25	210-280
High sulfate	Nickel sulfate, 75-110 Sodium sulfate, 75-110 Ammonium chloride, 15-35 Boric acid, 15	5.3-5.8	20-32	0.5-2.5	. . .	. . .	. . .	. . .
Black nickel (sulfate bath)	Nickel sulfate, 75 Zinc sulfate, 30 Ammonium sulfate, 35 Sodium thiocyanate, 15	5.6	24-32	0.15	. . .	. . .	. . .	. . .
Black nickel	Nickel chloride, 75 Zinc chloride, 30	5.0	24-32	0.15-0.6	. . .	. . .	. . .	. . .

(chloride bath)	Ammonium chloride, 30 Sodium thiocyanate, 15							
Nickel phosphorus	Nickel sulfate, 170 or 330 Nickel chloride, 35-55 Boric acid, 0 or 4 Phosphoric acid, 50 or 0 Phosphorous acid, 2-40	0.5-3.0	60-95	2-5	. . .	. . .	. . .	. . .

(a) The formulas of the compounds in the table are as follows: nickel fluoborate, $Ni(BF_4)_2$; nickel sulfate, $NiSO_4{\cdot}6H_2O$; nickel chloride, $NiCl_2{\cdot}6H_2O$; boric acid, H_3BO_3; ammonium chloride, NH_4Cl; ammonium sulfate, $(NH_4)_2SO_4$; sodium sulfate, Na_2SO_4; phosphoric acid, H_3PO_4; phosphorous acid, H_3PO_3; zinc sulfate, $ZnSO_4{\cdot}7H_2O$; zinc chloride, $ZnCl_2$; sodium thiocyanate, NaSCN.

Fluoborate. The fluoborate solution listed in Table 6 can be used over a wide range of nickel concentrations, temperatures, and current densities. The fluoborate anion is aggressive, and some materials that contact the solution are chemically attacked. Silica filter aids cannot be used on a continuous basis, although cellulose filters are satisfactory. Lead, titanium, and high-silicon cast iron are readily attacked. Stainless steels containing 20% Cr, 25 to 30% Ni, and 2 to 3% Mo are resistant. Anode materials can be encased in Vinyon, polypropylene, or Orlon anode bags to prevent insoluble particles and anode residues from entering the plating solution; nylon bags are unsuitable. Only sleeve-type glass electrodes for pH measurement should be used because of the formation of relatively insoluble potassium fluoborate with permanent junction types. The mechanical and physical properties of deposits produced by the fluoborate bath are similar to those from Watts solutions. The nickel fluoborate solution has been used primarily for high-speed deposition of thick nickel.

Hard Nickel. Developed especially for engineering applications, this solution is applied where controlled hardness, improved abrasion resistance, greater tensile strength, and good ductility are required (without the use of sulfur-containing organic addition agents). Close control of pH, temperature, and current density is necessary for this bath to maintain the desired hardness values. The tensile strength increases and the ductility decreases with an increase in pH and a decrease in temperature. The internal stress is slightly higher than in deposits from Watts solutions. The disadvantages of the hard nickel bath are its tendency to form nodules on edges and the low annealing temperature (230 °C, or 450 °F) of its deposits. Hard nickel deposits are used primarily for buildup or salvage purposes. For optimum results, the ammonium ion concentration should be maintained at 8 g/L (1.1 oz/gal). In those applications where the part being plated is not going to be exposed to elevated temperatures in service, it is simpler to add organic compounds such as saccharin, p-toluene sulfonamide, p-benzene sulfonamide, or other carriers to Watts or sulfamate solutions to achieve hardness without increased internal stress. Because the additives introduce 0.03% S (or more), this approach cannot be used for parts that will be exposed to high temperatures where sulfur severely embrittles the nickel deposit.

All-Chloride. The principal advantage of the all-chloride bath (Table 6) is its ability to operate effectively at high cathode current densities. Other advantages include its high conductivity, its slightly better throwing power, and a reduced tendency to form nodular growths on edges. Deposits from this electrolyte are smoother, finer-grain, harder, and stronger than those from Watts solutions, and more highly stressed. Because of the partial solubility of lead chloride, lead cannot be used in contact with the all-chloride solution. Mists from this solution are corrosive to the superstructure, vents, and other plant equipment, if not well protected. The solution has been used to some extent for salvaging undersize or worn shafts and gears.

All-sulfate has been applied for electrodepositing nickel where the principal or auxiliary anodes are insoluble. For example, insoluble auxiliary or conforming anodes may be required to plate the insides of steel pipes and fittings. To prevent pitting, hydrogen peroxide may be added to all-sulfate solutions, provided they contain no wetting agents or organic stress reducers. Oxygen is evolved at insoluble anodes in the all-sulfate solution, and as a result, the nickel concentration and pH decrease during plating. The pH is controlled and the nickel ion concentration is maintained by adding nickel carbonate. Another procedure that has been used in low-pH solutions replenishes the nickel electrolytically

by employing a replenishment tank with nickel anodes; the current in the replenishment tank is periodically reversed to keep the nickel anodes actively dissolving in the absence of chlorides. The insoluble anodes in all-sulfate solutions may be lead, carbon, graphite, or platinum. If a small anode area is required, solid platinum (in the form of wire) may be used; for large anode areas, platinum-plated or platinum-clad titanium is recommended. In some forms, carbon and graphite are too fragile; lead has the disadvantage of forming loose oxide layers, especially if it is immersed in other solutions in the course of a plating cycle. In chloride-free solution, pure nickel is almost insoluble and may function as an internal anode if properly bagged.

Sulfate/Chloride. The sulfate/chloride solution given in Table 6 has roughly equivalent amounts of nickel sulfate and nickel chloride and was developed to overcome some of the disadvantages of the all-chloride solution. It has high conductivity and can be operated at high current densities. Although the internal stress of the deposits is higher than in deposits from Watts solutions, the stress is lower than in the all-chloride solution. The other properties are about midway between those for deposits from Watts and all-chloride solutions. Lead may not be used for equipment in contact with this solution because of the high chloride content.

High Sulfate. The high-sulfate bath was developed for plating nickel directly on zinc-base die castings. It may also be used to plate nickel on aluminum that has been given a zincate or comparable surface preparation treatment. The high sulfate and low nickel contents, together with the high pH, provide good throwing power with little attack of the zinc. The deposits are less ductile and more highly stressed than nickel deposited from a Watts bath. For this reason, high sulfate nickel is sometimes used as a thin undercoating for more ductile nickel. In general, the deposition of copper from a cyanide solution directly on zinc-base die castings prior to the deposition of nickel is simpler and more reliable.

Black Nickel. There are at least two formulations for producing black nickel deposits; these incorporate zinc and thiocyanate (CNS^-) ions. Table 6 gives the composition and operating conditions for a sulfate and a chloride black nickel plating bath. The process was developed for decorative reasons--color matching and blending. The black nickel deposit has little wear or corrosion resistance and is usually deposited over a layer of nickel deposited from a bright or dull nickel plating solution. It is in commercial use, but it is limited in its applications.

Nickel phosphorus solutions result in the electrodeposition of nickel phosphorus alloys that are analogous to electroless deposits using sodium hypophosphite as the reducing agent. The hardness of the electrolytic deposits can be increased by heat treatment in the same way that the hardness of electroless nickel deposits can be increased, with maximum hardness occurring at 400 °C (750 °F). The phosphorus content of the deposits is best controlled by frequent additions of phosphite or phosphorous acid. The electrodeposition of nickel phosphorus alloys is receiving increased attention because deposits with greater than 10% P are amorphous and therefore have enhanced resistance to corrosion.

Nickel Alloy Plating and Composites. Although discussion of alloy plating is beyond the scope of this article, it should be noted that nickel alloy plating processes of commercial importance include nickel-iron (without brighteners), nickel-cobalt, nickel-palladium, and tin-nickel. An alloy plating process that is growing in importance is zinc-nickel, containing 8 to 12% Ni. In addition, the incorporation of inert particles within a nickel matrix is possible, and coatings that incorporate silicon carbide, diamonds, mica, polytetrafluoroethylene, and other materials are being applied for engineering purposes. Detailed information is available in the articles "Nickel Alloy Plating" and "Zinc Alloy Plating" in this Volume.

Quality Control of Nickel Plating

Achieving high quality involves controlling the bath composition, the purity of the plating solution, and the thickness and uniformity of the deposits. Eliminating rejects, troubleshooting, and the testing of deposits are important aspects of process and product control.

Control of Solution Composition. Control of the composition of the plating bath is one of the most important factors contributing to the quality of nickel deposits. At the outset, the bath must be prepared to the specified composition, adjusted to the proper pH, and purified before use. Thereafter, the composition and pH of the solution must be controlled within specified limits, and contamination by metallic and organic substances must be prevented.

Purification Techniques and Starting Up a New Bath. Before any freshly prepared nickel plating bath is used, contaminants such as iron, copper, zinc, and organics present in trace quantities in commercial salts must be removed to obtain the best results. Several treatments are available for purifying a freshly prepared nickel plating solution.

High-pH treatment consists of adding nickel carbonate to the hot solution until a pH of 5.0 to 5.5 is obtained. This precipitates the hydroxides of metals such as iron, aluminum, and silicon, which in turn frequently absorb other impurities. Addition of hydrogen peroxide oxidizes iron to the ferric state, making it more easily precipitated at high pH, and frequently destroys organic impurities.

Treatment with activated carbon removes organic impurities.

Electrolytic purification removes most of the harmful metallic and organic impurities. A complete purification procedure for a Watts solution would comprise the following steps:

1. Use a separate treatment tank (not the plating tank) to dissolve the nickel sulfate and nickel chloride in hot water at 38 to 49 °C (100 to 120 °F) to about 80% of desired volume.
2. Add 1 to 2 m/L (0.8 to 1.6 pints/100 gal) of 30% hydrogen peroxide (agitate briefly and allow to settle for 1 h).
3. Add 1.2 to 2.4 g/L (1 to 2 lb/100 gal) activated carbon and agitate thoroughly.
4. Heat to 66 °C (150 °F), then add 1.2 to 2.4 g/L (1 to 2 lb/100 gal) of nickel carbonate to the solution, with agitation to adjust the pH to 5.2 to 5.5. More nickel carbonate may be required and the mixture should be stirred to assist the dissolution of the carbonate. Allow to settle 8 to 16 h.
5. Filtering into the plating tank.
6. Add and dissolve boric acid; add water to bring bath up to its desired volume.
7. Electrolytically purify by using a large area of nickel plated corrugated steel sheets as cathodes. The average cathode current density should be 0.5 A/dm^2 (5 A/ft^2), and treatment should continue until 0.5 to 1.3 A · h/L (2 to 5 A · h/gal) have passed through the solution. The solution should be agitated and the temperature held at 49 to 60 °C (120 to 140 °F). It is useful to prepare deposits at normal current densities at some point to check appearance, stress, and sulfur content. If not acceptable, continue dummying until the properties are acceptable.
8. Remove the dummy cathodes and adjust the pH of the solution to the desired value.

Controlling the Main Constituents. The following basic constituents of nickel plating baths must be regularly controlled: the nickel metal content; the chloride concentration; the boric acid; and any organic addition agents. Nickel metal concentration is maintained between 60 and 80 g/L (8.0 and 10.5 oz/gal) in most commercial applications. It is desirable to have a minimum of 23 g/L (3 oz/gal) of nickel chloride in the solution to promote anode corrosion. (The chloride content is not critical for anode corrosion when sulfur-activated anode materials are used.) Boric acid is the most commonly used buffering agent for nickel plating baths. Boric acid is effective in stabilizing the pH in the cathode film within the ranges normally required for best plating performance. It is available in a purified form and is inexpensive. Organic addition agents must be controlled within the limits specified by the suppliers of proprietary processes, and they must be replenished due to losses from dragout, electrolytic consumption, and the effects of carbon filtration (or batch treatment).

Procedures exist for chemical analysis of nickel, chloride, boric acid, and organic addition agents in nickel plating solutions, and modern instrumental techniques are available to monitor the main ingredients on a regular basis with improved precision. High-performance liquid chromatography is one of the improved techniques for controlling organics that is growing in popularity.

Controlling pH, Temperature, Current Density, and Water Quality. The pH of the nickel plating solution will rise during normal operation of the bath, necessitating regular additions of acid to maintain the pH within the prescribed limits. A decrease in pH accompanied by a decrease in nickel ion concentration indicates that the process is not functioning properly.

The operating temperature may have a significant effect on the properties of the deposits, and it should be maintained within specified limits (±2 °C) of the recommended value. In general, most commercial nickel plating baths are operated between 38 to 60 °C (100 to 140 °F).

The nickel plating process should be operated at specified current densities by estimating the surface area of the parts and calculating the total current required. The practice of operating the process at a fixed voltage is not recommended.

Controlling cathode current density is essential for accurately predicting average nickel thickness, for achieving uniform coating thickness on complicated shapes, and for producing deposits with consistent and predictable properties.

Since current density determines the rate of deposition, it must be as uniform as possible to achieve uniformly thick nickel deposits. The nickel plating solution has an electrical resistance, and almost all components to be plated have prominent surfaces that are nearer the anode than recessed areas. The current density is greater at the prominences because the anode-to-cathode distance is shorter and therefore has less electrical resistance. The apportioning of the current in this way is called *current distribution.* This means that the recessed areas receive a thinner nickel deposit than the prominent ones. Current distribution is controlled by proper rack design and proper placement of components on those racks, by the use of nonconducting shields and baffles, and by the use of auxiliary anodes, when necessary. With care, relatively good thickness distribution can be achieved.

The quality of the water used in making up the bath and in replacing water lost by evaporation is important. Demineralized water should be used, especially if the local tap water has a high calcium content (greater than 200 ppm). Filtering the water before it is added to the plating tank is a useful precaution to eliminate particles that can cause rough deposits.

Controlling Impurities. Inorganic, organic, and gaseous impurities may be introduced into nickel plating solutions during normal operations. Continuing efforts to eliminate the sources of these impurities from the plating shop can improve the quality of the deposits, as well as productivity and profitability. The presence of small quantities of inorganic or organic contamination may result in plating defects.

Inorganic contaminants arise from numerous sources, including nickel salts of technical grade, hard water, carryover from acid dip tanks, airborne dust, bipolar attack of metallic immersion heaters, corrosion of the tank material through cracks in the lining, corrosion of anode bars, and dirt from structures above the tank and from parts that fall into the solution and are not removed. The following table lists maximum limits for metallic impurities in nickel plating baths:

Contaminant	Maximum concentration, ppm
Aluminum	60
Chromium	10
Copper	30
Iron	50
Lead	2
Zinc	20
Calcium	[a]

Note: The limits may be different when several contaminants are present at the same time, and complexing agents are a part of the solution formulation.

(a) pH-dependent; will precipitate at the saturation point

The degree of contamination by many inorganic materials may be controlled by continuous filtration and dummying, that is, by electrolysis of the plating solution at 0.2 to 0.5 A/dm^2 (2 to 5 A/ft^2). This may be accomplished on a batch basis or continuously by installing a dummy compartment and overflow dam at one end of the plating tank. Solution from the filter is pumped into the bottom of the dummy compartment, up past the corrugated cathode sheets, over the dam, into the plating section of the tank, out through a bottom outlet at the far end of the tank, and back to the filter. Solid particles and soluble metallic impurities (for example, copper, zinc, lead) are removed simultaneously by this procedure.

Organic contaminants may arise from many sources, including buffing compounds, lubricating oil dropped from overhead equipment, sizing from anode bags, weaving lubricants on plastic anode bags, uncured rack coatings or stopoff lacquers, adhesives on certain types of masking tape, decomposition products from wetting agents, organic stabilizers in hydrogen peroxide, paint spray, and new or patched rubber tank linings. Many organic contaminants can be effectively removed from nickel plating solutions by adsorption on activated carbon on either a batch or a continuous basis. On a batch basis, the solution is transferred to a spare tank, heated to 60 to 71 °C (140 to 160 °F), stirred for several hours with a slurry of 6 g/L (5 lb/100 gal) minimum of activated carbon, permitted to settle, and then filtered back into the plating tank. It is usually necessary to do a complete chemical analysis and adjust the composition of the solution after this type of treatment.

For solutions in which organic contamination is a recurring problem, continuous circulation of the solution through a filter, coated at frequent intervals with small amounts of fresh activated carbon, is recommended. When continuous carbon filtration is used, the wetting agent in the solution must be replenished and controlled more carefully, to prevent pitting of the nickel deposits.

Gaseous contamination of nickel plating solutions usually consists of dissolved air or carbon dioxide. Dissolved air in small amounts may lead to a type of pitting characterized by a teardrop pattern. Dissolved air in the plating solution usually can be traced to entrainment of air in the pumping system when the solution is circulated. If this occurs, the circulating pump and valves should be checked and modified, if necessary. Nickel plating solutions can be purged of dissolved air by heating to a temperature at least 6 °C (10 °F) higher than the normal operating temperature for several hours. The solution is cooled to the operating temperature before plating is resumed. Dissolved carbon dioxide in a nickel plating solution is usually found after nickel carbonate has been added to raise the pH, and it is liberated from warm nickel plating solutions after several hours. If solutions containing carbon dioxide are scheduled for immediate use, they should be purged by a combination of heating and air agitation for approximately 1 h at 6 °C (10 °F) or more above the normal plating temperature.

Effects of Impurities on Bright Nickel Plating. The presence of impurities is especially troublesome in decorative nickel plating. Contamination by zinc, aluminum, and copper is most often caused by the dissolution of zinc-base die castings that have fallen from racks into the plating tank and have been permitted to remain there. Inadequate rinsing before nickel plating increases the drag-in of metallic elements. The presence of cadmium and lead may be attributed to a number of sources, including lead-lined equipment and tanks, impure salts, and drag-in of other plating solutions on poorly rinsed racks. Chromium is almost always carried into the nickel solution on rack tips that have not been chromium stripped, or on poorly maintained racks that have been used in a chromium plating tank and have trapped chromium plating solution in holes, pockets, and tears in the rack coating.

Metallic contaminants affect bright nickel deposition in several ways. Aluminum and silicon produce hazes, generally in areas of medium to high current density. Aluminum and silicon may also cause a fine roughness called "salt and pepper" or "stardust." Iron produces various degrees of roughness, particularly at high pH. Calcium contributes to needlelike roughness as a result of the precipitation of calcium sulfate when calcium in solution exceeds the saturation point of 0.5 g/L (0.06 oz/gal) at 60 °C (140 °F). Chromium as chromate causes dark streaks, high-current-density gassing, and possibly peeling. After reduction to the trivalent form by reaction with organic materials in the solution or at the cathode, chromium may produce hazing and roughness effects similar to those produced by iron, silicon, and aluminum. Copper, zinc, cadmium, and lead affect areas of low current density, producing hazes and dark-to-black deposits.

Organic contaminants may also produce hazes or cloudiness on a bright deposit, or they can result in a degradation of mechanical properties. Haze defects may appear at any current density, or they may be confined to narrow current density ranges.

Mechanical defects producing hairline cracks, called *macrocracking,* may be encountered if the coating is sufficiently stressed as a result of solution contamination. These cracks usually appear in areas of heavier plating thickness (higher current density) but are not necessarily confined to those areas.

Eliminating Rejects/Troubleshooting. The production of defective plated parts or rejects may be associated with the presence in solution of soluble and insoluble impurities. The nature of the coating defect is often an indication of the source of the problem. Common defects include roughness, pitting, blistering (often associated with poor preparation of the surface prior to plating), high stress and low ductility, discoloration, burning at high-current-density areas, and failure to meet thickness specifications.

Roughness is usually caused by the incorporation of insoluble particles in the deposit. In bright nickel baths, chlorine generated at an auxiliary anode that is close to the cathode can react with organic additives to form an insoluble material that is incorporated in the deposit. Insoluble particles may enter the solution from many sources: incomplete polishing of the base metal so that slivers of metal protrude from the surface, incomplete cleaning of the surface so that soil particles remain on the surface, detached flakes of deposit from improperly cleaned racks, dust carried into the tank from metal polishing operations and other activities, insoluble salts and metallic residues from the anode, and others.

Roughness from incomplete polishing, cleaning, and inadequate rack maintenance is avoided by good housekeeping, regular inspection, and control. Roughness caused by dust can be controlled by isolating surface preparation and metal polishing operations from the plating area, by providing a supply of clean air, and by removing dirt from areas near and above the tanks. Roughness caused by the precipitation of calcium sulfate can be avoided by using demineralized water. Continuous filtration of the plating solution so as to turn over the solution at least once an hour is important for minimizing roughness problems. Anode residues must be retained within anode bags, and care should be taken not to damage the bags or allow the solution level to rise above the tops of the bags.

Pitting is caused by many factors, including adhesion of air or hydrogen bubbles to the parts being plated. Air should be expelled as already mentioned. Pitting from adherent hydrogen bubbles can result from a solution that is chemically out of balance, has too low a pH, or is inadequately agitated. Other sources of pitting include incorrect racking of complicated components, too low a concentration of wetting or antipitting agents, the use of incompatible wetting agents, the presence of organic contaminants, the presence of copper ions and other inorganic impurities, incomplete cleaning of the base material, and incomplete dissolution of organic additives that may form oily globules. Pitting is therefore avoided by maintaining the composition of the plating solution within specified limits, controlling the pH and temperature, and preventing impurities of all kinds from entering the solution.

Blistering may be associated with poor adhesion resulting from poor or incorrect surface preparation prior to plating. Nickel can be deposited adherently on most metals and alloys, plastics, and other materials by following standard methods of preparation and activation, including the proper use of intermediate deposits such as cyanide copper, acid copper, and acid nickel chloride strikes. Standard procedures for the preparation of materials prior to electroplating can be found in handbooks and in the *Annual Book of ASTM Standards,* Volume 0.205. Blistering may also be related to incomplete removal of grease, dirt, or oxides, formation of metal soaps from polishing compounds, or formation of silica films from cleaning solutions. In the case of zinc-base die castings or aluminum castings, blistering during or immediately after plating may be due to surface porosity and imperfections that trap plating solution under the coating.

High stress and low ductility usually occur when organic addition agents are out of balance, and also because of the presence of organic and inorganic impurities. Solutions must be maintained in a high state of purity.

Discoloration in low-current-density areas is most likely the consequence of metallic contamination of the plating solution. The effects can be evaluated systematically by plating over a reproducible range of current densities on a Hull cell cathode. Hull cells are available from plating supply houses and are shaped so that nickel can be deposited onto a standard panel over a predictable range of current densities. The variation in current density over the face of the panel is achieved by placing the panel at a specified angle to the anode. Bent panels that are L-shape and plated with the recessed area facing the anode can also be used to assess discoloration at low-current-density areas, and they may provide information on roughness problems.

Burning at high current densities can be caused by applying the full load on the rectifier to the lowest parts on a rack as it is lowered into the tank. This can be controlled by applying a reduced load or ramping the current during immersion of the rack. Burning can also be caused by exceeding the recommended maximum cathode current density, the presence of phosphates in solution introduced via contaminated activated carbon, or incorrect levels of organic additives.

Failure to meet thickness specifications is most frequently due to the application of too low a current and/or too short a plating time. This can be avoided by measuring the area of the parts to be plated, then calculating the total current required for a specified current density and plating for the appropriate time (see Table 1). Another major cause of failure to meet thickness requirements is nonuniform distribution of current leading to insufficient deposition in low-current-density areas. Poor electrical contacts and stray currents can also cause thin deposits, and anode and cathode bars, hooks, and contacts should be kept clean.

Controlling and Testing Deposit Properties. The requirements for testing electrodeposited nickel coatings may vary significantly, depending on the application. In almost all decorative applications, the appearance and the thickness of the deposit should be controlled and monitored on a regular basis. The plated surface must be free of defects such as blisters, roughness, pits, cracks, discoloration, stains, and unplated areas. It must also have the required finish--bright, satin, or semibright. Quality can only be maintained by checking the thickness of a specified number of plated parts. In decorative, electrodeposited multilayer coatings, it is also important to control the sulfur contents of the deposits, the relative thicknesses of individual layers, the ductility of the semibright nickel layer, and the difference in the electrochemical potentials between individual layers. Requirements for corrosion performance and adhesion may also be specified and may require additional testing.

In engineering and electroforming applications, it may be necessary to monitor the mechanical properties, including hardness, tensile strength, ductility, and internal stress, as well as wear resistance and other properties. Some of the more important test methods are briefly outlined below. Additional details can be found in the standard test methods collected in the *Annual Book of ASTM Standards.*

Thickness may be measured using a variety of techniques. The coulometric method described in ISO 2177 and ASTM B 504 can be used to measure the chromium and nickel thicknesses, as well as the thickness of copper undercoats, if present. The coulometric method measures the quantity of electrical energy required to deplate a small, carefully defined area of the component under test. A cell is sealed to the test surface and filled with the appropriate electrolyte, and a cathode is inserted. The component is made the anode, and the circuit is connected to the power supply via an electronic coulometer. By integrating time in seconds with the current passing, the electronic coulometer provides a direct reading in coulombs; modern instruments provide a direct reading of thickness. The completion of the deplating is shown by a marked change in the applied voltage. For routine control of production, it is convenient to monitor nickel thickness nondestructively by means of a magnetic gage, calibrating the gage at intervals with standard samples. Instruments for measuring thickness by beta backscatter, X-ray spectrometry, and eddy current techniques are also available. The traditional method of measuring thickness by microscopic examination of a metallographically prepared cross section of the plated part is still employed, but it is time-consuming, expensive, and destructive.

The simultaneous thickness and electrochemical potential (STEP) test was developed to measure the difference in electrochemical potential between semibright and bright nickel layers in multilayer nickel deposits on parts that are plated in production. It is similar to the coulometric method just described. By including a reference electrode in the circuit, however, it is possible to measure the electrochemical potential of the material being dissolved at the same time that the thickness of the individual layers is being measured. For example, with a double-layer nickel coating, a relatively large change in potential occurs when the bright nickel layer has dissolved and the semibright nickel layer begins to be attacked. The potential difference is related to the overall corrosion resistance of the double-layer coating and should be greater than 100 mV. Details can be found in ASTM B 764.

Corrosion testing may be specified and may require the plater to perform accelerated corrosion tests on a specified number of production parts as part of an overall quality assurance requirement. Three accelerated corrosion tests are recognized internationally: the Copper-Accelerated Acetic Acid Salt Spray (CASS), the Corrodkote, and the Acetic Acid Salt Spray tests. The CASS test is the one most widely used. The CASS and Corrodkote tests were developed when conventional chromium was the only type of chromium available; when the accelerated tests are used to evaluate microdiscontinuous chromium coatings, the surface appearance deteriorates more rapidly than in real-world environments. Details of these three tests can be found in ISO 1456 as well as in ASTM standards. The salt spray tests involve the application of the corrosive solution in the form of a spray or fog inside a fog cabinet or room made or lined with glass, rubber, or resistant plastics. The Corrodkote test involves applying a corrosive slurry to parts and exposing them to high, controlled humidity in a suitable chamber or cabinet; the slurry is formulated to simulate road mud containing corrosive salts. The CASS and Corrodkote tests were developed to control the quality of decorative, electrodeposited nickel-chromium-plated parts for exterior automotive use under severe conditions of corrosion and abrasion. CASS and other corrosion test requirements are specified in ASTM B 456 for nickel-plus-chromium coatings applied to steel, zinc alloys, or copper alloys. Similar information for nickel-plus-chromium coatings on plastics is given in ASTM B 604.

Ductility testing is used in decorative nickel plating to test that the percent elongation of semibright nickel deposits is greater than 8, and to verify that bright nickel solutions are in good working condition. The simple test described in ISO 1456 and in ASTM B 489 is based on bending a test strip of the deposit over a mandrel of specified diameter until the two ends of the strip are parallel. Other tests based on hydraulic or mechanical bulge testing are available. The percent elongation can also be determined by traditional mechanical testing by machining a test sample from relatively thick electroformed nickel and subjecting it to a tensile test. Because ductility is affected by the thickness of the coating, ductility should be measured at the actual thickness specified in a specific end use.

Other useful tests described in ASTM standards include adhesion (B 571), internal stress measurements with the spiral contractometer (B 636), and microhardness testing (B 578), among others.

Nickel Anode Materials

Most nickel plating processes are operated with soluble nickel anode materials. Nickel from the anode is converted into ions that enter the plating solution to replace those discharged at the cathode. In addition, the anode distributes current to the parts being plated and influences metal distribution.

The simplest way to satisfy anode requirements is to suspend nickel bars from hooks placed on an anode bar so that the nickel, not the hook, is immersed in the plating solution. Nickel anode materials are encased in cloth anode bags to prevent insoluble anode residues from entering the solution and causing roughness at the cathode. The use of bars or electrolytic nickel strip is still practiced but has been supplanted in most regions of the world by the use of titanium anode baskets. The baskets used in nickel plating are generally made of titanium mesh strengthened by solid strips of titanium at tops, bottoms, and edges. The baskets are encased in cloth anode bags, suspended on the anode bar by hooks that are an integral part of the baskets, and loaded with small pieces of nickel. The mesh facilitates the free flow of plating solution. Baskets that incorporate hoppers at the tops facilitate basket loading and help prevent pieces of nickel from falling into the tank.

Titanium anode baskets were quickly accepted because of their many advantages. The basket anode is large and unchanging, ensuring a uniform anode area giving constant current distribution and consistent thickness for repeat batches of the same work. Anode maintenance involves topping-up the load to keep the baskets filled. Conforming baskets can be made in virtually any size and shape. The anode-to-cathode distance can be made constant, thereby contributing to good current distribution. Lowest-cost, primary forms of nickel can be used to fill the baskets. Baskets can be semiautomatically or automatically filled with nickel, and that practice is growing in progressive plating shops. One limitation is that titanium cannot be used in concentrated fluoborate solutions or those containing fluoride ions; small amounts of fluoride in solution activate titanium, causing it to corrode.

The available forms of nickel for titanium baskets include high-purity electrolytic nickel squares about 25 × 25 mm, pure electrolytic nickel in button-like shapes about 22 mm in diameter, and sulfur-activated, electrolytic nickel button-shape pieces about 25 mm in diameter. Other popular forms of nickel for plating with baskets are made in spherical shapes by a gas-refining process; the spherical forms are also available in sulfur-free and sulfur-containing grades.

The sulfur-activated forms dissolve relatively uniformly at high current densities and at 100% anode efficiency even in the absence of chloride ions, whereas sulfur-free forms dissolve nonuniformly and require the presence of chloride ions in solution to dissolve efficiently. The need for chloride ions is due to the tendency for pure nickel to become passive in nickel sulfate solutions. Although the tendency for passivity persists even in the presence of chlorides, the chloride ion attacks the passive oxide film that forms when current flows through the anode, and nickel can be dissolved through pits on the surface. The sulfur-containing materials do not form oxide films, and they dissolve at low anode potentials. The small amount of sulfur in the nickel lowers the surface resistance to current flow, the practical effect being to reduce power costs. The unique advantage of the spherical forms of nickel is product flowability, which facilitates automatic basket loading and filling of conforming, semicylindrical, and other complicated basket shapes.

The anode affects the quality of nickel primarily through its effect on current distribution and thickness uniformity. Most anode materials available today are made to strict specifications of purity and are unlikely to introduce significant amounts of impurities into the solution.

Environmental, Health, and Safety Considerations

Strict environmental regulations are being imposed on the plating industry worldwide. The major problem facing nickel platers is to prevent nickel and other metallic ions from entering the environment via plant effluents. The most widely used method of removing metallic elements from effluents is to precipitate nickel and other metals in sludges as hydroxides or sulfides. The solid waste is then disposed of in landfills. Because the number of landfill sites is limited, and because disposal of solid waste is expensive, the recovery of metallic elements by applying reverse osmosis, ion exchange, electrotwinning, and other methods is economically appealing. Nickel producers accept nickel-containing sludges for recycling through smelters or special plants. The recovery of metallic elements is technically possible and will become important in the future.

Environmental regulations vary from state to state. Platers need to become familiar with all applicable local regulations and comply with them. Although there was great resistance to compliance in the early 1970s, most electroplaters in the United States are complying with existing regulations. In some cases, the recycling and recovery of salts and metals, coupled with the conservation of water and energy, have led to economies in plating operations that partially offset the cost of compliance.

The adoption and enforcement of strict environmental regulations arises from concern with the possible effects of metal contaminants on human health. Although the general perception is that these health effects are completely understood, the reality is that our knowledge is extremely limited. It is only when metals are present in high concentrations and in very specific forms that they are definitely known to be toxic.

In the nickel plating shop, three types of exposure are possible: Nickel and its compounds may be inadvertently ingested, nickel-containing solutions may be allowed to remain on the skin for long periods of time, and nickel and its compounds may be taken into the body by breathing. Although nickel and its compounds are not considered acutely toxic, it is advisable to avoid ingesting even small amounts of these substances by taking some simple precautions--wearing work gloves, washing one's hands before eating, and not eating in the workplace. Some workers may develop a skin rash or dermatitis after persistent contact with nickel and its salts. People who have become so sensitized should avoid contact with nickel and its compounds. To avoid becoming sensitized, one should limit skin contact with nickel and its compounds. In the plating shop, this may mean wearing work gloves and washing one's hands immediately after coming in contact with nickel plating solutions.

On the basis of available information, enhanced risk of cancer appears to be confined to the inhalation of high concentrations of dusts containing nickel subsulfides and oxides under conditions previously existing in certain nickel refineries. Although similar health problems have not been observed in plating shops and other workplaces where nickel is found, it is recommended that precautions be taken to avoid dispersing nickel-containing dusts or sprays into the air. Airborne concentrations of nickel should be kept below the permissible exposure limits established by law. This is not only the law, but good common sense. Simple housekeeping and personal hygiene can help prevent the release of toxic substances to the environment and minimize the possible effects of metallic contaminants on human health.

Iron Plating

Sue Troup-Packman, Hughes Research Laboratories

Introduction

IRON has been electrodeposited for many years. One of the earliest references to iron electroplating is in Langbein's *Electrodeposition of Metals,* published in 1894 as the English translation of a German treatise. In that translation there is a reference to "Mr. Alfred Smee (who made) many discoveries in the deposition of antimony, platinum, gold, silver, iron, copper and zinc. In publishing his experiments, in 1841, he originated the very appropriate term 'electro-metallurgy' for the process of working in metals by means of electrolysis" (Ref 1). A paper published in 1930 was titled "The Production of Electrolytic Iron Printing Plates" (Ref 2). It appears, though, that the largest body of published papers and patents were written in the 1950s and 1960s, although a small number of new papers on this topic are published every year.

Iron has been electroplated from a variety of electrolytes. These include chloride, sulfate, sulfamate, fluoroborate, sulfonate, and various combinations of these electrolytes. Perhaps the widest use of iron plating has been in electroforming, where thicknesses of 6 mm (0.25 in.) are common. The bath parameters of these electroplating solutions are as varied as the parts that are plated in them, and the resulting coatings have widely divergent characteristics according to the specific characteristics desired in the finished product.

Acknowledgements

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References

1. G. Langbein and W. Brannt, *A Complete Treatise on the Electro-Deposition of Metals,* Henry Carey Baird, 1894, p 5
2. W. Safranek, *The Properties of Electrodeposited Metals and Alloys,* 2nd ed., American Electroplaters and Surface Finishers Society, 1986, p 215

Advantages and Limitations

Iron is the least expensive metal available. This is partly because it makes up 5% of the earth's crust, making it second in abundance to aluminum among the metals and fourth in abundance behind oxygen, silicon, and aluminum among the elements. Iron, which largely constitutes the core, is the most abundant element in the Earth as a whole (about 35%). This abundance, plus the fact that iron is easily extracted from concentrated ore sources, is what makes it so inexpensive. In addition, the human body contains approximately 4.5 g of iron. The average adult human requires 10 to 20 mg of dietary iron each day to maintain good health. This human requirement, coupled with the vast abundance of iron around us, makes iron an unlikely candidate for environmental controls, at least on the metal itself. Also, the physical properties of the deposited metal can be altered very easily by adjustments in electrolyte, temperature, pH, and addition agents. The ability to "design" a coating to meet a specific need, coupled with the environmental friendliness of iron, has caused a recent upsurge in interest in this electrodeposited metal.

The primary limitations of iron electrodeposition are the innate corrosion properties that affect all iron and steel, although electrodeposited iron appears to be more corrosion resistant than ordinary iron, probably because of its higher purity. Even with better resistance, a protective coating of some kind must be applied to the deposit to prevent corrosion.

An additional limitation seems to be obtaining consistent properties from one batch of parts to another. There is evidence that iron baths function best when they are run in a full production mode. Intermittent operation creates problems in restoring the electrolyte to proper operating condition. Many baths are highly corrosive to ordinary equipment. Pitting and roughness can be a problem if the bath is not controlled properly. Extreme brittleness can result from the presence of codeposited hydrated Fe(III) or Fe(II) oxide as well as codeposition of organic additive breakdown products.

Principal Applications

Today the principal applications for electrodeposited iron are in the production of solder gun tips, the electroplating of iron onto aluminum automobile engine parts, and the electroforming of iron foils for certain magnetic applications. In the past there was a large market for electroformed stampers, engraving plates, and textile rollers, but these iron applications have been almost totally replaced by nickel plating. However, as environmental concerns about nickel increase, a return to iron plating will become increasingly probable. Interest is increasing in the use of nickel-iron alloys containing up to 40% Fe as a substitute for the more expensive and potentially toxic nickel deposits.

Process Description

Table 1 shows some typical iron plating bath parameters. It should be noted that the addition of various organic additives can change the properties of the deposit to a high degree. These are addressed in the Section "Properties of the Deposited Materials and Modified Surfaces" in this article.

Table 1 Typical iron plating solutions

Bath type	Composition	pH	Temperature, °C	Current density

	Component	g/L	Molarity		°C	A/m^2	A/ft^2
Sulfate	Fe^{++}	48	0.86	2.8-3.5	32-65	215-430	20-40
	[a]	240	0.86				
Double sulfate	Fe^{++}	36-51	0.64-0.92	2.5-3.5	24-65	215-645	20-60
	[b]	250-400	0.64-1.2				
Chloride	Fe^{++}	84-125	1.5-2.25	0.5-1.0	85 min	215-1075	20-100
	[c]	300-450	1.5-2.25				
	[d]	300	2.7				
Sulfate-chloride	Fe^{++}	60	1.08	2.5-3.5	27-70	215-540	20-50
	[a]	250	0.9				
	[c]	36	0.18				
	[e]	20	0.37				
Fluoborate	Fe^{++}	55	1	3.0-3.5	57-63	430-970	40-90
	[f]	227	1				
	[g]	10	0.17				
Sulfamate	Fe^{++}	75	1.35	2.5-3.5	60 max	215-430	20-40
	[h]	30-38	0.25-0.32				
Sulfonate	Fe^{++}	150	2.7	1.2-1.8	60-82	430-860	40-80
	[g]	50	0.81				
	[i]	275	2.7				

(a) Ferrous sulfate (7-hydrate).

(b) Ferrous ammonium sulfate (6-hydrate).

(c) Ferrous chloride (4-hydrate).

(d) Calcium chloride.

(e) Ammonium chloride.

(f) Ferrous fluoborate.

(g) Sodium chloride.

(h) Ammonium sulfamate.

(i) Ferrous sulfonate

In addition, there are many baths that have been reported for both the electrolytic and electroless deposition of iron alloys. Alloys are attracting more interest as replacements for nickel, but this chapter will address only electrodeposited pure iron deposits.

Processing Equipment

Because many of the electrolytes used in iron plating are very corrosive, it is necessary to choose the most corrosion-resistant materials for the processing equipment. This means at least a lined steel or stainless steel tank. However, considering the potential problems with liners, it is advisable to have tanks made out of polypropylene. The high temperatures of some of the baths make polyethylene a poor choice for tank construction.

Filters should be chlorinated polyvinyl chloride or polypropylene. Magnetically coupled pumps do not work well because of the high molar concentration of most of the solutions. Centrifugal pumps require seals, which do not hold up well in hot acidic solutions. In-tank pump and filter assemblies are highly recommended because any solution that leaves the tank and dries leaves a red-brown stain that can be a major problem in maintaining good housekeeping. There should be provision for regular carbon treatment. Care must be exercised to prevent the pump from aspirating air that aggravates the problem of oxidation.

Agitation can be mechanical or provided by the pump and filter. Air agitation should not be used because it will increase the oxidation of the ferrous to ferric iron that causes brittle, dark deposits.

Heaters should be Teflon-covered titanium except for those to be used in fluoroborate baths, which should be Teflon-coated stainless steel. Steam-heated tanks usually do not get enough for baths with higher temperatures, but they are acceptable for lower-temperature baths.

Anodes should be pure electrolytic iron (often called ARMCO iron) and should be bagged with glass fiber (except in fluoborate solutions) or Dynel anode bags to retain the sludge that comes from the anodes. In certain cases low-carbon steel anodes can be used, but these can cause incorporation of carbon into the deposit, which could cause the deposit to be very hard. This could be a problem if one of the required deposit characteristics is low hardness.

Properties of the Deposited Materials and / or Modified Surfaces

Table 2 shows some of the characteristics of deposits produced in various baths. It also shows a few instances where postplate heat treatment was used to change the stress characteristics of a deposit and some of the changes that additives can make in a deposit.

Table 2 Properties of electrodeposited iron coatings

Basic bath	Additives	Ultimate tensile strength		Elongation, %	Hardness, HV
		MPa	ksi		
Sulfate	None	572-614	83-89	3.0-3.5	250
	NaCl	354	51.4	5.5	200
	Boric acid + urea	. . .	. . .	. . .	480-720
	Oxalic acid	. . .	. . .	. . .	600-615
	NaCl + citric acid[(a)]	. . .	. . .	. . .	1000-1100
Double sulfate	NaCl + antioxidant	. . .	. . .	. . .	600-700
Chloride	None	421-434	61-63	5.0-18.0	<100
	NaCl	448-593	65-86	4.0-18.0	150-530
	Glycerol	786-883	114-128	. . .	360-380
Sulfate-chloride	Amidopyrine[(b)]	. . .	. . .	. . .	500-750
Fluoborate	Boric acid	. . .	. . .	. . .	575
Sulfamate	Formic acid[(c)]	676-1068	98-155	. . .	1200-1500
Sulfonate	Antioxidant 15 g/L	. . .	. . .	. . .	650-750
	Antioxidant 1.5 g/L	. . .	. . .	. . .	350-400

(a) Properties are for parts stress relieved by heat treatment for 1 h at 250 °C (480 °F).

(b) Properties are for parts stress relieved by heat treatment for 2 h at 200-300 °C (392-572 °F).

(c) Properties are for parts stress relieved by heat treatment for 24 h at 190 °C (374 °F).

Other additives can be used in various combinations with various baths. Organic additives (acetic acid, arginine, dextrin, glycerin, glycine, saccharin, sugar, and thiourea) are grain refiners as a general rule. They induce stress by the inclusion of their breakdown products in the coating. Inorganic additives (manganese chloride and potassium chloride) increase conductivity. A wetting agent (sodium lauryl sulfate) can be used to reduce pitting. The additive characteristics overlap each other and can change with current density, temperature, pH, and concentration.

References cited in this section

3. F. Lowenheim, *Electroplating,* McGraw-Hill Book Co., 1978, p 333-341

4. S.T. Packman, unpublished data

Environmental Considerations

Iron metal does not pose any special waste disposal considerations unless associated radicals are hazardous (Ref 3). In fact, most publicly owned treatment works (POTWs) like to see iron introduced into the sewer system because it acts as a "getter" for the sulfides in the system, thereby reducing the hydrogen sulfide that can form. The only waste treatment required for iron baths is the adjustment of the pH to a value within the operating range specified in a facility's waste disposal permit. The only exception to this rule is the fluoroborate bath, which could introduce fluorides to the waste disposal system. Most POTWs have fluoride limits that have to be considered when designing a waste disposal system. Boron also has limits in some geographical areas. Local permitting agencies can provide detailed information. Compared to other metal finishing operations, iron is very easy to keep in compliance.

Reference cited in this section

3. F. Lowenheim, *Electroplating,* McGraw-Hill Book Co., 1978, p 333-341

Health and Safety Considerations

As in all metal finishing operations, good judgment should be exercised when operating an iron plating bath. Eye protection, clothing protection, and gloves should be used. Most of the baths are highly corrosive and can have detrimental effects on surrounding equipment. This is especially true of the chloride and fluoroborate baths. High corrosion potentials coupled with current efficiencies in the range of 82 to 87% probably indicate that air emission equipment is necessary. The sulfate, sulfamate, and sulfonate baths are less corrosive and, even though they run at low pH, should require only general ventilation equipment.

Cadmium Plating

Revised by Milton F. Stevenson, Sr., Anoplate Corporation

Introduction

Electrodeposits of cadmium are used to protect steel and cast iron against corrosion. Because cadmium is anodic to iron, the underlying ferrous metal is protected at the expense of the cadmium plate even if the cadmium becomes scratched or nicked, exposing the substrate.

Cadmium is usually applied as a thin coating (less than 25 μm or 1000 μin. thick) intended to withstand atmospheric corrosion. It is seldom used as an undercoating for other metals, and its resistance to corrosion by most chemicals is low.

Besides having excellent corrosion protective properties, cadmium has many useful engineering properties, including natural lubricity. When corrosion products are formed on cadmium-electroplated parts, they are not voluminous, and there is minimal change in dimension. These two properties are responsible for the wide use of cadmium on moving parts or threaded assemblies.

Cadmium has excellent electrical conductivity and low contact resistance. Noncorrosive fluxes can be used to produce top-quality soldered sections. Steel that is coated with cadmium can be formed and shaped because of the ductility of the cadmium. Malleable iron, cast iron, powdered metals, and other hard-to-plate surfaces can be coated with cadmium, and materials used for adhesives bond very well to cadmium-coated surfaces.

Cadmium is highly toxic, and health, safety, and environmental concerns are driving the reduction or elimination of its use for many applications. See the section "Toxicity of Cadmium" in this article and the article "Cadmium Elimination" in this Volume for more information.

Plating Baths

Most cadmium plating is done in cyanide baths, which generally are made by dissolving cadmium oxide in a sodium cyanide solution. Sodium cyanide provides conductivity and makes the corrosion of the cadmium anodes possible.

Cyanide Baths. Compositions and operating conditions of four cyanide baths are given in Tables 1(a) and 1(b). Note that for each of these baths a ratio of total sodium cyanide to cadmium metal is indicated; maintenance of the recommended ratio is important to the operating characteristics of the bath.

Table 1(a) Compositions of cadmium plating cyanide solutions

Solution No.	Ratio of total sodium cyanide to cadmium metal	Composition[(a)]									
		Cadmium oxide		Cadmium metal		Sodium cyanide		Sodium hydroxide[(b)]		Sodium carbonate[(c)]	
		g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal
1	4:1	23	3	19.8	2.62	78.6	10.4	14.4	1.90	30-75	4-10
2	7:1	23	3	19.8	2.62	139	18.4	14.4	1.90	30-45	4-6
3	5:1	26	3.5	23.1	3.06	116	15.3	16.6	2.19	30-60	4-8

(a) Metal-organic agents are added to cyanide solutions to produce fine-grain deposits. The addition of excessive quantities of these agents should be avoided, because this will cause deposits to be of inferior quality and to have poor resistance to corrosion. The addition of these agents to solutions used for plating cast iron is not recommended.

(b) Sodium hydroxide produced by the cadmium oxide used. In barrel plating, 7.5 g/L (1 oz/gal) is added for conductivity.

(c) Sodium carbonate produced by decomposition of sodium cyanide and absorption of carbon dioxide, and by poor anode efficiency. Excess sodium carbonate causes anode polarization, rough coatings, and lower efficiency. Excess sodium carbonate may be reduced by freezing, or by treatment with calcium sulfate.

Table 1(b) Operating conditions of cadmium plating cyanide solutions

Solutions No.	Current density[a]				Operating temperature		Remarks
	Range		Average				
	A/m^2	A/ft^2	A/m^2	A/ft^2	°C	°F	
1	55-650	5-60	270	25	27-32	80-90	For use in still tanks. Good efficiency, fair throwing power. Also used in bright barrel plating
2	110-860	10-80	270	25	27-32	80-90	For use in still tanks and automatic plating. High throwing power, uniform deposits, fair efficiency. Not for use in barrel plating
3	55-970	5-90	380	35	24-29	75-85	Primarily for use in still tanks, but can be used in automatic plating and barrel plating. High efficiency and good throwing power
4	55-	5-	540	50	27-	80-	Used for plating cast iron. High speed and high efficiency[b]

(a) For uniform deposits from cyanide solutions, the use of a current density of at least 215 A/m^2 (20 A/ft^2) is recommended. Agitation and cooling of solution are required at high current densities.

(b) Agitation and cooling are required when current density is high (above 215 A/m^2, or 20 A/ft^2).

For still tank or automatic plating of steel, selection of a bath on the basis of cyanide-to-metal ratio depends on the type of work being plated and the results desired:

- For parts with no recesses and when protection of the basis metal is the sole requirement, Solution 1 in Table 1(a) (ratio, 4 to 1) is recommended.
- For plating parts with deep recesses and when a bright, uniform finish is required, Solution 2 in Table 1(a) (ratio, 7 to 1) is recommended.
- For all-purpose bright plating of various shapes, Solution 3 in Table 1(a) (ratio, 5 to 1) is recommended.
- For high-speed, high-efficiency plating, Solution 4 in Table 1(a) (ratio, 4.5 to 1) is recommended.

Although the use of brighteners produces maximum improvement in uniformity and throwing power (that is, the ability of an electroplating solution to deposit metal uniformly on an irregularly shaped cathode) in Solution 3 in Tables 1(a) and 1(b), brighteners also improve these properties in Solutions 1 and 2.

Normally, the sodium hydroxide content of cyanide baths is not critical. Usual limits are 7.5 to 26 g/L (1.0 to 3.5 oz/gal); the preferred concentration for best results is 15 ± 4 g/L (2 ± 0.5 oz/gal). Sodium hydroxide contributes to conductivity and, in excess, affects the current-density range for obtaining bright plate. Analytical procedures useful in the maintenance of cyanide baths are outlined in the section "Chemical Analysis of Cyanide Cadmium Plating Baths" in this article.

In recent years, the need for pollution control of cyanide solutions has led to the development of noncyanide cadmium electroplating baths, shown in Table 2. Noncyanide baths generate little hydrogen embrittlement and are used to electroplate hardened, high-strength steels. Both the sulfate and the fluoborate baths have been used for some time as a substitute for cyanide baths, and working data are available. The fluoborate bath is characterized by high cathode

efficiency, good stability, and relatively little production of hydrogen embrittlement (see the section "Selective Plating" in this article). The major disadvantage of the fluoborate bath is its poor throwing power. It is widely used in barrel plating operations. If this bath is used for still plating at high current density, air agitation is desirable. Wire and strip geometries can readily be plated in a fluoborate bath. Practically all of the other acid-type baths shown in Table 2 are supplied to electroplaters as proprietary baths. Because each proprietary bath has its own peculiarities, it is advisable to obtain all proper operating information from the supplier to obtain the desired results.

Table 2 Concentration of commercial noncyanide cadmium plating baths

Bath	Proprietary[(a)]		Fluoborate[(b)]		Acid sulfate[(c)]
	g/L	oz/gal	g/L	oz/gal	
Ammonium chloride	11-23	1.5-3.0	. . .	. . .	. . .
Ammonium fluoborate	. . .	. . .	60	8	. . .
Ammonium sulfate	75-115	10-15	. . .	. . .	. . .
Boric acid	. . .	. . .	27	3.6	. . .
Cadmium	4-11	0.5-1.5	95	12.6	. . .
Cadmium fluoborate	. . .	. . .	244	32.2	. . .
Cadmium oxide	. . .	. . .	. . .	. . .	7.6-11 g/L (1.0-1.5 oz/gal)

(a) Proprietary requires a current density of 22 to 160 A/m^2 (2 to 15 A/ft^2) and an operating temperature of 16 to 38 °C (61 to 100 °F).

(b) Fluoborate requires a current density of 325 to 650 A/m^2 (30 to 60 A/ft^2) and an operating temperature of 21 to 38 °C (70 to 100 °F).

(c) Acid sulfate requires a current density of 110 to 660 A/m^2 (10 to 61 A/ft^2) and an operating temperature of 16 to 32 °C (61 to 90 °F).

Brighteners. The most widely used, and probably the safest, brightening agents for cyanide baths are organics such as:

- Aldehydes
- Ketones
- Alcohols
- Furfural
- Dextrin
- Gelatin
- Milk sugar

- Molasses
- Piperonal
- Some sulfonic acids

These materials form complexes with the electrolyte in cyanide baths and influence the orientation and growth of electrodeposited crystals, resulting in the formation of fine longitudinal crystals, and hence a bright deposit. Care should be taken not to add the brighteners in too large an amount. Too much brightener can result in dullness, pitting, blistering, and general poor quality and appearance. It is difficult to remove the excess brightener. Many organic brighteners are available as proprietary materials. When these are used, manufacturers' recommendations regarding amounts and other conditions of use should be followed.

Another method of brightening consists of the use of trace quantities of metallic nickel, cobalt, molybdenum, and selenium. The concentration of these elements in the bath is much more critical than the concentration of the organic brighteners. Poor bright dipping qualities or poor ductility and corrosion resistance of the coating may result from an excess of these metals. Certain proprietary brighteners contain both metallic and organic compounds. Brighteners for the noncyanide baths are also proprietary products.

Rough or pitted deposits should not be encountered in a well-balanced, carefully operated bath. However, if the concentration of metal is too low or the ratio of metal to cyanide varies from recommended values, roughness may result. Other factors that may contribute are contamination by dust, dirt, oil, metallic particles, or soap. Excessive concentrations of sodium carbonate and too high a temperature or current density also promote surface roughness.

Pitted deposits usually are the result of metallic impurities or an excessive amount of decomposed organic addition agents. The interfering metals are antimony, lead, silver, arsenic, tin and thallium. Pitting may also result from the presence of nitrates.

Correction of roughness or pitting may require a complete solution clean-up, including removal of excess sodium carbonate, purification with zinc dust, treatment with activated carbon, and filtration.

Formation and Elimination of Carbonate. Sodium carbonate forms in the cyanide bath as a result of the decomposition of sodium cyanide and the reaction of sodium cyanide with carbon dioxide from the air. The preferred method of agitation, if used, is mechanical because air agitation accelerates the buildup of carbonates.The buildup also results from failure to keep ball anode racks full or from the use of a large area of insoluble steel anodes.

Maximum concentrations of sodium carbonate that can be present in the bath without adverse effect on operating efficiency and deposit characteristics depend on the metal content of the bath. For example, carbonate can be present in concentrations up to 60 g/L (8 oz/gal) if the metal content is 19 g/L (2.5 oz/gal), and up to 30 g/L (4 oz/gal) if metal content is 30 g/L (4oz/gal), without deleterious effects. Exceeding these concentrations results in anode polarization, depletion of the metal content of the bath, and poor, irregular, and dull deposits.

To remove carbonates, the preferred method is to freeze them out by reducing the temperature to 1 to 3 °C (35 to 40 °F) in an outside treatment tank. This lowers the solubility of the carbonates, and the resulting precipitate is allowed to settle. The next step is to pump or filter the clear solution back to the plating tank, readjust the solution based on analysis, and properly dispose of the settled precipitate and solution. It is also possible to remove carbonates by treating the solution with calcium sulfate or calcium cyanide. The equipment supplier should be consulted about which procedure should be applied. Continuous purification equipment that maintains a preset level of carbonate is now available in state-of-the-art equipment.

Purification and Filtration. Whenever it is convenient, continuous filtration is advisable. If a solution is contaminated by impurities such as copper, tin, lead, or other metals, the following treatment is recommended.

Transfer the solution to an auxiliary tank of the same size as the plating tank; stir in 0.7 to 1 kg (1.5 to 2 lb) of purified zinc dust per 400 L (100 gal). Continue to stir for about 1 h, then allow to settle for no more than 6 h. Filter through a well-packed filter. If the solution contains excess organic impurities, such as decomposed brighteners, it should be treated with activated carbon and filtered. Pumps and filter parts should be made of iron or steel for alkaline cyanide baths. The solution attacks brass or bronze, and heavy copper contamination results.

Anodes

The anode system for cadmium plating from a cyanide solution consists of ball-shape cadmium anodes in a spiral cage of bare steel (Fig. 1). The spherical shape provides a large surface area in relation to weight, without a large investment in cadmium. Ball anodes also make it possible to maintain an approximately constant anode area, and little or no anode scrap is produced. Cadmium balls are usually 50 mm (2 in.) in diameter and weigh 0.6 kg ($1\frac{1}{4}$ lb) per ball.

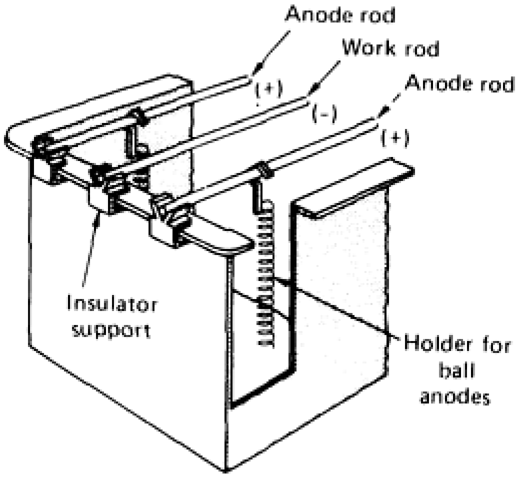


Fig. 1 Unagitated plating tank with spiral steel holders to secure cadmium ball anodes

If a cadmium cyanide solution is to be left idle for an extended period of time (a week or more), the steel anode cages should be removed from the solution, because the galvanic cell set up between the steel and the cadmium anodes will accelerate chemical dissolution of the anodes when the current is off.

When cadmium is plated from an acid solution, such as the fluoborate bath, ball anodes in uncoated steel cages cannot be used, because the steel would dissolve. Rather, bar anodes of elliptical or oval cross section, 460 to 2440 mm (18 to 96 in.) long, are used.

The use of bar anodes in a cyanide solution results in a high percentage of waste, because they must be removed and replaced when the cross-sectional area decreases, or they will dissolve preferentially at the solution level and drop to the bottom of the plating tank.

Purity of the anode is of great importance, especially if a bright deposit is to be produced. The typical composition range for cadmium anodes is as follows:

Element	Composition, %
Cadmium	99.95-99.97
Lead	0.008-0.03
Iron	0.005-0.008

Copper	0.002-0.01
Arsenic	0-0.001
Zinc	0-0.001

Anode composition complying with Federal Specification QQ-A-671 is:

Element(s)	**Composition**
Cadmium	99.9% min
Silver, lead, tin	0.05% max (total)
Arsenic, antimony, thallium	0.005% max

Insoluble anodes, which are made of low-carbon steel strip or wire, offer no particular advantage except where inside anodes are necessary or for special applications in which they are required because of a need to reduce metal concentration in the plating bath. When insoluble anodes are used, their total area should be 10 to 15% of the total anode area. Insoluble anodes accelerate the formation of carbonate.

Current Density

Cyanide cadmium baths may be operated over a wide range of cathode current densities, as indicated in Table 1(b). In a properly formulated bath operated within its intended current-density range, the cathode efficiency is 90% ± about 5%. Thus, to apply a 25 μ(1000 μin.) deposit of cadmium requires 120 A · h/m^2 (11 A · h/ft^2).

The ranges of current density given in Table 1(b) are suggested limiting values. Choice of current density is governed mainly by the type of work being plated; for example, low current densities are suitable for small lightweight parts, current densities up to 430 A/m^2 (40 A/ft^2) for medium-weight parts of fairly uniform shape, and high current densities for uniformly shaped heavy parts such as cylinders and shafts.

Baths containing 19 g/L (2.5 oz/gal) of cadmium are suitable for general use at current densities up to 270 A/m^2 (25 A/ft^2); higher concentrations of cadmium, up to 38 g/L (5 oz/gal), permit operation at higher current density.

A bath containing 19 g/L (2.5 oz/gal) of cadmium is suitable for barrel plating, where average current density may be about 55 A/m^2 (25 A/ft^2). Such a bath is also suitable for many still tank or automatic plating applications in which current densities do not exceed 270 A/m^2 (25 A/ft^2). At higher current densities, burning may result, with attendant dull, rough deposits that lack decorative and protective qualities. Where higher current densities are required, baths of higher metal content should be used.

Too low a current density (less than 55 A/m^2, or 5 A/ft^2) particularly in still tank or automatic plating, can result in excessively long plating times and inferior appearance of deposits.

The recommended range of current densities for plating with a fluoborate bath is 320 to 650 A/m^2 (30 to 60 A/ft^2). Even near 650 A/m^2 (60 A/ft^2), however, the bath has poor throwing power.

Deposition Rates

Among plating baths used commercially to deposit common metals (other than precious metals), cadmium cyanide baths are high in both throwing and covering power; only alkaline tin and cyanide copper have greater throwing power. Based on Haring-Blum cell measurements, the throwing power of cadmium cyanide baths is rated between 40 and 45%, with a distance ratio of 5. Therefore, the distance between the anode and the work is not critical, although as the distance is increased, current density and efficiency decrease, and current distribution is altered.

Table 3 lists the times required to plate cadmium deposits from 3 to 18 μm (120 to 720 μin.) thick. These times are predicated on 90% cathode efficiency.

Table 3 Time for plating cadmium to a given thickness at various current densities

Data based on 90% cathode efficiency, in a cyanide bath

Thickness of plate		**Plating time in minutes at current density specified**					
μm	**μin.**	**54 A/m^2 (5 A/ft^2)**	**110 A/m^2 (10 A/ft^2)**	**160 A/m^2 (15 A/ft^2)**	**215 A/m^2 (20 A/ft^2)**	**270 A/m^2 (25 A/ft^2)**	**325 A/m^2 (30 A/ft^2)**
3	120	13.0	6.5	4.3	3.2	2.6	2.2
5	200	26.0	13.0	8.6	6.4	5.2	4.4
8	320	39.0	19.5	13.9	9.6	7.8	6.6
10	400	52.0	26.0	18.2	12.8	10.4	8.8
13	520	65.0	32.5	22.5	16.0	13.0	11.0
15	600	78.0	39.0	25.8	19.2	15.6	13.2
18	720	91.0	45.5	30.4	22.4	18.2	15.4

Bath Temperature

Typical operating temperature ranges for cyanide baths are given in Table 1(b). Data for noncyanide baths are shown in Table 2. In general, satisfactory plating results are obtained by controlling bath temperature within ±3 °C (±5 °F) during plating. When greater precision is required, temperature should be controlled within ±1 °C (±2 °F).

Plating Equipment

Considerations specific to the operation of cadmium cyanide baths in conventional plating equipment are discussed here, with attention to the materials of construction used.

Still Tanks. Usually, unlined steel tanks are used for alkaline cadmium plating; however, steel tanks with plastic linings are useful in preventing stray tank currents. Another advantage is that lined tanks may satisfy the diking requirements of the Occupational Safety and Health Administration (OSHA). Double tanks and containment berms must be considered with the current regulations. Rubber and plastics used for tank linings should be tested for compatibility with the plating bath, to prevent contamination from constituents of the lining. Vinyl plastisols are compatible, commercially available, and require no further testing.

Filters and cooling coils may also be made of steel. Equipment for fume control should be used; such equipment in some cases is required by local ordinances. A typical tank arrangement is shown in Fig. 1. Equipment for baths other than the cyanide must be made acid-resistant.

Barrels may be made of hard rubber, polypropylene, acrylic resins, phenol-formaldehyde or melamine-formaldehyde laminates, or expanded or perforated sheet steel coated with vinyl plastisol. The plastisol coating is about 3.2 mm ($\frac{1}{8}$ in.) thick and is resistant to the standard barrel plating solutions and temperatures. Usually, doors and wall ends are of the same material.

Perforated cylinders for oblique barrels also have perforated bottoms and are made of the same materials used for perforated cylinders of horizontal barrels.

Anodes used for barrel plating may be bar- or ball-shape. For maximum current density, the anodes are curved to shorten the path of the current. Curved solid anodes are placed on insulated supports, whereas anode balls are placed in curved holders tied together at the lower ends.

Figure 2 illustrates schematically the use of barrel equipment for cadmium plating. Although not shown in the illustration, barrel installations are equipped with plate coils to remove the excess heat caused by the high current used in the plating bath.

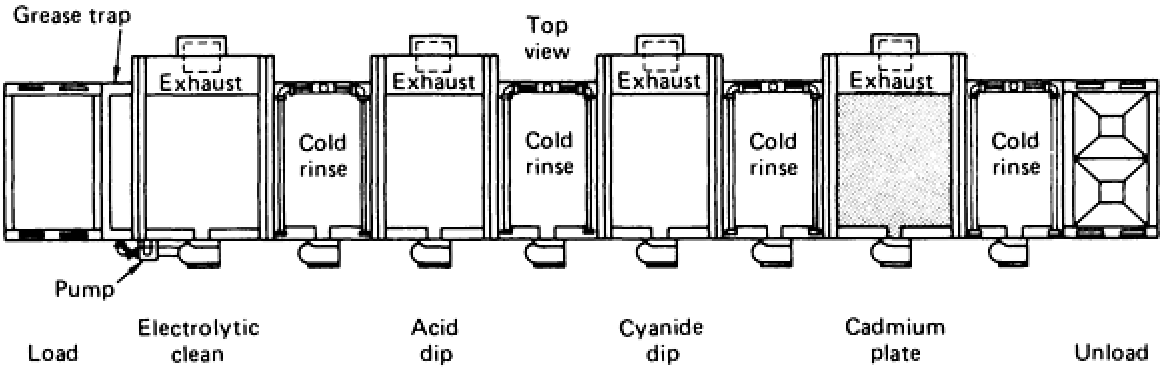


Fig. 2 Schematic showing cadmium plating installation that incorporates the barrel method

Automatic plating machines may be of either the straight-line or the return type. In straight-line plating machines, the work is loaded at one end, carried through the various phases of the cleaning and finishing cycles, and unloaded at the opposite end. Such a machine is considered a heavy-duty unit, because it can be designed for large racks and heavy loads.

Loading and unloading of the return machine is performed in the same area; the work follows an elliptical path, as indicated by the schematic layout of Fig. 3. This unit can be designed for either light or heavy loads.

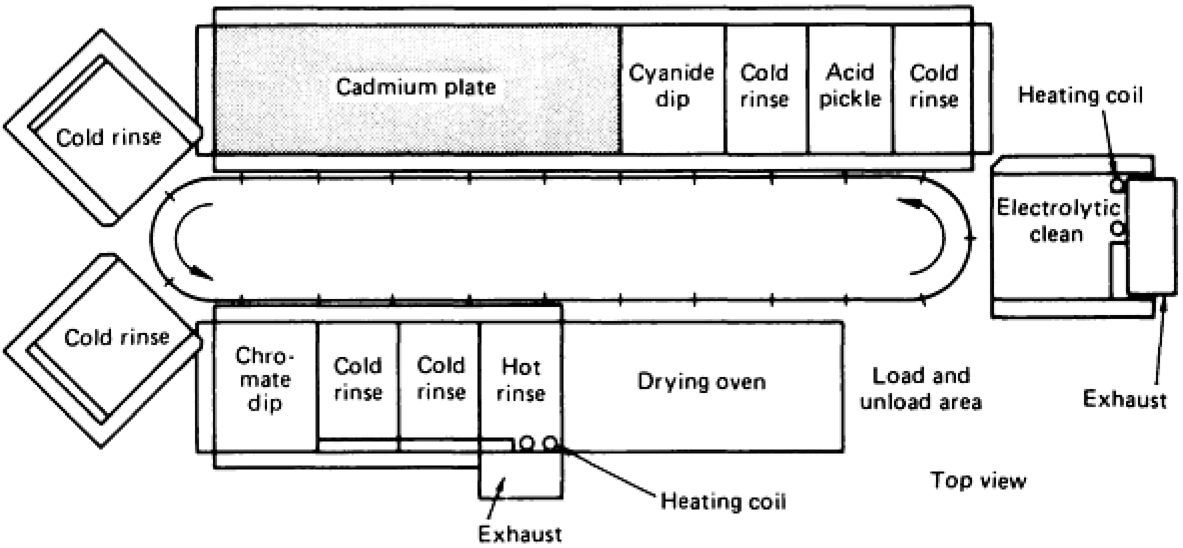


Fig. 3 Schematic showing process sequence for automatic cadmium plating installation

Both types of automatic machines may be continuous, with the work load in constant motion, or intermittent, in which case the motion of the carriers stops for a predetermined time after the work is immersed in each solution.

Power for cadmium plating is provided by rectifiers, which can be of silicon-controlled-rectifier (SCR) thyristor or tapswitch type. If the SCR type is used, attention should be paid to reducing ripple through a filter choke. This is necessary because bright cadmium is sensitive to a high-ripple current, which produces a dull finish on coatings plated in the medium- and high-current density range.

The rectifier elements are silicon. SCR rectifiers offer the advantage of remote control, finer control, computer interface, and constant current-voltage availability. Tap switch rectifiers offer the advantage of lower cost and eliminate the need for ripple filter chokes.

Rinse Tanks. Although longer tank life will be obtained if rinse tanks are lined or coated with polyvinyl chloride or rubber, all rinsing, with the exception of the rinse following hydrochloric acid pickling, may be done in unlined steel tanks. The use of unlined steel tanks for rinsing following pickling or acid plating is not recommended.

Racking of parts for cadmium plating is subject to the same considerations as in the electrodeposition of other metals. Information on design and use of plating racks is available in the article "Industrial (Hard) Chromium Plating" in this Volume.

Maintenance. Table 4 is a typical schedule of maintenance for plating and auxiliary equipment.

Table 4 Recommended maintenance schedule for plating and auxiliary equipment

Daily
Check anodes; replenish when necessary. Check all contacts, anode and cathode. Check solution levels. Check bath temperatures and controls. Check bath composition, if possible, using chemical analysis and plating cell test., Probe tank bottom for lost parts. Check motors for signs of overheating, arcing, or failure. Check amperage and voltage to work.

Check lubrication on automatic equipment.

Weekly
Probe tank bottom for lost parts, if not checked daily. Check rubber tank linings for damage. Filter plating bath, unless constant filtration is used. Check bath analysis, chemically and with plating cell, and make additions and corrections, if these functions are not performed more frequently. Oil equipment. Clean all contacts. Check for preventive-maintenance items that cannot be repaired during the week. Dump and replenish cleaning lines where necessary

Monthly
Pump plating solution to purification tank; treat for impurities, if necessary. Inspect tank linings while plating tanks are empty; repair if necessary. Inspect and clean heat exchangers or plate coils if accumulation or buildup exists. Blow out and check rectifier stacks for condition and power delivery. Check for arcing or scored armatures on generators. Blow out coils. Perform general preventive maintenance examination of all equipment.

Semiannually
Clean out exhaust systems. Repair exhaust fans. Check all motors. Repaint where necessary. Inspect and clean out all floor drains. Check for leaks and cross connections between cyanide and acid drains. Check all items usually covered on annual or semiannual overhaul, such as solenoid valves, limit switches, relays, and automatic electrical equipment.

Selection of Plating Method

Selection of plating method involves both technical and economic factors. Still plating, with parts racked, is the oldest and most universally used plating method. Barrel plating, limited to smaller parts that can be tumbled in the plating bath, is popular because many parts can be plated at one time. Automatic hoist units offer a means of mechanizing the still-tank rack or the barrel.

Still tanks are suitable for all types of work. They are used for small production quantities, in general, and for all quantities of parts that cannot be plated in barrel or automatic systems, because of a need for auxiliary anodes or special handling or because plating dimensions are critical.

Example 1: Cadmium Plating of Valve Bodies and Baffle Plates in Still Tanks.

Valve bodies and baffle plates are typical of many parts that are plated in still tanks (see Table 5). To cadmium plate the production quantities of these parts given in Table 5, the equipment required is:

Equipment	Specification
Plating tank (1440 L, or 380 gal)	2.7 by 0.76 by 0.76 m (9 by 2 $\frac{1}{2}$ by 2 $\frac{1}{2}$ ft)
Other tanks (420 L, or 110 gal)	0.91 by 0.76 by 0.76 m (3 by 2 $\frac{1}{2}$ by 2 $\frac{1}{2}$ ft)
Power rectifier (600 A)	1.5 to 6 V
Dimensions of rectifier	0.76 by 0.91 by 2.1 m (2 $\frac{1}{2}$ by 3 by 7 ft)
Total floor space of equipment and access area	2.0 by 4.6 m (6 $\frac{1}{2}$ by 15 ft)
Number of racks	15

Other tanks include a cleaning tank, an acid pickle tank, a hot-water rinse tank, and three cold-water rinse tanks.

Table 5 Equipment requirements for cadmium plating of valve bodies and baffle plates in still tanks

Production requirements	Valve body	Baffle plate
Weight per piece	1.1 kg (2 $\frac{1}{2}$ lb)	0.2 kg (0.5 lb)
Pieces plated per hour	210	175
Area plated per hour	6.5 m^2 (70 ft^2)	11.1 m^2 (120 ft^2)
Minimum thickness	8 μm (320 μin.)	4 μm (160 μin.)

Barrel plating may be used for parts up to 100 mm (4 in.) long and 50 mm (2 in.) thick. Parts such as machine bolts, nuts, and washers are ideal for barrel plating. Conversely, intricate shapes, such as ornaments and complex castings of brittle metals with small sections that fracture easily, should not be barrel plated; the tumbling action may damage these parts, and variation in plating thickness and appearance may result. Intricate designs incorporating recessed or shielded

areas may present problems in plating coverage, luster, and appearance. Barrel plating is not applicable for parts requiring heavy plate. Usually, 8 to 13 μm (320 to 520 μin.) is the maximum thickness of plate applied.

Example 2: Barrel Plating of Small Coil Springs and Brush Holders.

Small coil springs and brush holders are illustrative of parts suitable for barrel plating. Production requirements for plating these parts in horizontal barrels are given in Table 6. Equipment specifications are as follows:

Equipment	**Specification**
Plating tank (1330 L, or 350 gal)	1.8 by 1.2 by 0.76 m (6 by 4 by $2\frac{1}{2}$ ft)
Other tanks (605 L, or 160 gal)	0.91 by 1.2 by 0.76 m (3 by 4 by $2\frac{1}{2}$ ft)
Power rectifier (2000 A)	9 to 15 V
Dimensions of rectifier	0.91 by 1.2 by 2.4 m (3 by 4 by 8 ft)
Centrifugal dryer	0.61 by 0.61 by 0.76 m (2 by 2 by $2\frac{1}{2}$ ft)
Baking oven	1.2 by 0.91 by 2.4 m (4 by 3 by 8 ft)
Equipment floor space	12 m^2 (125 ft^2)
Access area behind line	6.3 m^2 (68 ft^2)
Access area in front	9.3 m^2 (100 ft^2)

Other tanks in the list above refer to cleaning tanks, acid pickle tanks, hot-water tanks, and three cold-water rinse tanks.

Table 6 Production requirements for cadmium plating of coil springs and brush holders in a horizontal barrel

Production requirements	**Coil spring**	**Brush holder**

Weight per piece	14 g ($\frac{1}{2}$ oz)	9 g ($\frac{5}{16}$ oz)
Pieces plated per hour	7200	3800
Area plated per hour	22 m^2 (240 ft^2)	17 m^2 (180 ft^2)
Minimum thickness	4 μm (160 μin.)	8 μm (320 μin.)

Automatic Plating. The primary selection factor for automatic plating is cost. The volume of work must be sufficient to warrant installation of the equipment.

Example 3: Cadmium Plating of Voltage-Regulator Bases on Automatic Equipment.

Voltage-regulator bases were cadmium plated, to a minimum thickness of 3.8 μm (152 μin.), in automatic equipment at the rate of 2640 pieces/h.

Production requirements:

Factor	**Specification**
Weight per piece	170 g (0.37 lb)
Pieces plated per hour	2640
Area to be plated per hour	53 m^2 (570 ft^2)
Minimum plate thickness	4 μm (160 μin.)

Equipment requirements:

Factor	**Specification**
Dimensions of full automatic plating unit	21 by 3.4 by 2.8 m(70 by 11 by 9 ft)
Width of access space on sides of unit	0.76 m (3 ft)

Width of access space on load end of unit	3.1 m (10 ft)
Motor-generator set	15 V, 7500 A
Dimensions of motor-generator set	3.1 by 3.1 by 2.4 m(10 by 10 by 8 ft)

Example 4: Cadmium Plating of Electrical-Outlet Receptacles with Automatic Equipment.

A quantity of 12,000 to 14,000 electrical-outlet receptacles per eight-hour day were required in order to justify the use of a small automatic plating system of 3800L (1000 gal) solution capacity with a single lane of rods and workpieces and plating 4 to 5 μm (160 to 200 μin.) of cadmium. When the size and shape of the parts are such that either automatic or still-tank plating processes may be used, the racking requirement is often the most important factor in determining the relative economy of still-tank and automatic plating. Two kinds of automated plating equipment are available, the regular return machine and the programmed hoist unit, which is an automated straight-line unit. The latter equipment is much less expensive to purchase.

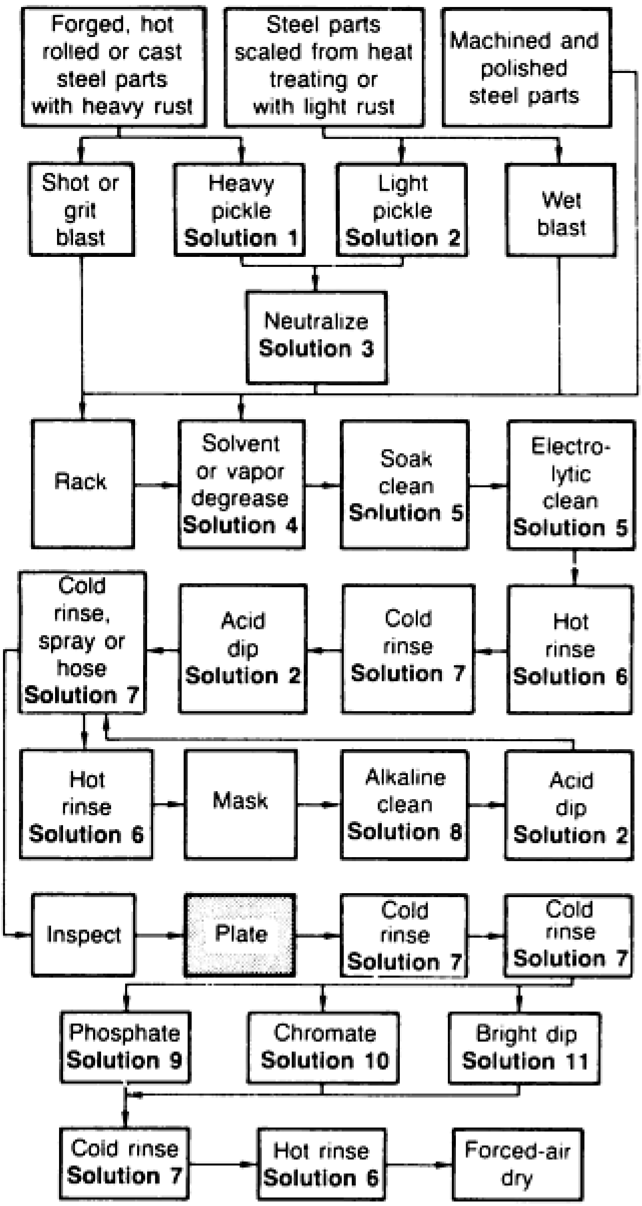
Cleaning and rinsing are essential operations in any plating sequence. Figures 2 and 3 show the number of tanks or stations required for such operations in typical barrel and automatic processes. In Fig. 4, where cleaning, rinsing, and postplating operations are indicated for various initial conditions of the work surface, the plating step itself is a rather inconspicuous item in the flow chart of the total finishing process. Table 7 shows variations in processing techniques for still-tank, barrel, or automatic plating to a thickness of less than 13 μm (520 μin.).

Table 7 Conditions for plating cadmium to a thickness of less than 13 μm (520 μin.)

Process variable	Still tank	Barrel	Automatic
Soak cleaning			
Alkali, g/L (oz/gal)	53 (6)	106 (12)	70 (8)
Temperature, °C (°F)	82 (180)	82 (180)	82 (180)
Time, min	2-3	5	3-5
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	$\frac{1}{2}$
Electrolytic cleaning			
Alkali, g/L (oz/gal)	70 (8)	. . .	70 (8)

Temperature, °C (°F)	82 (180)	. . .	82 (180)
Time, min	$\frac{1}{2}$-1	. . .	1-3
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	1
Acid dipping			
HCl, vol%	10-50	10-50	10-50
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{8}$-1	3	$\frac{1}{2}$ to >1
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	1
Cyanide dipping			
NaCN, g/L (oz/gal)	30-45 (4-6)	30-45 (4-6)	30-45 (4-6)
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	1
Plating			
Temperature, °C (°F)	29 (85)	29 (85)	29 (85)

Current density, A/m^2 (A/ft^2)	270 (25)	9-15 V	270 (25)
Time, min	10	30	10
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	3	$\frac{1}{2}$
Rinsing			
Temperature	Ambient	Ambient	Ambient
Time, min	$\frac{1}{4}$	2	$\frac{1}{2}$
Bright dipping			
HNO_3, vol%	$\frac{1}{4}$-$\frac{1}{2}$	$\frac{1}{4}$-$\frac{1}{2}$	$\frac{1}{4}$-$\frac{1}{2}$
Temperature, °C (°F)	82 (180)	Ambient	Ambient
Time, min	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{2}$
Rinsing			
Temperature, °C (°F)	. . .	71-82 (160-180)	82 (180)
Time, min	. . .	2	$\frac{1}{2}$
Drying			
Temperature, °C (°F)	82-105 (180-220)	82-105 (180-220)	82-105 (180-220)
Time, min	1-3	5	1-3



Solution No.	Composition	Amount	Temperature		Immersion time
			°C	°F	
1	H_2SO_4	8-12 vol%	71-93	160-200	10-120 s
2	HCl	20-50 vol%	RT	RT	10-120 s
3	Na_2CO_3	75-90 g/L (10-12 oz/gal)	RT	RT	15-60 s[(a)]

4	Petroleum solvent	. . .	RT	RT	$\frac{1}{2}$-3 min
5	Alkali(b)	60-75 g/L(b) (8-10 oz/gal)	82-93(b)	180-200(b)	$\frac{1}{2}$-3 min
6	Water	. . .	82-93(c)	180-200(c)	5-15 s
7	Water(d)	. . .	RT	RT	5-15 s
8	Alkali	60-75 g/L (8-10 oz/gal)	66 max	150 max	$\frac{1}{2}$-1 min
9	(e)	(e)	(e)	(e)	$\frac{1}{2}$-1 min
10	(e)	(e)	(e)	(e)	30 s
11	NaCN	45-60 g/L (6-8 oz/gal)	RT	RT	5-15 s

Note: For cast iron, the solutions, conditions, and procedure are the same as for steel, except that cast iron parts, after being thoroughly washed in cold water following the acid dip, are dipped for 5 s in a room-temperature (RT) cyanide solution (NaCN, 45 to 60 g/L, or 6 to 8 oz/gal) and then again rinsed in cold water, before proceeding to inspection, plating, and post-treatments.

(a) When solution is sprayed, time is 5 to 15 s.

(b) Heavy-duty cleaner. For electrolytic cleaning, concentration of alkali is 45 to 60 g/L (6 to 8 oz/gal), temperature is 82 °C (180 °F), and time is 1 to 3 min.

(c) When a spray rinse is used, water temperature is 71 to 82 °C (160 to 180 °F).

(d) Immersion or spray rinsing.

(e) Proprietary compounds

Fig. 4 Flow diagram showing cadmium plating operation relative to overall cleaning and post-treatment operations for steel and cast iron components

In the case of Fig. 2, 3, and 4 and Table 7, it is important to consider double or triple overflow rinses to control both water usage and pollution control costs. The use of dead rinses, following process tanks, is equally important.

Variations in Plate Thickness

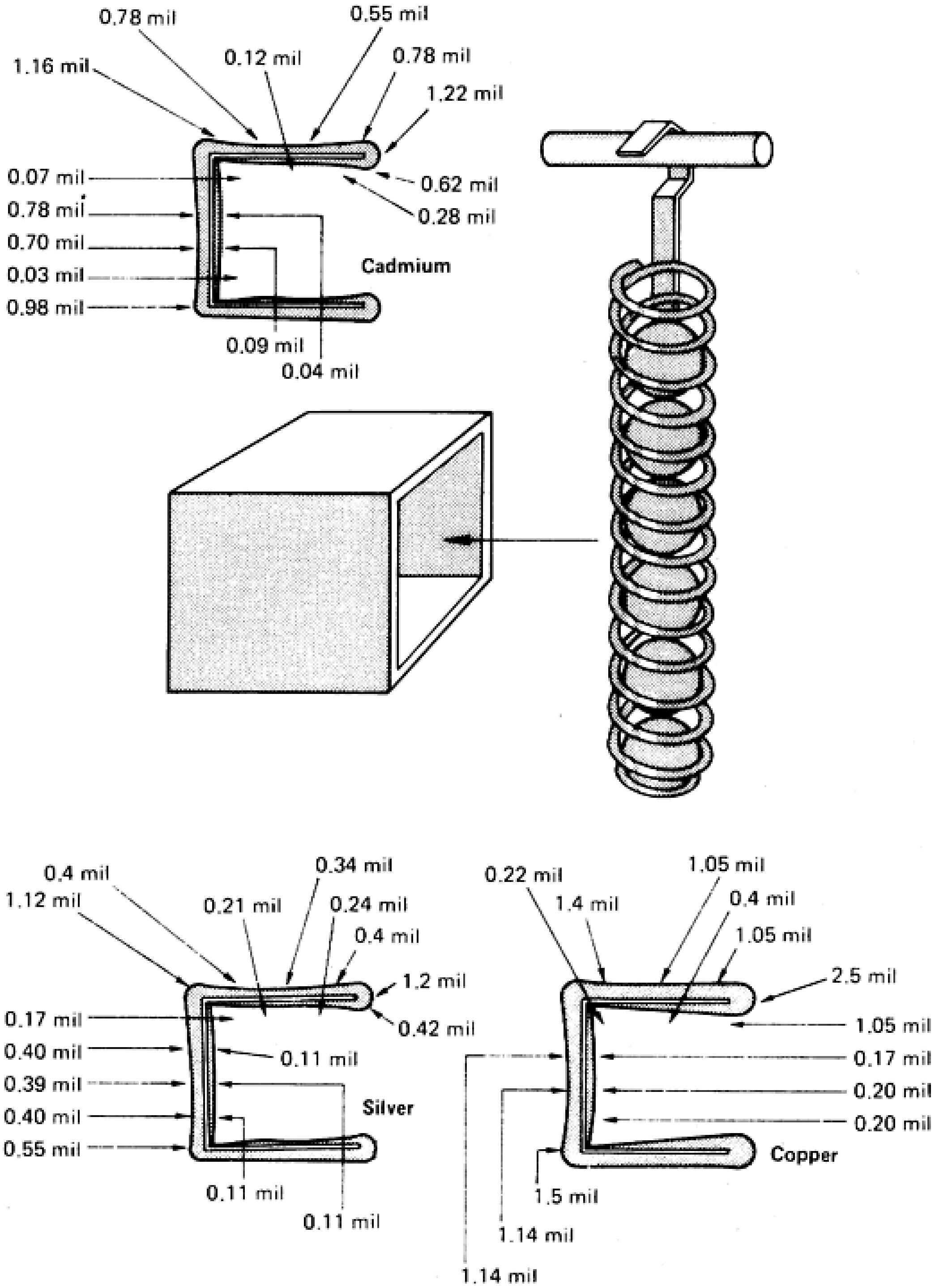
For adequate protection of steel, the thicknesses of cadmium in Table 8 are recommended. The shape of a part can markedly influence uniformity of the electrodeposit. Parts of simple design, such as socket wrenches and bathroom hardware, can be plated with a high degree of uniformity of plate thickness. On such parts, about 90% uniformity would be anticipated.

Table 8 Recommended thicknesses of cadmium

Environmental exposure	Description	Thickness		Uses
		µm	µin.	
Mild	Exposure to indoor atmospheres with rare condensation. Minimum wear and abrasion	5	200	Springs, lock washers, fasteners
Moderate	Exposure mostly to dry indoor atmospheres. Subject to occasional condensation, wear, or abrasion	8	320	Television and radio chassis, threaded parts, screws, bolts, radio parts instruments
Severe	Exposure to condensation, infrequent wetting by rain, cleaners	13	520	Washing machine parts, military hardware, electronic parts for tropical service
Very severe	Frequent exposure to moisture, saline solutions, and	25	1000	. . .

Threaded fasteners present a special problem, because of variations in contour and because of tolerance requirements. These items ordinarily are barrel plated, and thicknesses of 3 to 4 µm (120 to 160 µin.) are usually specified.

Throwing Power. The effect of shape on uniformity of deposit thickness is exemplified by the open-ended box (100 mm, or 4 in., cube) of Fig. 5. The open end of the box is pointed toward one of the anodes, to produce the most desirable condition for this shape without auxiliary thief rings, shields, bipolar anodes, insoluble anodes, or other devices. Results of plating such boxes with cadmium, silver, and copper, all deposited from cyanide baths, are shown in Fig. 5. These diagrams illustrate two facts: thickness of plate varies significantly from place to place on the simplest shape; and various plating baths have different throwing powers or abilities to plate uniformly over the surface, regardless of shape.



Plating bath	Thickness ratio[(a)]	
	Side	Bottom
Cadmium	1:4.25	1:12

Copper	1:3.0	1:6
Silver	1:2.5	1:5

(a) Ratio of average plate thickness of inside of average plate thickness on outside

Fig. 5 Plate thickness deposited on the cross section of a cube-shape workpiece to show throwing power of cadmium relative to that of silver or copper in a cyanide bath. Open ends of the 100 mm (4 in.) cubes were pointed toward ball anodes during plating.

The data on cyanide baths tabulated in Fig. 5 show that cadmium has appreciably less throwing power than silver or copper. However, cyanide cadmium has greater throwing power than nickel, chromium, iron, cyanide zinc, acid tin, acid cadmium, acid copper, or acid zinc. Normally, metals plated from cyanide or alkaline baths are more uniformly distributed than metals from acid baths. As design becomes more complex, uniform thickness of plate is more difficult to achieve without the use of special conforming anodes.

Example 5: Plate Thickness Variation in a Workpiece Plated without Use of Conforming Anodes.

A cylindrical, cup-shape production part that was plated without the use of conforming anodes is shown in Fig. 6. Thickness of plate varied from a minimum of 6 μm (240 μin.) to a maximum of 25 μm (1000 μin.).

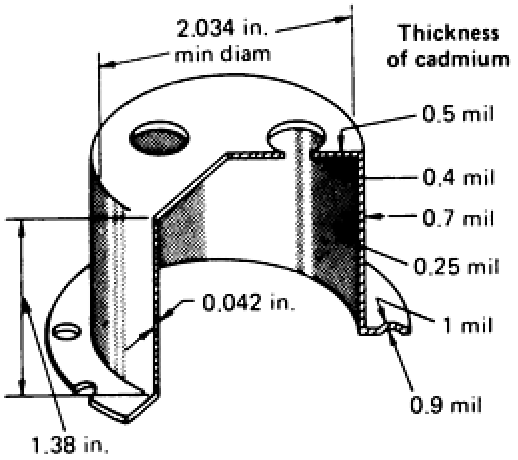


Fig. 6 Variations in plate thickness obtained on a workpiece plated without the use of conforming anodes

Conforming Anodes. Parts of complex shape with stringent dimensional requirements, such as those shown in Fig. 7 and 8, require the use of special techniques, conforming anodes, and shields, in order to obtain the required uniformity of plate thickness.

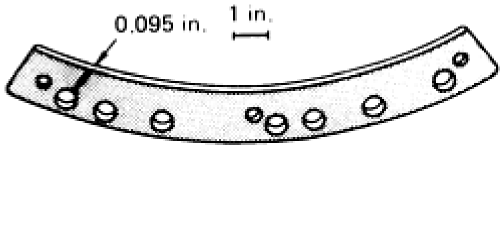


Fig. 7 Application of shields to obtain shim having a uniform cadmium plating. The 305 mm (12 in.) long and 38 mm (1 in.) wide shim was plated to the required thickness of 13 ± 5 μm (520 ± 200 μin.).

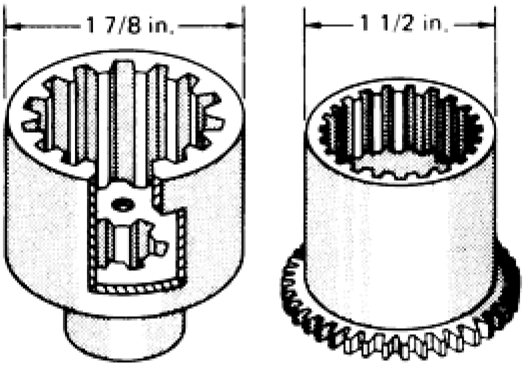


Fig. 8 Couplings that were uniformly cadmium plated with the aid of a 6.4 mm ($\frac{1}{4}$ in.) diameter anode centered in the bore during the plating operation. Plating thickness ranges from 8 to 13 μm (320 to 520 μin.).

Example 6: Application of Shields to Produce Uniform Cadmium-Plated Shim.

A shim, 305 mm (12 in.) long by 40 mm ($1\frac{1}{2}$ in.) wide by 2.4 mm (0.095 in.) thick, is shown in Fig. 7. Parallelism of all sides, as well as plate thickness, was extremely critical. When this part was plated in a simple rack, plate thickness varied from 13 μm (520 μin.) at the center to 50 to 75 μm (0.002 to 0.003 μin.) at the edges and ends.

By using shields that approximated the outline of the shim, it was possible to plate cadmium all over to a depth of 13 ± 5 μm (520 ± 200 μin.). The part was gently agitated in a still bath.

Example 7: Uniform Internal and External Cadmium Plating of Splined Couplings.

A coupling that required 8 to 13 μm (320 to 520 μin.) all over, except for the last 6.4 mm ($\frac{1}{4}$ in.) of the outside diameter of the small end, is shown in Fig. 8. The internal splines on both large and small bores were checked with plug gages and a single-tooth gage to ensure uniformity of plate thickness. To obtain the required uniformity, a 6.4 mm ($\frac{1}{4}$ in.) diameter anode was centered in the bore during plating. Although the outer surface of the large end of the coupling accumulated a heavier coating than other areas, general plate-thickness uniformity met requirements.

Example 8: Uniform Cadmium Plating of Coupling Leaving External Teeth Unplated.

A coupling that, except for the external teeth, was cadmium plated all over to a specified depth of 8 to 13 μm (320 to 520 μin.) is also shown in Fig. 8. Spline and internal bore dimensions were critical and had to be held to a tolerance of ±5 μm (±200 μin.) after plating. Again, uniformity of plate thickness was achieved by centering a 6.4 mm ($\frac{1}{4}$ in.) diameter anode in the bore during plating.

Simple cylindrical, cuboid, and channel shapes, such as those shown in Fig. 9, usually require conforming anodes in order to achieve complete coverage of plate and reasonable plating uniformity. Dimensional limits that definitely require the use of an internal anode are indicated for each geometric shape.

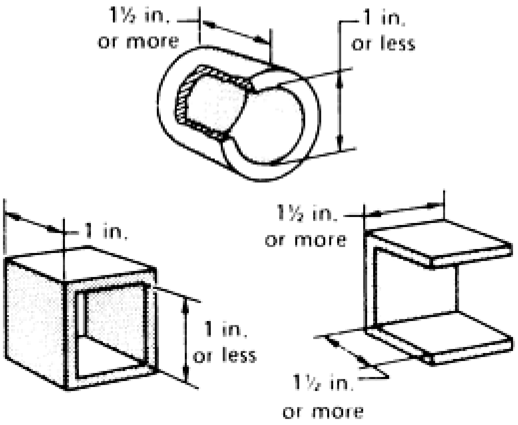


Fig. 9 Typical workpiece configurations with accompanying dimensions that require the use of conforming anodes to ensure uniform plate thickness

Normal Variations. Even under preferred production conditions, some variation in plate thickness must be anticipated. Usually, this normal scatter is acceptable and falls within the specified range of allowable variation.

In general, barrel plating produces greater variations in thickness than still plating. In barrel plating, factors such as the weight, size, and shape of the part usually exert a greater influence on uniformity of plate thickness than they do in still or automatic plating.

Screws, nuts, and other small parts of fairly regular shape will usually coat uniformly in barrel plating. Parts that are likely to nest because they have large flat areas or cup-shape recesses exhibit wide variations in coating thickness. Variations decrease somewhat as the thickness of plate increases.

Variations in plate thickness obtained on production parts are detailed in the example that follows:

Example 9: Histogram Showing Thickness Distribution of 90 Cadmium-Plated Components.

The small cylindrical part shown in Fig. 10 was plated in a horizontal barrel. The load contained about 5000 pieces. Thickness of plate was measured with a magnetic gage on 90 parts from each load. Plating thickness ranged from 5 to 14 μm (200 to 560 μin.).

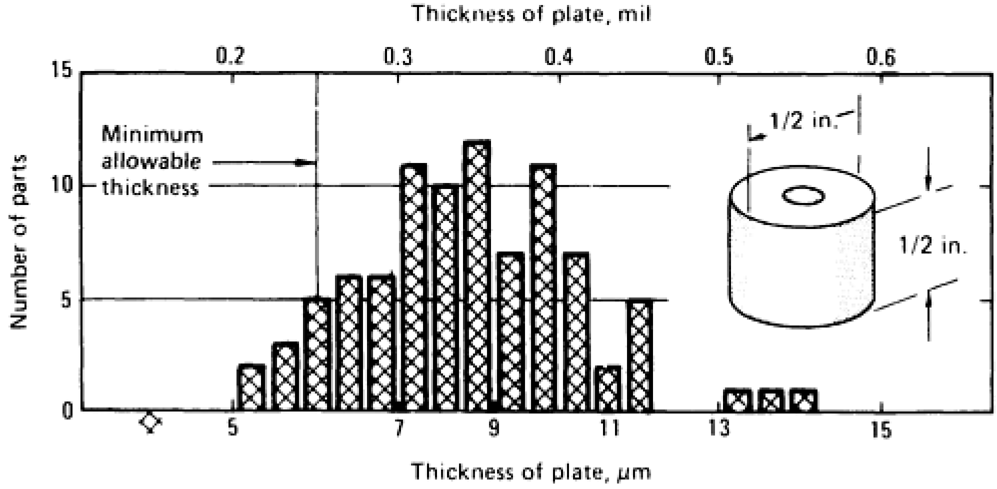


Fig. 10 Thickness distribution for cadmium plating of 90 samples that were evaluated from a 5000-piece

production lot

Other Application Factors

Aside from considerations of cost of very large plating systems, there are no size limitations on parts that can be cadmium plated, provided a tank of adequate size and other essential equipment are available. When a very large part is to be plated, jet plating methods may sometimes be used, rather than constructing a very large plating tank. In the jet technique, a steady stream of solution impinges against the part to be plated until the required thickness of plate is obtained. Because of the rapid movement of the solution, very high current densities can be used. The quality of the plate is comparable to that obtained by conventional methods.

Another technique that can be used on large parts is selective (or brush) plating. Detailed information is available in the article "Selective Plating" in this Volume.

Hardness. The hardness of the basis metal has little or no effect on the successful deposition of cadmium. However, the harder steels are likely to be more highly alloyed and may produce difficult-to-remove smuts from excessive pickling or chemical cleaning. Pickling is also a source of hydrogen embrittlement, which may be particularly harmful to hardened and stressed parts.

Springs often are electroplated with cadmium for protection against corrosion and abrasion. The following example deals with failure of a cadmium-plated compression spring that was not properly treated to release hydrogen.

Example 10: Baking of Cadmium-Plated 6150 Alloy Steel to Eliminate Hydrogen Embrittlement.

A spring used in a high-temperature relief valve under intermittent loading had dimensions and specifications as follows: wire size, 8.76 mm (0.345 in.); outside diameter of spring, 50 mm (2 in.); length, 75 mm (3 in.); six coils; 6150 alloy steel at 43 HRC; stress relieved immediately after coiling. The plating sequence was:

1. Alkaline clean.
2. Rinse in cold water.
3. Electroplate with cadmium 8 μm (320 μin.) thick.
4. Rinse in hot water.
5. Relieve hydrogen embrittlement in boiling water $\frac{1}{2}$ h.

The spring broke with a shatter fracture typical of that caused by hydrogen embrittlement. The corrective action was to bake the spring at 190 °C (375 °F) for 5 h.

For additional information on this subject, refer to the section "Hydrogen Embrittlement" in this article.

Service Temperature. Cadmium-plated, high-strength steel parts that are subjected to heavy loading should never be used at temperatures above 230 °C (450 °F). Cadmium melts at 320 °C (610 °F); at temperatures approaching 260 °C (500 °F), damage occurs that adversely affects mechanical properties.

Diffused Coatings. The aviation industry has developed an application for cadmium for low-alloy steel jet engine parts. The substrate is first plated with 10 μm (400 μin.) of nickel and then 5 μm (200 μin.) of cadmium. The alloy is diffused at 340 °C (645 °F) for about 1 h. Coverage with nickel must be complete, because cadmium can detrimentally affect the steel substrate when heated above the melting point of cadmium. In this way, an alloy with a very high melting point can be formed. Low-alloy steel parts that operate in jet engines at a temperature of 540 °C (1005 °F) were coated with this diffused alloy. After operating for 1 h at 540 °C (1005 °F), the parts withstood 100 h of salt spray without rusting. Cadmium can also be plated on copper and zinc, as well as on nickel.

Solderability. Although cadmium usually solders well with solders of the 60% tin, 40% lead type, using an inactive rosin flux, its performance may sometimes be unaccountably erratic. Solderability can be improved and made more

consistent by predepositing a thin (3 to 4 μm, or 120 to 160 μin.) layer of copper. If the final cadmium deposit is at least 4 μm (160 μin.) thick, the copper coating will not adversely affect corrosion resistance in mild indoor atmospheres. It is important for health and safety reasons to see the section "Toxicity of Cadmium" in this article.

Cadmium on Stainless. Cadmium can be successfully plated over stainless steels and heat-resisting chromium-nickel alloys if the basis metal is first activated and given a light coating of nickel in a nickel chloride-hydrochloric acid bath (U.S. Patent 2,437,409). Composition and operating conditions for this bath are as follows:

Factor	Specification
Nickel chloride	240 g/L (32 oz/gal)
Hydrochloric acid (1.16 sp gr)	120 g/L (16 oz/gal)
Temperature	Room temperature
Current density	55 to 2150 A/m^2 (50 to 200 A/ft^2)
Time	2 to 4 min
Anodes	Nickel

Plating of Cast Iron

Cast iron is difficult to plate because of the graphite flakes or nodules in the microstructure. The larger the graphite inclusions, the more difficult the plating operation. Cast iron parts with unmachined surfaces should be cleaned by mechanical methods, such as shot blasting or tumbling, before plating. Heavy pickling should be avoided if possible, because it produces smut that is difficult to remove. However, light pickling is required after abrasive cleaning, to activate the surface for plating.

Pickling should be followed by a thorough water rinse and a cyanide dip (see note in the table accompanying Fig. 4). Any carryover of acid to the cyanide dip must be avoided, because the combination of these chemicals generates a highly poisonous hydrocyanic gas. The fluoborate solution described in Tables 1(a) and 1(b) is excellent for plating cast iron parts without deep recesses. The cyanide solutions in Tables 1(a) and 1(b) also may be used, provided no metal-organic grain-refining agents have been added. Current density on the high side of the indicated ranges is recommended, to establish a continuous film of cadmium on the iron as soon as possible.

Cadmium Versus Zinc

In rural areas, cadmium and zinc are generally considered to offer equal protection. However, zinc is superior to cadmium in industrial environments (Table 9). In uncontaminated marine atmospheres, zinc and cadmium give approximately equal protection. When the comparison is made at a distance of 24 m (80 ft) from the ocean, cadmium gives significantly greater protection than zinc. Although it is used to a limited extent in the paper and textile industries, cadmium plate has poor resistance to chemicals commonly used in these processes and also to the chemicals of the petroleum and pharmaceutical industries.

Table 9 Protection against rusting imparted to steel in selected atmospheres by 25μm (1000μin.) of cadmium plate or zinc plate

Test location	Atmosphere	Time required for 5 to 10% rusting, yr	
		Cadmium	Zinc
New York, NY	Industrial	2	4
Pittsburgh, PA	Industrial	3	4
Sandy Hook, NJ	Marine, Industrial	6	5
State College, PA	Rural	>11	>11
Key West, FL	Marine	>7	>9

Source:ASTM

One reason for preferring cadmium to zinc is that cadmium plate forms a smaller amount of corrosion products than zinc, particularly in marine atmospheres. Cadmium also retains its initial appearance for a longer time. This is an important consideration in applications where a buildup of corrosion products would have a detrimental effect, such as preventing the flow of current in electrical components or the movement of closely fitting parts such as hinges. For such applications, cadmium should be chosen in preference to zinc. Cadmium is preferable to zinc for plating cast iron.

Cadmium Substitutes

There is increased pressure, both domestically and internationally, for reduced usage, or even elimination of cadmium plating for health, safety, and environmental reasons. There have been several zinc alloy baths developed that work for specific applications, but none duplicates all the properties of cadmium. There are many instances, however, where the use of cadmium plating is not essential and zinc or zinc alloy deposits could be substituted, because both give adequate anodic protection, and there was no functional purpose when cadmium was chosen in the first place.

Chemical Analysis of Cyanide Cadmium Plating Baths

Table 10 lists analytical tests that may be applied to cyanide cadmium plating baths to determine their contents of cadmium metal, sodium cyanide, sodium hydroxide, and sodium carbonate.

Table 10 Analytical tests for determining concentration of selected chemical constituents of cyanide cadmium plating baths

Test constituent	Component			
	Cadmium metal	Sodium cyanide (total)	Sodium Hydroxide	Sodium Carbonate
Reagents	Hydrochloric or sulfuric acid (concentrated) Ammonium hydroxide (concentrated) Eriochrome black "T" indicator (0.5% solution in alcohol) Formaldehyde (8% solution in water)	Ammonium hydroxide (concentrated) Potassium iodide (10% solution in water) Silver nitrate (13 g/L, or	LaMotte sulfo-orange indicator Sulfuric acid, standard (0.94	Barium chloride (10% solution in water) Methyl orange-xylene cyanole

	Disodium dihydrogen ethylenediaminetetraacetate dihydrate (EDTA), 0.575*M* solution (21.4 g/L, or 2.85 oz/gal)	1.7 oz/gal solution in water)	*N*)	indicator solution Hydrochloric acid, standard (0.7 *N*)
Procedure	1. Pipette exactly 2 mL (0.07 oz) of plating bath into a 250 mL (8.5 oz) Erlenmeyer flask, and dilute to about 100 mL (3.4 oz) with distilled water. 2. Neutralize this dilution to a faint white precipitate with hydrochloric or sulfuric acid. This can be conveniently done from the burette of standard sulfuric acid (0.94 *N* used for the caustic titration, or by the addition of a 50% solution of hydrochloric acid from an eyedropper. If no precipitate appears, as may happen with a new bath, thymolphthalein can be used as an indicator and will change from blue to colorless on neutralization. 3. Add 10 mL (0.34 oz) of concentrated ammonium hydroxide and about $\frac{3}{4}$ mL of Eriochrome indicator. 4. Zero the burette. 5. Add 8 mL (0.27 oz) of 8% formaldehyde solution. 6. Titrate immediately with EDTA solution. The color change is from red to blue, and it is sharpest when the solution is titrated as soon as possible after the formaldehyde has been added. A rapid titration will also give a sharper end point. Occasionally, the presence of impurities in the bath will prevent the attainment of a clear blue end point, but the color will prevent the attainment of a clear blue end point, but the color change is still sharp, from a red to a purplish blue.	1. Pipette a 2 mL (0.07 oz)sample of plating bath into a 250 mL (8.5 oz) flask. 2. Add to the sample about 50 mL (1.7 oz) distilled water, 5 to 7 mL (0.17 to 0.24 oz) of ammonium hydroxide, and 2 to 3 mL (0.07 to 0.10 oz) of potassium iodide solution. 3. Titrate with silver nitrate solution to the first stable faint yellowish turbidity.	1. Pipette 10 mL (0.34 oz) of the plating bath into a 250 ml (8.5 oz) flask. 2. Add to the sample about $\frac{1}{2}$ mL (0.017 oz) of indicator solution. 3. Titrate with the sulfuric acid to the color change from orange to yellow.	1. Pipette 10 mL (0.34 oz) of plating bath into a 250 mL (8.5 oz) beaker, add to it about 100 mL (3.4 oz) of water, and heat to boiling. 2. Stir into boiling bath dilution about 20 mL of barium chloride solution; cover mixture; allow to stand warm for about $\frac{1}{4}$ to $\frac{1}{2}$ h. 3. Filter, using No. 41 Whatman filter paper, and wash precipitate and flask at least 2 or 3 times with hot distilled water. 4. Place paper and precipitate in the original beaker, add about 10 mL (0.34 oz) of hot distilled water and 3 or 4 drops of indicator. 5. Titrate with the hydrochloric acid (while stirring) to the first permanent color change from green to purple.
Calculation	Milliliters of EDTA solution used × 0.432 = ounces per gallon, cadmium metal	Milliliters of silver nitrate used × 0.5 = ounces per gallon, total sodium cyanide	Milliliters of sulfuric acid used × 0.5 = ounces per gallon, sodium hydroxide	Milliliters of hydrochloric acid used × 0.5 = ounces per gallon, sodium carbonate

Methods for Measuring Thickness of Cadmium Plate

There are many nondestructive and destructive methods for measuring the thickness of cadmium deposits (Table 11). The most widely used are magnetic, coulometric, and eddy-current methods, as well as x-ray spectrometry and microscopic cross-sectioning. Other reliable methods, including the chemical drop test, may be used. Detailed information on most methods can be obtained from ASTM specification B 659-85 ("Standard Guide for Measuring Thickness of Metallic and Inorganic Coatings") (Ref 1) and ISO Standards.

Table 11 Methods applicable to measuring cadmium coating thickness on selected ferrous and nonferrous substrates per ASTM B 659

Substrates	**Measurement technique**

	Beta backscatter[(a)]	Coulometric[(b)]	Magnetic[(c)]
Magnetic steel (including corrosion-resisting steel)	X	X	X
Nonmagnetic stainless steels	X	X	. . .
Copper and alloys	X	X	. . .
Zinc and alloys	X	. . .	. . .
Aluminum and alloys	X	X	. . .
Magnesium and alloys	X	. . .	. . .
Nickel	X	X	. . .
Glass sealing nickel-cobalt-iron alloys (UNS No. K94610)	X	. . .	X
Nonmetals	X	X	. . .
Titanium	X	. . .	. . .

Source: Ref 1

(a) ASTM B 567; ISO 3543.

(b) ASTM B 504; ISO 2177.

(c) ASTM B 499; ISO 2178.

Reference cited in this section

1. 1989 Annual Book of ASTM Standards, Vol 2.05 *(Metallic and Inorganic Coatings; Metal Powders, Sintered P/M Structural Parts)*, ASTM, 1989, p 441-443

Solutions for Stripping Cadmium Plate

Electrodeposited cadmium can be stripped chemically from the basis metal by immersion in one of the following solutions: ammonium nitrate, inhibited hydrochloric acid, chromic acid with a sulfuric acid addition, and ammonium persulfate with an ammonium hydroxide addition. Electrolytic stripping is performed in a solution of sodium cyanide with an addition of sodium hydroxide. Compositions of these stripping solutions, and the immersion times to be used with them, are given in Table 12.

Table 12 Solutions for stripping electrodeposited cadmium

Solution[a]	Composition	Amount		Immersion time, min[b]
		g/L	oz/gal	
1	Ammonium nitrate	105-136	14-18	10-20
2[c]	Hydrochloric acid (1.18 sp gr), undiluted	. . .	. . .	10-20
	Antimony trioxide	15	2	. . .
3	Chromic acid	203	26.8	5-10
	Sulfuric acid (95%)	48[d]	6.4[e]	. . .
4	Ammonium persulfate	51	6.7	5-10
	Ammonium hydroxide	96.8[d]	12.8[e]	. . .
5[f]	Sodium cyanide	60-91	8-12	10-20
	Sodium hydroxide	15-30	2-4	. . .

(a) Solutions are listed in order of preference; all solutions are used at room temperature.

(b) Immersion times are for deposits 8 to 13 μm (320 to 520 μin.) thick.

(c) Solution should not be used on stressed or hardened parts.

(d) mL/L.

(e) fl oz/gal.

(f) Solution for stripping electrolytically; 540 to 1080 A/m^2 (50 to 100 A/ft^2) and 6 to 8 V; part to be stripped is made the anode.

Toxicity of Cadmium

Two hazardous consequences attend the use of cadmium in contact with food products: acute poisoning resulting from the ingestion of cadmium dissolved from containers or from food-handling equipment; and poisoning from the inhalation of fumes of cadmium oxide, if cadmium-plated vessels or food-handling equipment is heated.

Acute poisoning has resulted from the ingestion of cadmium salts derived from cadmium-plated vessels in which any acid foods have been stored for even short periods of time; therefore, cadmium should not be used on food containers of any

kind. Fatal poisoning is more apt to result from the inhalation of dust or fumes of cadmium salts and cadmium oxide. These are the kinds of exposure encountered in industrial operations when cadmium-plated parts are heated or soldered. Exposure to dust or fumes of cadmium should be avoided and safety / OSHA regulations should be followed. The complete regulatory text of the cadmium rule and appendixes is published in the Federal Register 57 (178): 42102-42463, 14 September 1992. Among its provisions, the rule requires employers to adhere to a new personal exposure limit (5 g/ μm^3), provide medical surveillance, monitor exposure level, and maintain proper records.

Deposits of cadmium on the sides or bottom of a tank previously used for cadmium plating should not be burned off, because the fumes from this operation are highly toxic. These deposits should be removed mechanically or deplated. For high-efficiency deplating, the solution used contains 45 to 60 g/L (6 to 8 oz/gal) of sodium cyanide and 23 to 30 g/L (3 to 4 oz/gal) of sodium hydroxide in water; the tank is the anode, and steel sheets or scrap steel parts are the cathodes. Just like the production solutions presented in Table 1(a), the resulting solution must be treated with the utmost care. The proper handling of cyanide solutions should be discussed with the proper vendors, and internal safety departments must train operators in the safe use of these solutions. Disposal issues must be part of waste treatment management practices. Additional information is available in the article "Cadmium Elimination" in this Volume.

Selective Plating

When plating must be applied to only certain areas of parts, the areas not to be plated must be stopped off or masked, which means they must be covered with materials that will not conduct current, such as waxes, lacquers, or rubber tape.

Waxes. Ordinarily, a petroleum-derived wax is used for stopping off. The wax must not contain any oil or other organic materials that will dissolve in the plating solution and contaminate it. It must also be capable of adhering tightly to the part, to prevent the plating solution from coming in contact with the stopped-off area.

Before being applied, the wax is heated in a pot to about 27 °C (80 °F) above its melting point, so that it does not solidify too rapidly and will adhere more readily. Still-better adhesion is obtained if parts are warmed on a hot plate before the wax is applied.

Parts must be positioned so that only the area to be coated is placed in the molten wax. This means that, normally, only end areas or protrusions can be stopped off with wax. The wax can be applied with camel's hair brushes, but this is time-consuming if many parts are to be treated. For a large number of similar parts, a fixture can be used that will dip each part to the proper depth.

A sharp, uniform demarcation between plated and nonplated areas can be obtained by the use of pressure-sensitive tape and wax, following either of two procedures:

- Apply the tape to the part so that the trailing edge of the tape follows the demarcation line; dip that portion of the part to be left unplated in molten wax so as to overlap the trailing edge of the tape slightly; and then remove the wax when it has solidified.
- Apply the tape to the part so that the leading edge follows the demarcation; dip that portion of the part to be left unplated in molten wax so as to overlap partly the trailing edge of the tape; and then, when the wax has solidified, plate the part without removing the tape.

Waxing must be done carefully, so that areas that are to be plated have no wax on them. If wax does get on areas to be plated, it must be thoroughly removed. After plating and postplating treatments, the wax is removed from parts by placing them in hot water.

Lacquers may be used instead of wax as stop-off coatings, but their use is generally limited to instances in which the plating bath is operated at a temperature at which the wax would melt. Lacquer is applied by dipping or painting the areas to be stopped off. Normally, two to four coats of lacquer must be applied. One disadvantage of lacquer is that it is difficult and time-consuming to get all of it off. Heavier coatings prevent leakage and make stripping easier.

Plastic Tape. For stopping off irregular areas of heavy parts that cannot be dipped or that are too large to be painted (e.g., splines, large shafts, or bearing shoulders), a plastic tape is used. The tape is wound tightly and stretched over the irregular areas. To prevent leakage, each turn should overlap the preceding one at least half-way. At the edge of the stop-

off area, a pressure-sensitive tape is used to form a sharp line and prevent the leakage of plating solution under the plastic tape.

Plastic tape is expensive to use. When many similar parts are to be selectively plated, rubber sheet, held in place by pressure-sensitive tape, may be used for stopping off areas not to be plated. Rubber stoppers, plastic plugs, or corks, sealed with wax, are used for stopping off internal areas of cylindrical parts. Rubber or plastic tubing can be used to stop off areas of small cylindrical parts.

Rinsing and Drying

Although one of the simplest operations in plating, rinsing is often the most difficult to accomplish. The primary requirements are that the rinsing be effective in removing the solutions used in the preceding tank and that no contaminants be introduced into the subsequent tank. Rinse baths, whether hot or cold, usually are provided with some means for constant changing of the water, good agitation, and skimming of the surface. Agitation of both the water and part is usually necessary. The surface skimmer may consist of jets of water shooting across the surface to rinse surface films into an overflow trough at the far side of the rinse tank. Water should enter at the bottom of one side of a rinse tank and escape over a weir outlet along the top at the opposite side of the tank. Constant monitoring of the water quality versus product quality is essential with the increased demand to lower water usage. The amount of contamination in rinse tanks can be regulated by controlling the flow of fresh water into the rinse through a valve actuated by a conductivity cell.

The temperature of the postplating rinse bath depends to some extent on the mass of the work being rinsed, because the workpiece must supply all the heat of evaporation for drying. Thin-gage materials require rinse temperatures of 93 to 100 °C (200 to 212 °F); otherwise, the workpiece cools before evaporation is complete. Parts made from thicker materials may be rinsed in water at 82 to 88 °C (180 to 190 °F).

Rapid and thorough drying of the plated work is important, to prevent water marks and stains and to eliminate the moisture from residual salt that may not have been entirely removed from crevices or recesses by rinsing. Residual salt and moisture can be a source of corrosion.

Drying practice is also influenced by the shape and orientation of the workpiece as it leaves the final rinse. In many applications, hot-water rinsing is followed with oven drying, wherein hot air is blown directly against the work. In automatic installations, oven temperatures are maintained at 105 °C (220 °F) or higher and the work passes through in 3 to 5 min. Centrifuges with a hot air blast are used for barrel-plated work.

Hydrogen Embrittlement

If an electrodeposited coating is to be applied to a highly stressed part or a high-strength (over 1100 MPa, or 160 ksi) heat-treated steel part, it is important that the processing not decrease the static or fatigue strength of the part. Hydrogen embrittlement does not affect fatigue life. Coatings having high residual stresses, such as chromium, affect fatigue life; however, this is not the case with cadmium.

Cadmium deposited from a cyanide solution is more likely to produce hydrogen embrittlement than any other commonly plated metal. Heat-treated steels, particularly those plated and used at 35 HRC and above, are susceptible to hydrogen embrittlement. Most susceptible is spring steel that has not been adequately stress relieved after forming. The requirements of Federal Specification QQ-P-416F may be used as a guide for stress relief before plating and hydrogen embrittlement post-treatment (Table 13). Other guidelines vary from these, but the latest revision (F) seems to be the most stringent.

Table 13 Heat treat specifications required to stress relieve cadmium-plated components

Hardness, HRC	Stress relief before plating			Hydrogen embrittlement relief (within 4 h of plating)		
	Temperature		Minimum time, h	Temperature		Minimum time, h
	°C	°F		°C	°F	

34-54	175-205	350-400	4	. . .	. . .	. . .
36-45	. . .	. . .	. . .	175-205	350-400	8 23[(a)]
46-54	. . .	. . .	. . .	175-205	350-400	23
>55	120-150	250-300	23	120-150	250-300	23

(a) Fasteners and bearings

Although the thickness of the plated deposit appears to have no direct bearing on hydrogen embrittlement, it is always more difficult to release the hydrogen (by baking) from heavy deposits.

By adhering to the following procedures, hydrogen embrittlement can be minimized or made inconsequential:

- Use mechanical cleaning methods, such as brushing, blasting, and tumbling.
- Wherever possible, avoid the use of strong acid-pickling solutions and extended exposure to acid pickling.
- If pickling is essential to the preparation of medium-strength and high-strength steel parts, bake the parts at 175 to 205 °C (350 to 400 °F) for 3 h after pickling and before plating.
- In plating, use the higher current densities to produce a more porous deposit; 755 A/m^2 (70 A/ft$^{2)}$ in a cyanide bath without brighteners has been satisfactory for steel at 46 HRC.
- After plating, bake parts at 175 to 205 °C (350 to 400 °F) for 3 to 24 h. The shorter baking periods are generally adequate for parts with a tensile strength below about 1520 MPa (220 ksi); longer baking periods are recommended for steel of tensile strength above about 1520 MPa (220 ksi) or for lower-strength parts if sharp notches or threads exist. Parts greater than 25 mm (1 in.) thick should also be baked for 24 h. The elapsed time between plating and baking must never exceed 8 h and should be carried out as soon as possible, preferably within 4 h.
- Plate parts to a thickness of about 5 μm (200 μin.), bake for 3 h at 195 °C (385 °F), activate in cyanide, and then complete the plating to the required final thickness.

The applications of shot peening and baking, as related to the hardness of the steel to be plated, are described in Federal Specification QQ-C-320 (Amendment 1) and are summarized in the article "Industrial (Hard) Chromium Plating" in this Volume.

Tests for Adhesion of Plated Coatings

The tests used for evaluating adhesion of plated coatings are largely qualitative. A bend test, described in Federal Specification QQ-P-416, involves observation of the degree of flaking that occurs as a specimen is bent. Additional tests are scrape/scratch, short blasts from a glass bead machine (reduced pressures), and bake/cold water quench, all of which tend to show blistering or peeling. In another test, a pressure-sensitive tape, such as surgical adhesive or masking tape, is attached to the plated surface. The tape is quickly stripped from the specimen by pulling it at right angles to the surface. If adhesion is poor, loose plate or blisters will appear as flecks on the surface of the adhesive.

Another good test for adhesion, on parts that have been baked after being plated, is a visual inspection for blisters in the plate. If a good bond has not been established, the plate will most often pull away from the basis metal and form blisters.

Chromate Conversion Coatings

The corrosion of cadmium plate can be retarded by applying a supplemental chemical conversion coating of the chromate type. The chromate films are produced by immersing the plated article in a solution containing chromic acid or other chromates and catalytic agents. These films provide protection against initial corrosion through the inhibitive properties of the water-soluble chromium compounds present. However, the chromate finish must not be applied before stress relieving or baking, because its beneficial effect will be destroyed by the elevated temperature.

Chromate conversion coatings are used in some instances to improve the bond between paint and cadmium-plated surfaces and to provide the plate with resistance to corrosion if gaps should occur in the paint film. However, wash primers will not adhere to chromate finishes, and baking painted chromate finishes will produce poor bonding.

Plate Discoloration. Cadmium tarnishes easily from handling and, at a lesser rate, from normal oxidation. Both types of tarnish may be prevented by the use of chromate conversion coatings. For maximum prevention of tarnish, an unmodified chromate film should be applied, if the iridescence or the light yellow coloration it imparts is not objectionable. Such a surface film also provides resistance against salt spray and humidity, and its application for this purpose is frequently standard practice. The clear film obtained by bleaching a chromate coating affords much poorer protection, but it is superior to an as-plated cadmium surface with respect to resistance to tarnishing, humidity, and salt spray.

With a plate thickness of 13 to 18 μm (520 to 720 μin.) and a chromate conversion coating, cadmium will provide adequate service in marine and humid tropical atmospheres. When long-term exposure is anticipated, a paint coating is desirable.

If a chromate treatment is used, only two cold-water rinse tanks are necessary after plating. The first may be for reclaiming the cadmium solution or for the treatment of water. The second rinse should be provided with sufficient flow and agitation to prevent carryover of cyanide into the chromate solution. After chromate dipping, three rinse tanks are required. Again, the first tank may be for reclaiming or waste treatment.

Yellow chromate finish is obtained by dipping in acidified sodium or potassium dichromate. Excellent corrosion protection and a superior base for organic finishing are obtained.

Clear chromate finish consists of 117 g (0.258 lb) of chromic acid and 1.2 g (2.6×10^{-3} lb) of sulfuric acid per liter (gallon) of water and provides good passivation and attractive appearance. Although the protective film is very thin, it prevents the formation of a white, powdery corrosion product on cadmium-plated parts in indoor or internal-component use.

Olive green coating is obtained in an acidified dichromate solution and is easily colored by any of the acid dyes.

Other Postplating Processes

Bright Dipping. The solution for bright dipping consists of $\frac{1}{4}$ to 1% of commercial-grade nitric acid (1.41 sp gr) and is used at room temperature. The acid neutralizes any alkaline salts on the surface and provides some passivation. It is used extensively because it does not interfere with solderability. Immersion times vary from 2 to 30 s.

A solution of acidified hydrogen peroxide is also used for bright dipping. It consists of 6 to 7% commercial-grade (35%) hydrogen peroxide acidified with about 0.25% H_2SO_4. It produces a bright luster and uniform finish but adversely affects resistance to atmospheric corrosion, ultimately resulting in the formation of a white powder. The solution is rather expensive and has a short life.

Phosphate treatment produces a supplementary conversion coating. The solution consists of 3 to 4% equivalent phosphoric acid at a pH of 3.5 to 4.2. The solution is maintained at a temperature of 71 to 88 °C (160 to 190 °F); immersion time ranges from 3 to 5 min. Following the acid dip, parts are water rinsed and then passivated for 2 to 3 min in a solution of sodium dichromate (0.8 to 1.5 g/L, or 0.1 to 0.2 oz/gal) or chromic acid (pH, 3.5 to 4.0) at a temperature of 66 to 77 °C (150 to 170 °F). The coating provides a good basis for organic finishes.

Molybdenum coating is performed in a proprietary bath containing molybdenum salts dissolved in a highly concentrated solution of ammonium chloride at 54 to 66 °C (130 to 150 °F). An attractive, adherent black finish is obtained.

Zinc Plating

Revised by A. Sato, Lea Ronal Inc.

Introduction

ZINC is anodic to iron and steel and therefore offers more protection when applied in thin films of 7 to 15 μm (0.3 to 0.5 mil) than similar thicknesses of nickel and other cathodic coatings, except in marine environments where it is surpassed by cadmium (which is somewhat less anodic than zinc to iron and steel). When compared to other metals it is relatively inexpensive and readily applied in barrel, tank, or continuous plating facilities. Zinc is often preferred for coating iron and steel parts when protection from either atmospheric or indoor corrosion is the primary objective. Electroplated zinc without subsequent treatment becomes dull gray in appearance after exposure to air. Bright zinc that has been subsequently given a chromate conversion coating or a coating of clear lacquer (or both) is sometimes used as a decorative finish. Such a finish, although less durable than heavy nickel chromium, in many instances offers better corrosion protection than thin coatings of nickel chromium, and at much lower cost.

Much recent attention has been focused on the development of techniques for electroplating alloys such as zinc-iron, zinc-nickel, and zinc-cobalt. The operating parameters and applications of these coatings is very similar to those for unalloyed zinc. More detailed information about these techniques is provided in the article "Zinc Alloy Plating" in this Volume.

Plating Baths

Commercial zinc plating is accomplished by a number of distinctively different systems: cyanide baths, alkaline noncyanide baths, and acid chloride baths. In the 1970s, most commercial zinc plating was done in conventional cyanide baths, but the passage of environmental control laws throughout the world has led to the continuing development and widespread use of other processes. Today, bright acid zinc plating (acid chloride bath) is possibly the fastest growing system in the field. Approximately half of the existing baths in developed nations use this technology and most new installations specify it.

The preplate cleaning and postplate chromate treatments are similar for all zinc processes; however, the baths themselves are radically different. Each separate system is reviewed in detail in this article, giving its composition and the advantages and disadvantages.

Cyanide Zinc Baths

Bright cyanide zinc baths may be divided into four broad classifications based on their cyanide content: regular cyanide zinc baths, midcyanide or half-strength cyanide baths, low-cyanide baths, and microcyanide zinc baths. Table 1 gives the general composition and operating conditions for these systems.

Table 1 Composition and operating conditions of cyanide zinc baths

Constituent	Standard cyanide bath[(a)]				Mid or half-strength cyanide bath[(b)]			
	Optimum		Range		Optimum		Range	
	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal
Preparation								
Zinc cyanide	61	8.1	54-86	7.2-11.5	30	4.0	27-34	3.6-4.5

Sodium cyanide	42	5.6	30-41	4.0-5.5	20	2.7	15-28	2.0-3.7
Sodium hydroxide	79	10.5	68-105	9.0-14.0	75	10.0	60-90	8.0-12.0
Sodium carbonate	15	2.0	15-60	2.0-8.0	15	2.0	15-60	2.0-8.0
Sodium polysulfide	2	0.3	2-3	0.3-0.4	2	0.3	2-3	0.3-0.4
Brightener	[g]	[g]	1-4	0.1-0.5	[g]	[g]	1-4	0.1-0.5
Analysis								
Zinc metal	34	4.5	30-48	4.0-6.4	17	2.3	15-19	2.0-2.5
Total sodium cyanide	93	12.4	75-113	10.0-15.1	45	6.0	38-57	5.0-7.6
Sodium hydroxide	79	10.5	68-105	9.0-14.0	75	10.0	60-90	8.0-12.0
Ratio: NaCN to Zn	2.75	0.37	2.0-3.0	0.3-0.4	2.6	0.3	2.0-3.0	0.2-0.4

Constituent	**Low-cyanide bath[c]**				**Microcyanide bath[d]**			
	Optimum		**Range**		**Optimum**		**Range**	
	g/L	**oz/gal**	**g/L**	**oz/gal**	**g/L**	**oz/gal**	**g/L**	**oz/gal**
Preparation								
Zinc cyanide	9.4[b]	1.3[e]	7.5-14[b]	1.0-1.9	[f]	[f]	[f]	[f]
Sodium cyanide	7.5	1.0	6.0-15.0	0.8-2.0	1.0	0.1	0.75-1.0	0.4-0.13
Sodium hydroxide	65	8.7	52-75	6.9-10.0	75	10.0	60-75	8-10
Sodium carbonate	15	2.0	15-60	2.0-8.0	. . .	. . .	. . .	. . .
Sodium polysulfide	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Brightener	[g]	[g]	1-4	0.1-0.5	[g]	[g]	1-5	0.1-0.7
Analysis								

Zinc metal	7.5	1.0	. . .	0.8-1.5	7.5	1.0	6.0-11.3	0.8-1.5
Total sodium cyanide	7.5	1.0	6.0-15.0	0.8-2.0	1.0	0.1	0.75-1.0	0.1-0.13
Sodium hydroxide	75	10	60-75	8.0-10.0	75	10.0	60-75	8-10
Ratio: NaCN to Zn	1.0	0.1	1.0	0.1	. . .	. . .	. . .	. . .

Note: Cathode current density: limiting 0.002 to 25 A/dm^2 (0.02 to 250 A/ft^2); average barrel 0.6 A/dm^2 (6 A/ft^2); average rack 2.0 to 5 A/dm^2 (20 to 50 ft^2). Bath voltage: 3 to 6 V, rack; 12 to 25 V, barrel.

(a) Operating temperature: 29 °C (84 °F) optimum; range of 21 to 40 °C (69 to 105 °F).

(b) Operating temperature: 29 °C (84 °F) optimum; range of 21 to 40 °C (69 to 105 °F).

(c) Operating temperature: 27 °C (79 °F) optimum; range of 21 to 35 °C (69 to 94 °F).

(d) Operating temperature: 27 °C (79 °F) optimum; range of 21 to 35 °C (69 to 94 °F).

(e) Zinc oxide.

(f) Dissolve zinc anodes in solution until desired concentration of zinc metal is obtained.

(g) As specified

Cyanide baths are prepared from zinc cyanide (or zinc oxide sodium cyanide), and sodium hydroxide, or from proprietary concentrates. Sodium polysulfide or tetrasulfide, commonly marketed as zinc purifier, is normally required in standard, midcyanide, and occasionally low-cyanide baths, to precipitate heavy metals such as lead and cadmium that may enter the baths as an anode impurity or through drag-in.

Standard cyanide zinc baths have a number of advantages. They have been the mainstay of the bright zinc plating industry since the early 1940s. A vast amount of information regarding standard cyanide bath technology is available, including information on the technology of operation, bath treatments, and troubleshooting.

The standard cyanide bath provides excellent throwing and covering power. The ability of the bath to cover at very low current densities is greater than that of any other zinc plating system. This capability depends on the bath composition, temperature, base metal, and proprietary additives used, but it is generally superior to that of the acid chloride systems. This advantage may be critical in plating complex shapes. This bath also tolerates marginal preplate cleaning better than the other systems.

Cyanide zinc formulas are highly flexible, and a wide variety of bath compositions can be prepared to meet diverse plating requirements. Zinc cyanide systems are highly alkaline and pose no corrosive problems to equipment. Steel tanks and anode baskets can be used for the bath, substantially reducing initial plant investment.

The cyanide system also has a number of disadvantages, including toxicity. With the possible exception of silver or cadmium cyanide baths, the standard cyanide zinc bath containing 90 g/L (12 oz/gal) of total sodium cyanide is

potentially the most toxic bath used in the plating industry. The health hazard posed by the high cyanide content and the cost for treating cyanide wastes have been the primary reasons for the development of the lower-cyanide baths and the switch to alkaline noncyanide and acid baths. Although the technology for waste treatment of cyanide baths is well developed, the cost for the initial treatment plant may be as much as or more than for the basic plating installation.

Another disadvantage is the relatively poor bath conductivity. The conductivity of the cyanide bath is substantially inferior to that of the acid bath, so substantial power savings may be had by using the latter.

The plating efficiency of the cyanide system varies greatly, depending on such factors as bath temperature, cyanide content, and current density. In barrel installations at current densities up to 2.5 A/dm^2 (25 A/ft^2), the efficiency can range within 75 to 90%. In rack installations, the efficiency rapidly drops below 50% at current densities above 6 A/dm^2 (60 A/ft^2).

Although the depth of brilliance obtained from the cyanide zinc bath has increased steadily since 1950, none of the additives shows any degree of the intrinsic leveling found in the acid chloride baths. The ultimate in depth of color and level deposits reached in the newer acid baths cannot be duplicated in the cyanide bath.

Midcyanide Zinc Baths. In an effort to reduce cyanide waste as well as treatment and operating costs, most cyanide zinc baths are currently at the so-called midcyanide, half-strength, or dilute cyanide bath concentration indicated in Table 1. Plating characteristics of midcyanide baths and regular cyanide baths are practically identical. The only drawback of the midcyanide bath, compared with the standard bath, is a somewhat lower tolerance to impurities and poor preplate cleaning. This drawback is seldom encountered in practice in the well-run plant. Greater ease of rinsing, substantially less dragout, and savings in bath preparation, maintenance, and effluent disposal costs are responsible for the prominence of this type of bath.

Low-cyanide zinc baths are generally defined as those baths operating at approximately 6 to 12 g/L (0.68 to 1.36 oz/gal) sodium cyanide and zinc metal. They are substantially different in plating characteristics from the midcyanide and standard cyanide baths. The plating additives normally used in regular and midstrength cyanide baths do not function well with low metal and cyanide contents. Special low-cyanide brighteners have been developed for these baths.

Low-cyanide zinc baths are more sensitive to extremes of operating temperatures than either the regular or midcyanide bath. The efficiency of the bath may be similar to that of a regular cyanide bath initially, but it tends to drop off more rapidly (especially at higher current densities) as the bath ages. Bright throwing power and covering power are slightly inferior to those of a standard midcyanide bath. However, most work that can be plated in the higher cyanide electrolytes can be plated in the low-cyanide bath. Despite the fact that low-cyanide baths have significantly lower metal and cyanide contents, they are less sensitive to impurity content than the standard or midcyanide bath. Heavy metal impurities are much less soluble at lower cyanide contents. The deposit from a low-cyanide bath is usually brighter than that from a regular or midcyanide system, especially at higher current densities. These baths are used extensively for rack plating of wire goods. Unlike the other cyanide systems, low-cyanide baths are quite sensitive to sulfide treatments to reduce impurities. Regular sulfide additions may reduce the plating brightness and precipitate zinc.

Microcyanide zinc baths are essentially a retrogression from the alkaline noncyanide zinc process discussed in the following section. In the early history of alkaline baths it was often difficult to operate within its somewhat limited parameters; many platers used a minimal amount of cyanide in these baths, 1.0 g/L (0.13 oz/gal), for example. This acted essentially as an additive, increasing the overall bright range of the baths. However, it negated the purpose of the alkaline noncyanide bath, which is to totally eliminate cyanide.

Preparation of Cyanide Zinc Baths

Bath may be prepared with cyanide zinc liquid concentrates that are diluted with water, and to which sodium hydroxide is normally added, or they may be prepared as follows:

1. Fill the makeup and/or plating tank approximately two-thirds full of tap water.
2. Slowly stir in the required amount of sodium hydroxide.
3. Add the required amount of sodium cyanide and mix until dissolved.
4. Prepare a slurry of the required amount of zinc oxide or zinc cyanide and slowly add to the bath. Mix until completely dissolved. Instead of zinc salts, the bath may be charged with steel baskets of zinc

anode balls that are allowed to dissolve into the solution until the desired metal content is reached.

5. Add an initial 15 g/L (2.0 oz/gal) sodium carbonate for rack plating baths.
6. Add approximately 0.25 to 0.50 g/L (0.03 to 0.06 oz/gal) of sodium polysulfide or zinc purifier for regular and midcyanide baths.
7. Run plating test panels and add the necessary amount of brightener to the bath. If a satisfactory deposit is obtained, place anodes for production.

Zinc baths prepared from impure zinc salts may require treatment with zinc dust and/or low-current-density dummying (the process of plating out bath impurities). Zinc dust should be added at the rate of 2 g/L (0.26 oz/gal) and the bath should be agitated for about 1 h. After settling, the bath should be filtered into the plating tank. Dummying is preferably done on steel cathode sheets at low current densities of 0.2 to 0.3 A/dm^2 (2 to 3 A/ft^2) for 12 to 24 h.

Cyanide Zinc Plating Brighteners

Zinc plating bath brighteners are almost exclusively proprietary mixtures of organic additives, usually combinations of polyepoxyamine reaction products, polyvinyl alcohols, aromatic aldehydes, and quaternary nicotinates. These materials are formulated for producing brightness at both low- and high-density areas and for stability at elevated temperatures. Metallic brighteners based on nickel and molybdenum are no longer commercially used in zinc systems, because their concentration in the deposit is highly critical. Proprietary additives should be used following the manufacturer's recommendations for bath operation. Some incompatibility between various proprietary additives may be encountered, and Hull Cell plating tests should always be used to test a given bath and evaluate new brighteners.

Alkaline Noncyanide Baths

Alkaline noncyanide baths are a logical development in the effort to produce a relatively nontoxic, cyanide-free zinc electrolyte. Approximately 15 to 20% of zinc plated at present is deposited from these baths. Bath composition and operating parameters of these electrolytes are given in Table 2. The operating characteristics of an alkaline noncyanide system depend to a great extent on the proprietary additives and brightening agents used in the bath, because the zinc deposit may actually contain 0.3 to 0.5 wt % C, which originates from these additives. This is ten times as much carbon as is found in deposits from the cyanide system.

Table 2 Composition and operating characteristics of alkaline noncyanide zinc baths

Constituent	Optimum[(a)]		Range[(b)]	
	g/L	oz/gal	g/L	oz/gal
Preparation				
Zinc oxide	9.4	1.3	7.5-21	1-2.8
Sodium hydroxide	65	8.6	65-90	8.6-12
Proprietary additive	[(c)]	[(c)]	3-5	0.4-0.7
Analysis				
Zinc metal	7.5	1.0	6.0-17.0	0.8-2.3

Sodium hydroxide	75.0	10.0	75-112	10.0-14.9

(a) Operating conditions: temperature, 27 °C (81 °F) optimum; cathode current density, 0.6 A/dm^2 (6 A/ft^2); bath voltages, 3 to 6 rack.

(b) Operating conditions: temperature, 21 to 35 °C (69 to 94 °F) range; cathode current density, 2.0 to 4.0 A/dm^2 (20 to 40 A/ft^2); bath voltages, 12 to 18 barrel.

(c) As specified

Alkaline noncyanide baths are inexpensive to prepare and maintain, and they produce bright deposits and cyanide-free effluents. An alkaline noncyanide zinc bath with a zinc metal content of 7.5 to 12 g/L (1.0 to 1.6 oz/gal) used at 3 A/dm^2 (30 A/ft^2) produces an acceptably bright deposit at efficiencies of approximately 80%, as shown in Fig. 1. However, if the metal content is allowed to drop 2 g/L (0.26 oz/gal), efficiency drops to below 60% at this current density. Raising the metal content much above 17 g/L (2.3 oz/gal) produces dull gray deposits, lower-current-density plating areas, and poor distribution; however, additives have been developed to address this problem. Increasing sodium hydroxide concentration increases efficiency, as shown in Fig. 2. However, excessively high concentrations will cause metal buildup on sharp-cornered edges. Alkaline noncyanide zinc is a practical plating bath having hundreds of thousands of gallons in use in large captive plating installations.

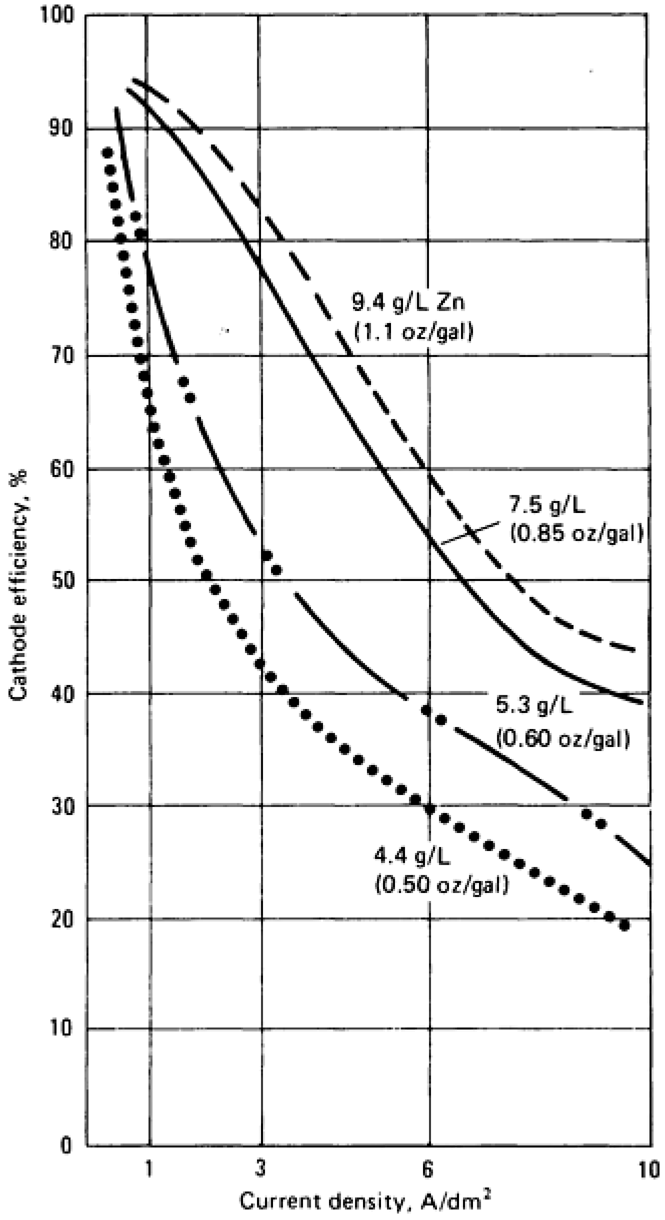


Fig. 1 Cathode current efficiency of alkaline noncyanide zinc baths as related to zinc metal contents. NaOH, 80 g/L (11 oz/gal); Na_2CO_3, 15 g/L (2 oz/gal)

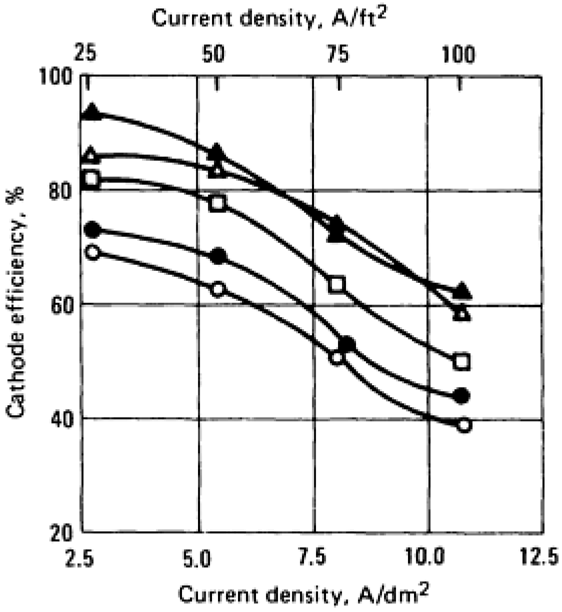


Fig. 2 Effect of zinc and sodium hydroxide concentration on the cathode efficiency of noncyanide zinc solutions. Temperature: 26 °C (77 °F). d : 7.5 g/L (1 oz/gal) Zn, 75 g/L (10 oz/gal) NaOH; •: 7.5 g/L (1.0 oz/gal) Zn, 150 g/L (20 oz/gal) NaOH; V : 11 g/L (1.5 oz/gal) Zn, 110 g/L (15 oz/gal) NaOH; ▲: 15 g/L (2.0 oz/gal) Zn, 150 g/L (20 oz/gal) NaOH; W : 11 g/L (1.5 oz/gal) Zn, 150 g/L (20 oz/gal) NaOH.

Operating Parameters of Standard Cyanide and Midcyanide Zinc Solutions

Anodes. Almost every physical form of zinc anode material has been used in cyanide zinc plating, the type and prevalence varying from country to country. In the United States, cast zinc balls approximately 50 mm (2 in.) in diameter, contained in spiral steel wire cages, are by far the most common anode material. A practical variation of this is the so-called flat top anode, with a flat surface to distinguish it from cadmium ball anodes. The use of ball anodes provides maximum anode area, ease of maintenance, and practically complete dissolution of the zinc anodes with no anode scrap formation.

One of the most economical forms of anode material is the large cast zinc slabs that form the prime material for subsequent ball or elliptical anode casting. Although these have the disadvantage of bulky handling and the need for specially fabricated anode baskets, their lower initial cost makes their use an important economic factor in the larger zinc plating shop.

Three grades of zinc for anodes are conventionally used for cyanide zinc plating: prime western, intermediate, and special high-grade zinc. The zinc contents of these are approximately 98.5%, 99.5%, and 99.99%, respectively. The usual impurities in zinc anodes are all heavy metals, which cause deposition problems unless continuously treated. Nearly troublefree results can consistently be obtained through the use of special high-grade zinc. A typical composition of special high-grade zinc is:

Constituent	Amount, %
Zinc	99.9930
Lead	0.0031

Cadmium	0.0017
Iron	0.0010
Copper	Trace

Control of Zinc Metal Content. Zinc anodes dissolve chemically as well as electrochemically in cyanide baths, so effective anode efficiency will be above 100%. This causes a buildup in zinc metal content, because cathode efficiencies are usually substantially less than 100%. A number of procedures have been developed to control this tendency.

In a conventional new zinc cyanide installation, approximately ten spiral anode ball containers should be used for every meter of anode rod. These should be filled initially, and after 1 or 2 weeks of operation they should be adjusted to compensate for anode corrosion and dragout losses so that the metal content remains as constant as possible. During shutdown periods in excess of 48 h, most cyanide zinc platers remove anodes from the bath. In large automatic installations, this may be done by using a submerged steel anode bar sitting in yokes that can be easily lifted by hoist mechanisms.

One of the prime causes of zinc metal buildup is the very active galvanic cell between the zinc anodes and the steel anode containers. This is evidenced by intense gassing in the area of anodes in a tank not in operation. Zinc buildup from this source can be eliminated by plating the anode containers with zinc before shutdown, which eliminates the galvanic couple.

Temperature. Probably no operating variable is as important and as often overlooked in the operation of cyanide zinc baths as operating temperature. Cyanide zinc solutions have been reported operating between the rather wide limits of 12 to 55 °C (54 to 130 °F), with the vast majority of baths operating between 23 to 32 °C (73 to 90 °F). The exact operating temperature for a given installation depends on the type of work processed, the finish desired, and the engineering characteristics of the plating system. Bath temperature has an effect on a great many variables in the cyanide zinc systems, so the optimum temperature is generally a compromise. Increasing the bath temperature:

- Increases cathode efficiency
- Increases bath conductivity
- Increases anode corrosion
- Produces duller deposits over a broad range of current densities
- Reduces covering power
- Reduces throwing power
- Increases breakdown of cyanide and addition agents

Lowering the bath temperature has the opposite effects. Thus, if a plater is primarily concerned with plating of pipe or conduit where deposit brilliance is not of great importance and covering and throwing power are not critical, operating the bath at the highest practical temperature to give optimum conductivity and plating efficiency would be preferred. For general bright plating of fabricated stampings, a lower bath temperature should be used, permitting the required excellent covering and throwing power and bright deposits.

The effects of higher bath temperature can be compensated to a substantial extent by increasing the total-cyanide-to-zinc ratio of the solution. The exact optimum ratio varies slightly for a given proprietary system, as shown in Table 3.

Table 3 Effect of bath temperature on total-cyanide-to-zinc ratio

Temperature	Total-NaCN-to-Zn ratio	Total-NaCN-to-Zn ratio

°C	°F	(standard cyanide bath)	(midcyanide bath)
22	72	2.6	2.2
26	79	2.7	2.3
30	86	2.8	2.4
34	93	2.9	2.5
38	100	3.0	2.6
42	108	3.2	2.7
46	115	3.3	3.0

Cathode Current Densities. Bright cyanide zinc solutions operate at wide-ranging cathode current densities varying from extremely low, less than 0.002 A/dm^2 (0.02 A/ft^2), to above 25 A/dm^2 (250 A/ft^2) without burning (i.e., the formation of dark, coarse electrodeposits). Current density limits depend on bath composition, temperature, cathode film movement, and addition agents used.

Average current densities vary but are approximately 0.6 A/dm^2 (6 A/ft^2) in barrel plating and 2 to 5 A/dm^2 (20 to 50 A/ft^2) in still or rack plating. Barrel zinc plating is a complex phenomenon in which a large mass of parts is constantly tumbled in the plating cylinder at varying distances from the cathode contact surfaces. At any given time, a part may have an infinitesimally low current density or it may even be deplating, and in another instant, near the outer surface of the tumbling mass, current density may approach 20.0 A/dm^2 (200 A/ft^2). In general, the bulk of deposition takes place in the lower current density range of 0.2 to 1 A/dm^2 (2 to 10 A/ft^2).

Average cathode current densities are generally easier to maintain in rack and still line operations and range from approximately 2 to 5 A/dm^2 (20 to 50 A/ft^2). However, the actual current density of any particular area of a given part will vary greatly, depending on part configuration, anode-to-cathode distance, bath shape, and other factors affecting the primary and secondary current distribution characteristics. In most cases, with proper attention to racking and work shape, current density variations can be kept within practical limits on fabricated parts so that if a minimum average thickness of 4 µm (0.15 mil) is required on a specific part, variations from approximately 2.5 to 8 µm (0.09 to 0.3 mil) occur at various areas on the part.

Cathode current efficiencies in barrel cyanide zinc plating vary between 75 and 93%, depending on temperature, formulation, and barrel current densities. In rack or still plating, however, there is quite a wide variation in current efficiencies when higher current densities are used, especially above 3 A/dm^2 (30 A/ft^2). The effects of zinc metal content, sodium hydroxide content, and the cyanide-to-zinc ratio on cathode current efficiency are shown in Fig. 3. As can be seen from the graphs, the current efficiency in the most commonly used baths drops dramatically from approximately 90% at 2.5 A/dm^2 (25 A/ft^2) to 50% at 5 A/dm^2 (50 A/ft^2). An improvement in current efficiency can be obtained by using a high-strength bath; however, this is offset by the relatively poor throwing power of the solution, higher brightener consumption, higher operating costs, and maintenance difficulties. The lower standard bath concentration, which gives practically identical results, is used for practically all plating installations except a selected few rack tanks that plate conduit or large flat surfaces with no critical recessed areas.

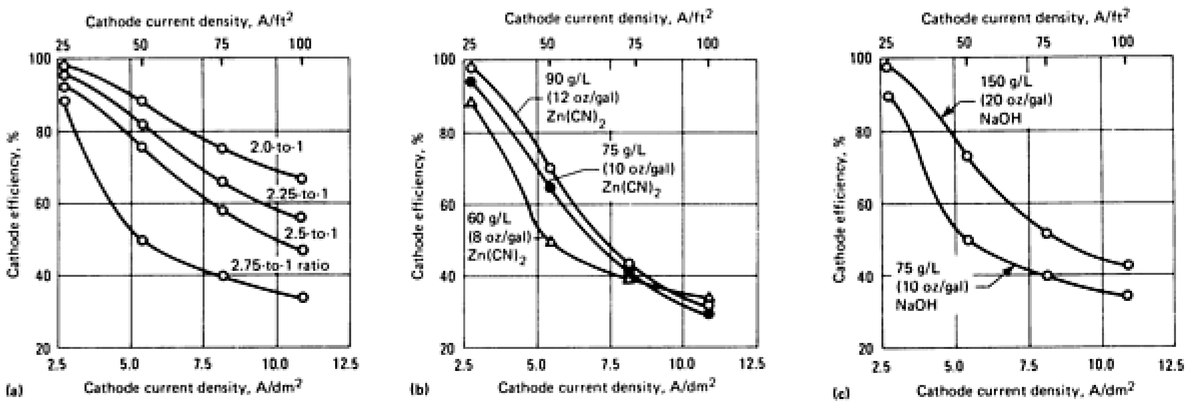


Fig. 3 Effects of bath composition variables and cathode current density on cathode efficiency in cyanide zinc plating. (a) Effect of NaCN/Zn ratio. 60 g/L (8 oz/gal) Zn (CN); 17.5 to 43.7 g/L (2.33 to 5.82 oz/gal) NaCN; 75.2 g/L (10 oz/gal) NaOH; 2.0-to-1 to 2.75-to-1 ratios of NaCN to zinc. Temperature: 30 °C (86 °F). (b) Effect of zinc metal content. 60.1, 75.2, and 90.2 g/L (8, 10, and 12 oz/gal) Zn (CN); 43.7, 54.6, and 65.5 g/L (5.82, 7.27, and 8.72 oz/gal) NaCN; 75.2 g/L (10 oz/gal) NaOH; 2.75-to-1 ratio of NaCN to zinc. Temperature: 30 °C (86 °F). (c) Effect of NaOH content. 60.1 g/L (8 oz/gal) Zn(CN); 43.6 g/L (5.8 oz/gal) NaCN; 150.4 and 75.2 g/L (20 and 10 oz/gal) NaOH; 2.75-to-1 ratio of NaCN to zinc. Temperature: 30 °C (86 °F)

Sodium carbonate is present in every cyanide and alkaline zinc solution. It enters the bath as an impurity from the makeup salts (sodium hydroxide and sodium cyanide may contain anywhere from 0.5 to 2% sodium carbonate) or as a deliberate addition to the initial bath (15 to 30 g/L, or 2.0 to 4 oz/gal).

The harmful effects of sodium carbonate in cyanide zinc plating are not as critical as in cyanide cadmium plating. Sodium carbonate does not begin to affect normal bath operation until it builds to above 75 to 105 g/L (10 to 14 oz/gal). Depending on overall bath composition and the type of work being done, a carbonate content in this range results in a slight decrease in current efficiency, especially at higher current densities, decreased bath conductivity, grainier deposits, and roughness, which becomes visible when the carbonate crystallizes out of cold solutions.

The carbonate content of zinc baths builds up by decomposition of sodium cyanide and absorption of carbon dioxide from the air reacting with the sodium hydroxide in the bath. Carbonates are best removed by one of the common cooling or refrigeration methods rather than by chemical methods, which are simple in theory but extremely cumbersome in practice. When an operating cyanide zinc bath has reached the point that excessive carbonates present a problem, it undoubtedly is contaminated with a great many other dragged-in impurities, and dilution is often a much quicker, although expensive, method of treatment. Alkaline noncyanide baths do not suffer from the effects of carbonate buildup.

Operating Parameters of Low-Cyanide Zinc Systems

Temperature control is as critical, if not more critical, in the low-cyanide bath as in the regular or midcyanide bath. The optimum operating temperature for most proprietary baths is 29 °C (84 °F), and the permissible range is more restricted than for the standard cyanide bath. Adequate cooling facilities are therefore mandatory and are more critical for low-cyanide than for the standard system.

Cathode Current Density. The average cathode current densities used in most low-cyanide processes are the same as in the standard cyanide bath. However, some proprietary baths do not have the extreme high-current-density capabilities of the standard cyanide bath, and burning on extremely high-current-density areas may be more of a problem with the low-cyanide bath than with the conventional baths.

Agitation. Unlike the standard cyanide bath, where agitation is usually nonexistent, air or mechanical agitation of the low-cyanide bath is common and is often quite useful in obtaining the optimum high-current-density plating range of the bath.

Filtration. Most low-cyanide baths appear to operate much more cleanly than the standard or midcyanide bath. The bath is a poor cleaner, and soils that may be removed and crystallized out of high-cyanide baths are not as readily affected by the low-cyanide bath.

Efficiency. The efficiency of the low-cyanide bath on aging is much more dependent on the particular addition agent used than the standard cyanide bath, because there is a substantial difference in various proprietary systems. In a new low-cyanide bath, current efficiency is slightly higher than that of a standard or midcyanide system. However, as the bath ages, current efficiency tends to drop, possibly because of the formation of additive breakdown products, and the efficiency of a bath after 2 or 3 months of operation may be as much as 30% below that of a higher cyanide system, especially at higher current densities. As in the standard cyanide bath, increasing the sodium hydroxide content, zinc metal content, and operating temperature increases the efficiency of the low-cyanide bath. However, increasing these variables has markedly harmful effects on the bright operating range of a low-cyanide bath that usually override the benefit of increased efficiency. The effects of bath constituents and temperature on the plating characteristics of the bright low-cyanide zinc systems are given in Table 4. Figure 4 shows the effect of sodium cyanide concentration on cathode efficiency.

Table 4 Effect of bath constituents and temperature on plating characteristics of bright, low-cyanide zinc plating

Variable	Cathode efficiency	Bright plating range	Bright low-current-density throwing power
Increasing sodium hydroxide	Increases	Slightly decreases	Negligible
Increasing zinc metal	Increases	Decreases	Decreases
Increasing sodium cyanide	Decreases	Increases	Increases
Increasing brightener	Increases	Increases	Increases
Increasing temperature	Increases	Decreases	Decreases

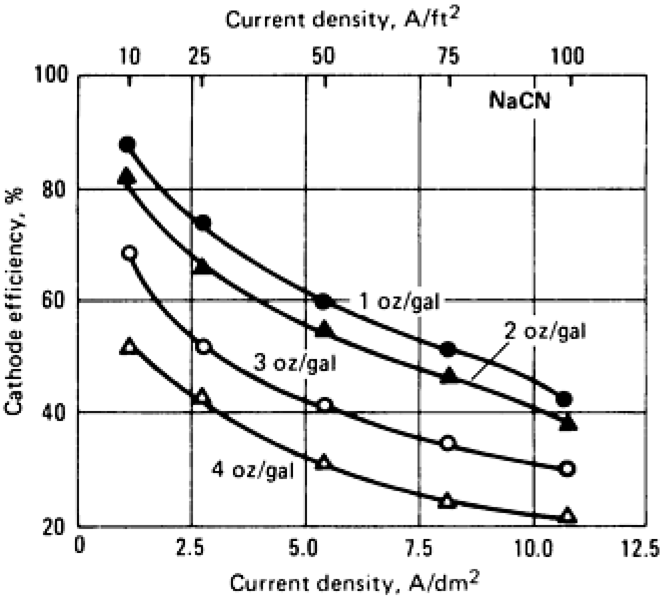


Fig. 4 Effect of sodium cyanide concentration on the cathode efficiency of low-cyanide zinc solutions. d :20 g/L

(2.5 oz/gal) NaCN; •:8 g/L (1 oz/gal) NaCN; ∨:30 g/L (4 oz/gal) NaCN; ▲:15 g/L (2 oz/gal) NaCN

Bright Throwing Power and Covering Power. The bright covering power of a low-cyanide bath operated at low current density is intrinsically not as good as that of a standard or midcyanide bath. In most operations, however, the difference is negligible except on extremely deep recessed parts. The vast majority of parts that can be adequately covered in a standard cyanide bath can be similarly plated in a low-cyanide bath without any production problems, such as excessively dull recessed areas or stripping by subsequent bright dipping.

Increasing the brightener and cyanide contents, within limits, improves the bright low-current-density deposition to a visible degree. Problems with bright throwing power at extremely low current densities are often solved by raising the cyanide content to approximately 15 g/L (2 oz/gal), which in effect returns the system to the lower range of the midcyanide bath.

Operating Parameters of Alkaline Noncyanide Zinc Baths

Temperature control is more critical in noncyanide zinc baths than in cyanide baths. The optimum temperature for most baths is approximately 29 °C (84 °F). Low operating temperatures result in no plating or, at most, very thin, milky white deposits. High operating temperatures rapidly narrow the bright plating current range, cause dullness at low current densities, and result in very high brightener consumption. However, because these temperature limitations for noncyanide zinc are within those commonly used in regular cyanide zinc, no additional refrigeration or cooling equipment is required for conversion to the process.

Operating Voltages. Normal voltages used in standard cyanide zinc plating are adequate for the noncyanide zinc bath, in both rack and barrel range. Normal voltage will be approximately 3 V with a range of 2 to 20 V, depending on part shape, anode-to-cathode relationship, temperature, barrelhole size, and variables that are unique to each operation.

Cathode Current Densities. The maximum allowable cathode current densities of the noncomplexing noncyanide bath closely approximate those of a standard cyanide bath. Current density ranges from 0.1 to more than 20 A/dm^2 (1 to 200 A/ft^2) can be obtained. This extremely wide plating range permits operation at an average current density of 2 to 4 A/dm^2 (20 to 40 A/ft^2) in rack plating, which makes a noncyanide system practical for high-production work.

Anodes. Standard zinc ball or slab anodes in steel containers are used in the noncyanide electrolyte. During the first 2 or 3 weeks of installation of noncyanide zinc baths, the anode area should be watched carefully to determine the appropriate anode area to maintain a stable analysis of zinc in the system. Whenever possible, zinc anodes should be removed during weekend shutdown periods to avoid excessive metal buildup.

Filtration of noncyanide baths is not an absolute necessity. However, the occurrence of roughness in these baths presents a greater potential problem than in regular cyanide baths. This is due to the nature of the deposit, which may become amorphous at very high current densities if the brightener is not maintained at an optimum level, and to anode polarization problems, which result in sloughing off of anode slimes, a more common occurrence in these baths. Carbon filtration may be required to remove organic contamination caused by marginal preplate cleaning practices. Filtration is also the preferred method for removing zinc dust used to treat metallic impurities in the system.

The bright plating range of the alkaline, noncyanide zinc bath is totally dependent on the particular additive used. Without any additive, the deposit from an alkaline, noncyanide bath is totally useless for commercial finishing, with a powdery, black amorphous deposit over the entire normal plating range.

Proper maintenance of the addition agent at the recommended level is extremely important in noncyanide alkaline zinc baths. A plater does not have the liberty of maintaining low levels of brightener in the bath and still obtaining passably bright deposits, as is the case in cyanide systems. Low brightener content rapidly leads to high- and medium-current-density burning, because in the noncyanide bath, as in the low-cyanide bath, burning and brightness are interdependent.

Cathode current efficiency of a noncyanide bath is a very critical function of the metal content (Fig. 1). At lower metal concentrations of approximately 4 g/L (0.5 oz/gal), efficiency is less than that of a standard cyanide bath, whereas at a metal content of approximately 9 g/L (1.2 oz/gal), efficiency is somewhat higher than in either regular or low-cyanide baths. Thus, if a plater can maintain metal content close to the 9 g/L (1.2 oz/gal) value, there will be no problem in obtaining deposition rates similar to those obtained with cyanide baths.

Acid Baths

The continuing development of acid zinc plating baths based on zinc chloride has radically altered the technology of zinc plating since the early 1970s. Acid zinc plating baths now constitute 40 to 50% of all zinc baths in most developed nations and are the fastest growing baths throughout the world. Acid zinc formulas and operating limits are given in Table 5. Bright acid zinc baths have a number of intrinsic advantages over the other zinc baths:

- They are the only zinc baths possessing any leveling ability, which, combined with their superb out-of-bath brightness, produces the most brilliant zinc deposits available.
- They can readily plate cast iron, malleable iron, and carbonitrided parts, which are difficult or impossible to plate from alkaline baths.
- They have much higher conductivity than alkaline baths, which produces substantial energy savings.
- Current efficiencies are 95 to 98%, normally much higher than in cyanide or alkaline processes, especially at higher current densities, as shown in Fig. 5.
- Minimal hydrogen embrittlement is produced than in other zinc baths because of the high current efficiency.
- Waste disposal procedures are minimal, consisting only of neutralization, at pH 8.5 to 9, and precipitation of zinc metal, when required.

The negative aspects of the acid chloride bath are that:

- The acid chloride electrolyte is corrosive. All equipment in contact with the bath, such as tanks and superstructures, must be coated with corrosion-resistant materials.
- Bleedout of entrapped plating solution occurs to some extent with every plating process. It can become a serious and limiting factor, prohibiting the use of acid chloride baths on some fabricated, stamped, or spot welded parts that entrap solution. Bleedout may occur months after plating, and the corrosive electrolyte can ruin the part. This potential problem should be carefully considered when complex assemblies are plated in acid chloride electrolytes.

Table 5 Composition and operating characteristics of acid chloride zinc plating baths

Constituent	Ammoniated bath Barrel		Ammoniated bath Rack	
	Optimum	Range	Optimum	Range
Preparation				
Zinc chloride	18 g/L (2.4 oz/gal)	15-25 g/L (2.0-3.8 oz/gal)	30 g/L (4.0 oz/gal)	19-56 g/L (2.5-7.5 oz/gal)
Ammonium chloride	120 g/L (16.0 oz/gal)	100-150 g/L (13.4-20.0 oz/gal)	180 g/L (24.0 oz/gal)	120-200 g/L (16.0-26.7 oz/gal)
Potassium chloride	. . .	. . .	. . .	. . .
Sodium chloride	. . .	. . .	. . .	. . .
Boric acid	. . .	. . .	. . .	. . .

Carrier brightener[(a)]	4 vol%	3-5%	3.5%	3-4%
Primary brightener[(a)]	0.25%	0.1-0.3%	0.25%	0.1-0.3%
pH	5.6	5.5-5.8	5.8	5.2-6.2
Analysis				
Zinc metal	9 g/L (1.2 oz/gal)	7.5-25 g/L (1.0-3.8 oz/gal)	14.5 g/L (1.9 oz/gal)	9-27 g/L (1.2-3.6 oz/gal)
Chloride ion	90 g/L (1.2 oz/gal)	75-112 g/L (10.0-14.9 oz/gal)	135 g/L (18.0 oz/gal)	90-161 g/L (12.0-21.5 oz/gal)
Boric acid	. . .	. . .	. . .	. . .
Operating conditions				
Temperature	24 °C (75 °F)	21-27 °C (69-79 °F)	24 °C (75 °F)	21-27 °C (69-79 °F)
Cathode current density	. . .	0.3-1.0 A/dm^2 (3-10 A/ft^2)	. . .	2.0-5 A/dm^2 (20-50 A/ft^2)
Voltage	. . .	4-12 V	. . .	1-5 V

Constituent	**Potassium bath**		**Mixed sodium ammonium Barrel bath**	
	Optimum	**Range**	**Optimum**	**Range**
Preparation				
Zinc chloride	71 g/L (9.5 oz/gal)	62-85 g/L (8.3-11.4 oz/gal)	34 g/L (4.5 oz/gal)	31-40 g/L (4.1-5.3 oz/gal)
Ammonium chloride	. . .	. . .	30 g/L (4.0 oz/gal)	25-35 g/L (3.3-4.7 oz/gal)
Potassium chloride	207 g/L (27.6 oz/gal)	186-255 g/L (24.8-34.0 oz/gal)	. . .	. . .
Sodium chloride	. . .	. . .	120 g/L (16.0 oz/gal)	100-140 g/L (13.3-18.7 oz/gal)
Boric acid	34 g/L (4.5 oz/gal)	30-38 g/L (4.0-5.1 oz/gal)	. . .	. . .

Carrier brightener[a]	4%	4-5%	4%	3-5%
Primary brightener[a]	0.25%	0.1-0.3%	0.2%	0.1-0.3%
pH	5.2	4.8-5.8	5.0	4.8-5.3
Analysis				
Zinc metal	34 g/L (4.5 oz/gal)	30-41 g/L (4.0-5.5 oz/gal)	16.5 g/L (2.2 oz/gal)	15-19 g/L (2.0-2.5 oz/gal)
Chloride ion	135 g/L (18.0 oz/gal)	120-165 g/L (16.0-22.0 oz/gal)	110 g/L (14.7 oz/gal)	93-130 g/L (12.4-17.4 oz/gal)
Boric acid	34 g/L (4.5 oz/gal)	30-38 g/L (4.0-5.1 oz/gal)	. . .	. . .
Operating conditions				
Temperature	27 °C (79 °F)	21-35 °C (69-94 °F)	27 °C (79 °F)	25-35 °C (76-94 °F)
Cathode current density	. . .	2.0-4 A/dm^2 (20-40 A/ft^2)	. . .	0.3-1 A/dm^2 (3-10 A/ft^2)
Voltage	. . .	1-5 V	. . .	4-12 V

(a) Carrier and primary brighteners for acid chloride are proprietary, and exact recommendations of manufacturer should be followed. Values given are representative.

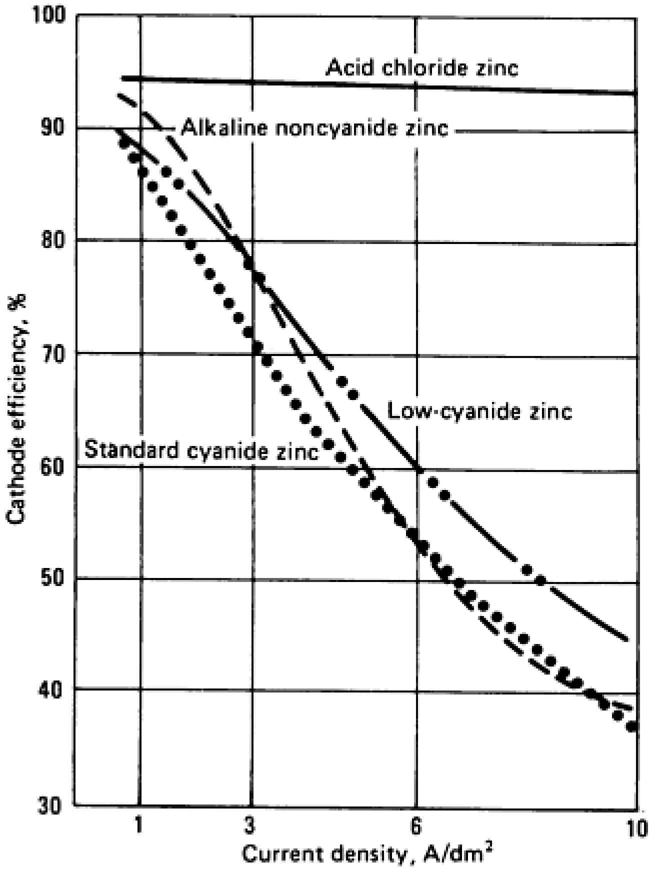


Fig. 5 Comparison of cathode current efficiencies of bright zinc plating electrolytes

Acid chloride zinc baths currently in use are principally of two types: those based on ammonium chloride and those based on potassium chloride. The ammonium-based baths, the first to be developed, can be operated at higher current densities than potassium baths. Both systems depend on a rather high concentration of wetting agents, 4 to 6 vol%, to solubilize the primary brighteners. This is more readily accomplished in the ammonia systems, which makes bath control somewhat easier. Ammonium ions, however, act as a complexing agent in waste streams containing nickel and copper effluents, and in many localities they must be disposed of by expensive chlorination. This was the essential reason for the development of the potassium chloride bath.

All bright acid chloride processes are proprietary, and some degree of incompatibility may be encountered between them. Conversion from an existing process should be done only after a Hull Cell plating test evaluation. Preplate cleaning, filtration, and rack designs for acid chloride baths should be equivalent to those required for nickel plating.

The latest acid chloride zinc baths to become available to the industry are those based on salt (sodium chloride) rather than the more expensive potassium chloride. In many of these baths, salt is substituted for a portion of either ammonium or potassium chloride, producing a mixed bath. Sodium acid chloride baths at present are generally restricted to barrel operation, because burning occurs much more readily in these baths at higher current densities. However, with the continuing development of additive technology, sodium acid chloride baths may challenge the widely used nonammoniated potassium bath in the near future.

Acid chloride zinc baths are now being explored as the basis of zinc alloy plating incorporating metals such as nickel and cobalt, to improve corrosion for specific applications and possibly eliminate standard chromate treating.

A number of zinc baths based on zinc sulfate and zinc fluoborate have been developed, but these have very limited applications. They are used principally for high-speed, continuous plating of wire and strip and are not commercially used for plating fabricated parts. Table 6 shows the compositions and operating conditions for some typical fluoborate and sulfate baths.

Table 6 Fluoborate and sulfate electroplating bath compositions

Constituent	Fluoborate[a]		Sulfate[b]	
	g/L	oz/gal	g/L	oz/gal
Zinc	65-105	9-14	135	18
Zinc fluoborate	225-375	30-50	. . .	. . .
Zinc sulfate	. . .	. . .	375	50
Ammonium fluoborate	30-45	4-6	. . .	. . .
Ammonium chloride	. . .	. . .	7.5-22.5	1-3
Addition agent	[c]	[c]	[c]	[c]

(a) At room temperature; 3.5 to 4 pH; at 20 to 60 A/dm^2 (200 to 600 A/ft^2).

(b) At 30 to 52 °C (85 to 125 °F); 3 to 4 pH; at 10 to 60 A/dm^2 (100 to 600 A/ft^2).

(c) As needed

Operating Parameters of Acid Chloride Zinc Baths

Anodes for acid chloride zinc should be special high grade, 99.99% Zn. Most installations use zinc ball or flat top anodes in titanium anode baskets. Baskets should not be used if the applied voltage on an installation exceeds 8 V, because there may be some attack on the baskets. Baskets should be kept filled to the solution level with zinc balls. Slab zinc anodes, drilled and tapped for titanium hooks, may also be used. Any areas of hooks or splines exposed to solution should be protective coated. Anode bags are optional but recommended for most processes, especially for rack plating where they are useful to minimize roughness. Bags may be made of polypropylene, Dynel, or nylon. Before being used they should be leached for 24 h in a 5% hydrochloric acid solution containing 0.1% of the carrier or wetting agent used in the particular plating bath.

Chemical Composition. Zinc, total chloride, pH, and boric acid, when used, should be controlled and maintained in the recommended ranges (see Table 5) by periodic replenishment using chemically pure materials. Excess zinc causes poor low-current-density deposits, and insufficient zinc causes high-current-density burning. Excess chloride may cause separation of brighteners, and insufficient chloride reduces the conductivity of solutions. Excessively high pH values cause the formation of precipitates and anode polarization, and excessively low pH values cause poor plating. Insufficient boric acid reduces the plating range.

Brighteners also have to be replenished by periodic additions. Because the chemical compositions of brighteners are proprietary, the suppliers specify concentrations and control procedures.

Agitation is recommended in acid chloride baths to achieve practical operating current densities. Solution circulation is recommended in barrel baths to supplement barrel rotation. In rack baths, solution circulation is usually accomplished by locating the intake and discharge of the filter at opposite ends of the plating tank. Cathode rod agitation is suitable for many hand-operated rack lines.

Air agitation is the preferred method for most installations. A low-pressure air blower should be used as a supply source.

Temperature control is more critical in acid zinc baths than in cyanide zinc baths, and auxiliary refrigeration should be provided to maintain the bath at its maximum recommended operating temperature, usually 35 °C (95 °F). Cooling coils in the bath itself should be Teflon or Teflon-coated tubing. Titanium coils may be used if they are isolated from the direct current source.

Operating an acid chloride bath above its maximum recommended temperature causes low overall brightness, usually beginning at low current densities and rapidly progressing over the entire part. High temperatures may also bring the bath above the cloud point of the brightener system. As the acid bath gets hot, additives start coming out of solution, giving the bath a milky or cloudy appearance and causing bath imbalance. Conversely, low temperatures, usually below 21 °C (70 °F), cause many baths to crystallize and cause organic additives to separate out of solution. This produces roughness and, in extreme cases, a sticky globular deposit on the bath and work, which clogs filters and completely curtails operations.

Cathode Current Efficiency. The high cathode current efficiency exhibited by acid chloride zinc baths is one of the most important properties of these baths. As shown in Fig. 5, the average cathode current efficiency for these baths is approximately 95 to 98% over the entire range of operable current densities. No other zinc plating system approaches this extremely high efficiency at higher current densities, which can lead to productivity increases of 15 to 50% over those obtainable with cyanide baths. In barrel plating, barrel loads can often be doubled in comparison with those for cyanide baths, and equivalent plating thickness can often be achieved in half the time.

pH control of acid zinc baths is usually monitored on a daily basis. Electrometric methods are preferred over test papers. The pH of a bath is lowered with a hydrochloric acid addition; when required, the pH may be raised with a potassium or ammonium hydroxide addition.

Iron contamination is a common problem in all acid chloride zinc baths. Iron is introduced into the bath from parts falling into the tank during operation, from attack by the solution on parts at current densities below the normal range, such as the inside of steel tubular parts, and from contaminated rinse waters used before plating. Iron contamination usually appears as dark deposits at high current densities; in barrel plating it appears as stained dark spots reproducing the perforations of the plating barrel. A high iron content turns the plating solution brown and murky.

Iron can be readily removed from acid chloride baths by oxidizing soluble ferrous iron to insoluble ferric hydroxide. This is accomplished by adding concentrated hydrogen peroxide to the bath, usually on a daily basis. Approximately 10 mL (0.34 fl oz) of 30% hydrogen peroxide should be used for every 100 L (26.4 gal.) of bath. The peroxide should be diluted with 4 to 5 parts water and dispersed over the bath surface. Dissolved potassium permanganate can be used instead of peroxide. The precipitated iron hydroxide should then be filtered from the bath using a 15 μm (0.6 mil) or smaller filter coated with diatomaceous earth or a similar filter aid.

Control of Plate Thickness

This section discusses the thicknesses of zinc specified for service in various indoor and outdoor atmospheres. Many combinations of variables must be considered in attempting to plate to a given thickness. To hold each variable at a steady value is virtually impossible under production conditions, so as one variable changes spontaneously, others must be adjusted to maintain uniformity of plate thickness. In automatic plating this is impractical, so the process is set up to give a certain minimum thickness under a great variety of conditions. This accounts for much of the thickness variation normally encountered in automatic plating of a run of identical pieces.

The shape and size of parts that may be plated all over, with or without the use of conforming anodes to attain uniformity of plate thickness, are essentially the same in zinc plating as in cadmium plating (see the article "Cadmium Plating" in this Volume).

Normal Variations. Preferred thicknesses in automatic zinc plating are usually minimum specified thicknesses, and there is little concern regarding the maximum thicknesses obtained. Thickness variations encountered should therefore be over the established minimum thickness.

For example, as shown in Fig. 6, tests were made on 75 samples, over a one-week period, of parts 100 mm (4 in.) long and 39 g (1.375 oz) that were automatically plated to a minimum specified thickness of 3.8 μm (0.15 mil). Although actual plate thicknesses ranged from 2.5 to 7.5 μm (0.1 to 0.3 mil), over 80% of the parts examined exceeded the target minimum.

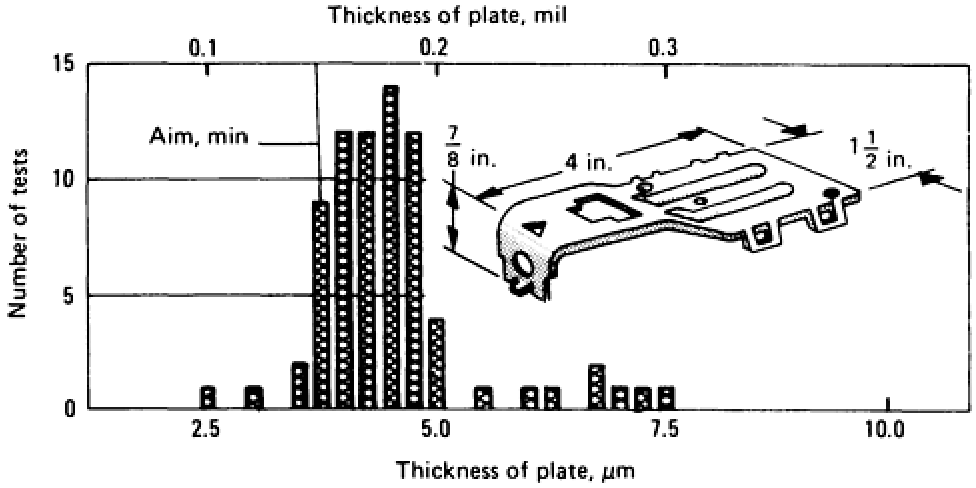


Fig. 6 Variation in thickness of zinc plate obtained in automatic plating in cyanide zinc bath, 75 tests

Thickness variations obtained in barrel plating are markedly affected by the tumbling characteristics of the part and by the density of the load in the plating barrel. Parts that can be tumbled readily are more likely to develop a uniform coating. As shown in Fig. 7, a minimum plate thickness of 12.5 μm (0.5 mil) was the target in barrel plating a 0.12 kg (0.26 lb) S-shape part made of 3 mm (0.125 in.) flat stock. Of 75 parts examined, all were found to be plated to thicknesses that exceeded the target minimum, and a few had thicknesses in excess of 34 μm (0.9 mil).

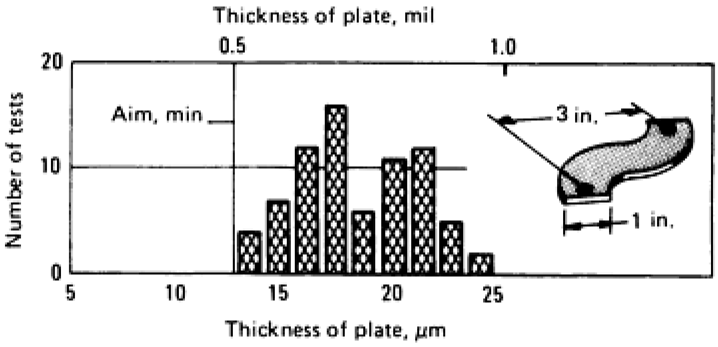


Fig. 7 Variation in thickness of zinc plate obtained in barrel plating a 3.2 mm ($\frac{1}{8}$ in.) thick part in a cyanide zinc

Similarities Between Cadmium and Zinc Plating

Except for differences in plating baths and in such operational details as current density and rates of deposition, alkaline cadmium and zinc plating are essentially similar processes. See the article "Cadmium Plating" in this Volume for a

detailed discussion of plating methods, equipment, and processing. Exceptions with respect to equipment and processing are described below.

Plating Equipment. The equipment requirements for zinc plating are the same as those noted for cadmium plating, except for the following:

- In barrel plating, zinc solutions require higher voltage and current density and therefore must be provided with greater cooling capacity to prevent overheating. Also, because the cyanide zinc bath generates much larger amounts of hydrogen, barrel design should incorporate safety features to prevent explosions.
- Fume hoods should be used on cyanide, low-cyanide, and, especially, alkaline noncyanide baths to exhaust caustic spray and toxic fumes.
- Barrels, tanks, and all superstructures coming into contact with acid chloride zinc plating baths should be coated with material able to resist acid corrosion. Polypropylene, polyethylene, polyvinyl chloride, and fiberglass are commonly used materials. Lead-lined tanks should never be used in these systems. Heating and cooling coils should be built of titanium that is electrically isolated from the tank, or of high-temperature Teflon.

Hydrogen embrittlement of steels is a major problem in all types of cyanide zinc plating. These formulas should not be used for spring tempered parts or other parts susceptible to this type of embrittlement. Spring-tempered parts and other susceptible parts should be plated in acid chloride electrolyte. When no embrittlement whatsoever can be tolerated, mechanically deposited zinc is the preferable alternative.

Processing Steps. Time requirements for various operations involved in still tank, barrel, and automatic methods of plating zinc to a thickness of less than 12.5 μm (0.5 mil) are given in Table 7.

Table 7 Process steps and time requirements for zinc plating operations

Times listed are for plating zinc to a thickness of less than 12.5 μm (0.5 mil).

Processing cycle	Time for each operation
Hand- or hoist-operated still tank	
Electrolytic cleaning	1-3 min
Cold water rinse	10-20 s
Acid pickle	30 s-2 min
Cold water rinse	10-20 s
Cold water rinse	10-20 s
Zinc plate	6-8 min
Cold water rinse	10-20 s

Cold water rinse	10-20 s
Chromate conversion coat	15-30 s
Cold water rinse	10-20 s
Hot water rinse	20-30 s
Air dry	1 min
Hand- or hoist-operated barrel line	
Soak clean	4 min
Electroclean	4 min
Cold water rinse	1-2 min
Acid pickle	2-3 min
Zinc plate	20-30 min
Cold water rinse	1-2 min
Cold water rinse	1-2 min
Chromate conversion coat	30 s-1 min
Cold water rinse	1-2 min
Hot water rinse	2-3 min
Centrifugal dry	3-5 min
Automatic barrel line	
Soak clean	6 min
Electroclean	3 min
Cold water rinse	2 min

Cold water rinse	2 min
Acid pickle	1 min
Neutralize dip	3 min
Cold water rinse	2 min
Zinc plate	30-40 min
Dragout rinse	2 min
Neutralize rinse	2 min
Cold water rinse	2 min
Nitric acid dip	30 s
Cold water rinse	2 min
Chromate dip	30 s
Cold water rinse	2 min
Hot water rinse	2 min
Centrifugal dry	3 min

Applications

In the presence of moisture, zinc becomes a sacrificial protecting agent when in contact with iron and other metals that are below zinc in the galvanic series. Attack is most severe when the electrolyte has high electrical conductivity (as in marine atmospheres) and when the area ratio of zinc to the other metals is small.

Plate Thickness. The life of a zinc coating in the atmosphere is nearly proportional to the coating thickness. Its rate of corrosion is highest in industrial areas, intermediate in marine environments, and lowest in rural locations. Corrosion is greatly increased by frequent dew and fog, particularly if the exposure is such that evaporation is slow.

Table 8 gives the estimated life of different thicknesses of unprotected zinc coatings on steel in different outdoor atmospheres. The majority of zinc-plated parts are coated with a thickness of 7.5 to 12.5 μm (0.3 to 0.5 mil). Typical applications employing thicknesses less than or greater than usual are given in Table 9.

Table 8 Estimated average service life of unprotected zinc coatings on steel in outdoor service

Condition	Coating thickness	Service, yr

	µm	**mil**	
Rural	5	0.2	3
	13	0.5	7
	25	1.0	14
	38	1.5	20
	50	2.0	30
Temperate marine	5	0.2	1
	13	0.5	3
	25	1.0	7
	38	1.5	10
	50	2.0	13
Industrial marine	5	0.2	1
	13	0.5	2
	25	1.0	4
	38	1.5	7
	50	2.0	9
Severe industrial	5	0.2	0.5
	13	0.5	1
	25	1.0	3
	38	1.5	4
	50	2.0	6

Table 9 Applications of zinc plating at thicknesses below or above 7 to 13 µm (0.3 to 0.5 mil)

Application	Plate thickness	
	µm	mil
Less than 7 µm (0.3 mil) of zinc		
Automobile ashtrays[(a)]	5-7	0.2-0.3
Birdcages[(b)]	5	0.2
Electrical outlet boxes[(c)]	4-13	0.15-0.5
Tacks	5	0.2
Tubular rivets[(d)]	5	0.2
More than 13 µm (0.5 mil) of zinc		
Conduit tubing[(e)]	30	1.2

(a) Chromated after plating.

(b) Chromated after plating; some parts dyed and lacquered.

(c) Bright chromated after plating.

(d) Chromated, clear or colored, after plating.

(e) Dipped in 0.5% HNO_3 or chromated after plating

Supplementary Coatings. Because corrosion is rapid in industrial and marine locations, zinc-plated parts that must endure for many years are usually protected by supplementary coatings. Steel with 5 µm (0.2 mil) of electroplated zinc is often painted to obtain a coating system for general outdoor service; a phosphate or chromate post-plating treatment ensures suitable adherence of paint to zinc.

In uncontaminated indoor atmospheres, zinc corrodes very little. A 5 µm (0.2 mil) coating has been known to protect steel framework on indoor cabinets for more than 20 years. Atmospheric contaminants accelerate corrosion of zinc if condensation occurs on cooler parts of structural members inside buildings. In 10 years or less, 12.5 µm (0.5 mil) of zinc may be dissipated. Zinc-plated steel in such locations is usually given a protective coating of paint.

A satisfactory coating for parts such as those on the inside of an office machine must afford protection in storage, assembly, and service. The cost is also important. Gears, cams, and other parts of the working mechanism can be plated with 3.8 to 6.3 μm (0.15 to 0.25 mil) of zinc to meet these requirements.

Chromate conversion coatings, colored or clear, are almost universally applied to zinc-plated parts for both indoor and outdoor use to retard corrosion from intermittent condensation, such as may occur in unheated warehouses. Chromate films minimize staining from fingerprints and provide a more permanent surface appearance than bare zinc.

Limitations. Zinc-plated steel is not used for equipment that is continually immersed in aqueous solutions. It must not be used in contact with foods and beverages because of dangerous health effects. Although zinc may be used in contact with gases such as carbon dioxide and sulfur dioxide at normal temperatures if moisture is absent, it has poor resistance to most common liquid chemicals and to chemicals of the petroleum and pharmaceutical industries.

Fasteners. Steel fasteners, such as screws, nuts, bolts, and washers, are often electroplated for corrosion resistance and appearance. If protection against atmospheric corrosion is the sole objective, zinc is the most economical coating metal. Coatings of 5 to 7.5 μm (0.2 to 0.3 mil) give protection for 20 years or more for indoor applications in the absence of frequent condensation of moisture. Chromate coatings are used to retard corrosion from condensates, provide a more permanent surface appearance, and prevent staining from fingerprints. For indoor use in industrial areas and in locations where condensation is prevalent, as in unheated buildings, corrosion may be rapid, and the zinc surface should be phosphated and then painted to extend its service beyond the few years that would be obtained by the unpainted coating. Unprotected zinc-plated screws should not be used to fasten bare parts if the service is to include marine exposure.

The dimensional tolerance of most threaded articles, such as nuts, bolts, screws, and similar fasteners with complementary threads, does not permit the application of coatings much thicker than 7.5 μm (0.3 mil). The limitation of coating thickness on threaded fasteners imposed by dimensional tolerance, including class or fit, should be considered whenever practicable, to prevent the application of thicker coatings than are generally permissible. If heavier coatings are required for satisfactory corrosion resistance, allowance must be made in the manufacture of the threaded fasteners for the tolerance necessary for plate buildup. If this is not practicable, phosphating before assembly and painting after assembly will increase service life. The approximate durability of 5 μm (0.2 mil) untreated coatings is given in Table 8.

Appearance. The appearance of electrodeposited zinc can be varied over a wide range, depending on bath composition, current density, the use of brighteners, and postplating treatments. The appearance of electroplated zinc is bright and silvery, and the deposit from the acid chloride baths is often initially indistinguishable from bright nickel chrome when plated.

Currently, nearly all zinc plating is followed by some type of chromate dip. These preserve the appearance of the part and vastly increase the bright shelf life of the surface. The cost of chromating is so minimal that its use has become practically universal. Presently, bright zinc deposits are used for a wide variety of low-cost consumer goods such as children's toys, bird cages, bicycles, and tools. Refrigerator shelves are commonly bright zinc plated, chromated, and lacquered. Without lacquer protection, even chromated bright zinc will tarnish and discolor quite rapidly when handled, and unlacquered bright zinc plate is not a good substitute for nickel chrome when a longlasting bright finish is desired. However, the vast majority of zinc plate is deposited primarily to impart corrosion resistance; brightness is not the primary factor for these applications.

Additional information about applications of electroplated zinc is provided in the article "Surface Engineering of Carbon and Alloy Steels" in this Volume.

Indium Plating

Allen W. Grobin, Jr., Grobin Associates, Inc.

Introduction

INDIUM is a soft, low-melting-point, silvery white metal with a brilliant metallic luster and a color resembling that of platinum. It alloys with most other metals to form a series of unique alloys, many of which are used as solders. It is soft enough to be readily marked by light fingernail pressure. Indium can be easily extruded at very low pressures: solders containing 50% In can be extruded as 1 mm (0.04 in.) wire at a pressure of 83 MPa (12 ksi). The hardness of indium is

0.9 to 1.0 on the modified Brinell scale, and it has a melting point of 156.7 °C (314.1 °F), a boiling point of 2000 °C (3632 °F), and a low vapor pressure.

Indium is ductile, malleable, crystalline, and diamagnetic. The pure metal gives a high pitched "cry" when bent. It wets glass and finds application in low-melting alloys and solders. It is used in making alkaline batteries, automotive trim, bearing alloys, electronic assemblies, germanium transistors, photoconductors, rectifiers, thermistors, vacuum seals, and group III-V compound semiconductors such as indium phosphide and indium arsenide. When rubbed together, two indium-plated parts will "cold weld" (autogenously join). This can be easily accomplished with freshly plated parts, but as surface oxides build up with time, more vigorous rubbing is required. This cold welding phenomenon is being explored for use in the surface mount technology of the electronics industry. Indium is electropositive to iron and steel and electronegative to tin. In an aqueous 3% sodium chloride solution of pH 6.7 to 7.2, indium has a half-cell static potential of -0.56 V referenced to that of a silver electrode given the value of zero. This places indium between cadmium and tin in the electromotive series of metals, which is used by materials and design engineers to identify and avoid potential galvanic corrosion problems.

Indium is particularly useful in making reliable electrical contact to aluminum. When indium-plated steel wire terminals are secured to aluminum, the high-resistance surface aluminum oxide cracks under the pressure and the indium extrudes into the oxide cracks, making direct metal-to-metal contact with the underlying aluminum. This application, which was widely used in the telephone industry, has diminished in use with that industry's switch to fiber optics. However, it is used for aluminum wire terminals in the electronics industry, particularly where the use of terminal fluids is undesirable. One relatively new use is for the plating of steel internal dished-tooth star-washer-ring-lug terminals for attachment to aluminum capacitors.

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Indium Electrodeposits

Indium electrodeposits provide excellent solderability, low electrical contact resistance, friction resistance, and atmospheric corrosion resistance when plated on aluminum, copper-base alloys, and steel, which are typically selected for their engineering properties. Indium can be readily electrodeposited from either acid or alkaline solutions. It is particularly useful for coating aluminum and other amphoteric metals; its alkaline corrosion resistance provides a wider measure of corrosion protection for these metals than that provided by cadmium, tin, or zinc.

Indium can be plated without special apparatus. Any shop or laboratory that has plating equipment can set up an indium plating tank without costly equipment. Any technician familiar with the plating of silver, copper, and so on finds indium plating quite easy to handle. However, barrel plating of small, lightweight items (e.g., ring lugs, wire terminations, and threaded fasteners and washers) may present a problem on occasion. This type of part may cold weld during the tumbling action of the barrel and end up as a solid indium-plated mass. The problem is easily overcome by adding gelatin or glue to the bath to increase its viscosity.

Plating Baths. The four most commonly used indium plating baths are indium cyanide, indium fluoborate, indium sulfamate, and indium sulfate. Table 1 compares these processes. The details of the processes are shown in Tables 2, 3, 4, and 5.

Table 1 Comparison of indium plating baths

Parameter	Bath salt			
	Cyanide	Fluoborate	Sulfamate	Sulfate
Throwing power	Excellent	Good	Excellent	Poor

Quality of plate	Excellent	Good	Excellent	Passable
Ease of solution analysis	Difficult	Easy	Easy	Easy
Critical temperature	No	21-32 °C (70-90 °F)	No	Controlled
Color of solution	Clear	Clear	Clear	Clear
Wettability	Easy	Difficult	Easy	Difficult
Anode	Insoluble	Indium	Indium	Indium
Cathode efficiency	40-50%	40-50%	90%	30-70%
Tendency to pit	No	No	No	Yes
Control of solution	Cyanide and metal	Metal and pH	Metal and pH	Metal and pH

Table 2 Indium cyanide plating bath

Constituent or parameter	**Value or condition**
Indium as metal	33 g/L (4.4 oz/gal)
Dextrose	33 g/L (4.4 oz/gal)
Total cyanide (KCN)	96 g/L (12.7 oz/gal)
Potassium hydroxide (KOH)	64 g/L (8.5 oz/gal)
Temperature (static)	Room temperature
Cathode efficiency	50-75%
Anodes	Plain steel
Throwing power	Excellent
Quality of plate	Excellent
Ease of solution analysis	Difficult

Critical temperature (working)	None, with or without agitation
Color of solution	Clear, pale yellow to dark amber
Wettability	Easy
Tendency to pit	None
Control of solution	Cyanide and metal by additions
Use	General
Current	162-216 A/m^2 (15-20 A/ft^2)
pH	High

Notes: (1) Because insoluble anodes are used, it is necessary to replace the indium metal content of this alkaline bath. Under normal conditions, addition of cyanide will not be required; however, it is best to keep the cyanide concentration at about 100 g/L (13.4 oz/gal) for efficient operation. (2) Plating efficiency of the bath will be maintained within a range suitable for normal plating until the indium content is reduced. The plating rate should be checked at regular intervals, because as the bath is depleted a decrease in rate of deposition is to be expected.

Table 3 Indium fluoborate plating bath

Constituent parameter	**Value or condition**
Indium fluoborate	236 g/L (31.5 oz/gal)
Boric acid	22-30 g/L (2.9-4.0 oz/gal)
Ammonium fluoborate	40-50 g/L (5.3-6.7 oz/gal)
pH (colorimetric)	1.0
Temperature (static)	21-32 °C (70-90 °F)
Cathode efficiency	40-75%
Anode efficiency	Indium, 100%
Throwing power	Good
Quality of plate	Good

Ease of solution analysis	Easy
Critical temperature (working)	21-32 °C (70-90 °F), with or without agitation
Color of solution	Clear
Wettability	Difficult
Tendency to pit	None
Control of solution	Metal and pH
Use	Experimental
Current density	540-1080 A/m^2 (50-100 A/ft^2)

Notes: (1) The pH of this bath is controlled by the addition of 42% fluoboric acid. (2) Some insoluble anodes (platinum or graphite) should be used because the anode and cathode efficiency are not in good relation.

Table 4 Indium sulfamate plating bath

Constituent or parameter	**Value or condition**
Indium sulfamate	105.36 g/L (14 oz/gal)
Sodium sulfamate	150 g/L (20 oz/gal)
Sulfamic acid	26.4 g/L (3.5 oz/gal)
Sodium chloride	45.84 g/L (6 oz/gal)
Dextrose	8.0 g/L (1 oz/gal)
Triethanolamine	2.29 g/L (0.3 oz/gal)
pH	1-3.5[a]
Temperature (static)	Room temperature
Cathode efficiency	90%
Anode efficiency	Indium, 100%

Throwing power	Excellent
Quality of plate	Excellent
Ease of solution analysis	Easy
Critical temperature (working)	None, with or without agitation
Color of solution	[(b)]
Wettability	Fairly easy
Tendency to pit	None
Control of solution	Metal and pH[(a)]
Use of solution	Experimental
Current density	108-216 A/m^2 (10-20 A/ft^2)[(c)]

(a) 1.5-2 preferred. The pH of this bath is controlled by the addition of sulfamic acid.

(b) Clear when new; after use will darken due to organic material breakdown. This has no effect on deposit. Filtering of bath can be done through activated charcoal to maintain clarity of bath.

(c) Optimum. If metal is increased, current density can be increased up to 1080 A/m^2 (100 A/ft^2).

Table 5 Indium sulfate plating bath

Constituent or parameter	**Value or condition**
Indium (as sulfate)	20 g/L (2.67 oz/gal min)
Sodium sulfate	10 g/L (1.3 oz/gal)
pH	2.0-2.5
Temperature (static)	Room temperature
Cathode efficiency	30-70%

Anode efficiency	Indium, 100%
Throwing power	Poor
Quality of plate	Passable
Ease of solution analysis	Easy
Critical temperature (working)	Controlled, with or without agitation
Color of solution	Clear
Wettability	Difficult
Tendency to pit	Yes
Control of solution	Metal and pH
Use	Experimental
Current density	216-432 A/m^2 (20-40 A/ft^2)

Notes: (1) The pH of this bath is controlled by the addition of sulfuric acid or sodium hydroxide as needed. (2) Some insoluble anodes (platinum or graphite) should be used because the anode and cathode efficiency are not in good relation.

Diffusion Treatment. The plating of indium on a clean, nonferrous surface does not necessarily end the operation. For some applications, such as bearing plating, the indium deposit is diffused into the base metal, forming a surface alloy. This is accomplished by placing the plated part in an oven or hot oil bath and heat treating it for about 2 h at a temperature slightly above the melting point of indium. Indium melts at 156.7 °C (314.1 °F), and the diffusion treatment is carried out at about 175 °C (350 °F). The processing time may be shortened by increasing the temperature, but only after the diffusion has actually begun. Failure to observe the proper temperature at the beginning of the diffusion process may lead to the formation of surface bubbles or droplets of indium, which are undesirable, particularly on a decorative finish. A number of factors govern the depth of diffusion:

- The amount of indium plated on the surface
- Temperature of heat treatment
- Time of diffusion treatment
- The diffusion coefficient for indium in the base metal

Indium Alloy Electrodeposits

A variety of indium alloy deposits have been reported in the literature. Included are alloys with antimony, arsenic, bismuth, cadmium, copper, gallium, lead, tin, and zinc. Of these, only indium-lead has had any degree of commercial importance.

Indium-lead electroplated alloy was developed as an improvement over the diffusion alloy that is formed by plating a thin layer of indium over lead on lead-containing bearings and diffusing the indium into the lead in a hot, 150 °C (300 °F) oil bath. The alloy reduces the corrosion of the lead-containing bearings by lubricating oils. An alloy containing an average

of about 4% In had high resistance to corrosion and was harder and had better antifriction properties than lead. However, the composition of the thermally diffused alloy was nonuniform. The electrodeposited indium-lead alloy provided greater uniformity of composition and showed only one-fourth the corrosion compared to the thermally diffused alloy.

Plating Baths. The two most successful indium-lead plating baths are indium-lead fluoborate and indium-lead sulfamate. Table 6 compares these processes. The details of the processes are shown in Tables 7 and 8.

Table 6 Comparison of indium-lead plating baths

Parameter	Bath salt	
	Fluoborate	Sulfamate
Indium content of deposit	11%	5%
Microhardness of deposit	2.5 kg/mm^2	[(a)]

(a) Not reported

Table 7 Indium-lead fluoborate plating bath

Constituent or parameter	Value or condition
Indium fluoborate	25 g/L (3.4 oz/gal)
Lead fluoborate	90 g/L (12.0 oz/gal)
Free fluoboric acid	15 g/L (2.0 oz/gal)
Glue	1.5 g/L (0.2 oz/gal)
Current density	100-300 A/m^2 (9-28 A/ft^2)
Temperature	20 °C (70 °F)

Table 8 Indium-lead sulfamate plating bath

Constituent or parameter	Value or condition
Indium sulfamate	20 g/L (2.67 oz/gal)
Lead sulfamate	1 g/L (0.13 oz/gal)

Soluble coffee[a]	5 g/L (0.67 oz/gal)
pH	1.5
Current density	100-300 A/m^2 (9-28 A/ft^2)

(a) Regular instant coffee powder

Nonaqueous Indium Plating Baths

The literature has reported the electrodeposition of indium and alloys such as indium-antimony, indium-gallium, and indium-bismuth from solutions of the metals dissolved in distilled ethylene glycol or glycerin. High-quality deposits have been reported with good current efficiencies.

Stripping Indium Plating

Diffused indium plate cannot be stripped from bronze. Undiffused indium on bronze can be removed with hydrochloric acid. Lead-indium plating, either diffused or undiffused, can be removed by immersion in a mixture of 9 parts glacial acetic acid and 1 part 30% hydrogen peroxide at room temperature. Indium and silver-indium alloy can be removed from steel by reversing the current in 30 g/L (4 oz/gal) solution of sodium cyanide at approximately 50 to 55 °C (122 to 131 °F). The silver-indium alloy can be removed in 1:1 nitric acid, but care must be taken to remove it from the bath before the steel is etched.

Specifications and Standards

No ASTM, ISO, or U.S. government specifications exist for indium plating. ASTM initiated a draft standard several years ago, but work was suspended due to lack of interest. The thickness ranges initially proposed were identical to those for tin (ASTM B 545). The SAE/AMS series has a specification for indium-lead plating, AMS 2415.

Hazards

The toxicity of indium and its compounds has not been extensively investigated. Animal tests indicate some degree of hazard, but for normal electroplating applications, usual good housekeeping practices should be sufficient. Indium should not be used in contact with food products because its solubility in food acids is high.

Tin Plating

Revised by Arthur J. Killmeyer, Tin Information Center of North America

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Introduction

TIN IS A VERSATILE, low-melting point, nontoxic metal that has valuable physical properties. It alloys readily with most other metals, and it forms many useful inorganic and organic chemical compounds because it is amphoteric. It has the largest melting point to boiling point range (from 232 to 2370 °C, or 450 to 4300 °F) of any metal. In conventional metallurgical applications, evaporation from a pot of liquid tin does not occur. Tin is used in a multitude of products, although the amount in which it is present is usually relatively small as a percentage of the total. Most manufacturers use some tin, and it is an essential material in industries such as communications, transportation, agriculture, food processing, and construction.

Electrodeposits

A thin coating of electrodeposited tin provides beneficial properties, such as excellent solderability, ductility, softness, and corrosion or tarnish resistance. In this way, the stronger materials that are required for their engineering properties can be enhanced by the desirable properties of tin on their surfaces. A tin deposit provides sacrificial protection to copper, nickel, and many other nonferrous metals and alloys. Tin also provides good protection to steel. However, because tin is normally cathodic to iron, the coating must be continuous and effectively pore-free. (This requirement does not apply to tinplate used for food packaging because the absence of oxygen inside tin-plated food containers prevents the electrochemical cell reactions that lead to corrosion.)

Thick, nonporous coatings of tin provide long-term protection in almost any application. The required coating thickness is established by the application. Thickness recommendations for tin coatings on metallic materials are given in Table 1. Tin coatings can be applied at thicknesses of less than 1 to 250 μm or greater.

Table 1 Recommended thicknesses for typical applications of tin deposits on metal substrates (ASTM B 545-92)

Class	Minimum thickness		Typical applications
	μm	μin.	
A	2.5	100	Mild service conditions, particularly where the significant surface is shielded from the atmosphere (as in electronic connector housings). Provides corrosion and tarnish resistance where greater thicknesses may be detrimental to the mechanical operation of the product (for example, small electrical spring contacts and relays). Class A often used for tin coatings that are not to be soldered, but must function as low-resistance electrical contact surfaces.
B	5	200	Mild service conditions with less severe requirements than grade C. Used as a precoating on solderable base metals to facilitate soldering of electrical components, surface preparation for protective painting, antigalling agent, and a stopoff in nitriding. Also found on baking pans after reflow.
C	8[(a)]	320[(a)]	Moderate exposure conditions, usually indoors, but more severe than class B. Used on electrical hardware (such as cases for relays and coils, transformer cans, screened cages, chassis, frames, and fittings) and for retention of the solderability of solderable articles during storage.
D	15[(b)]	600[(b)]	Severe service conditions, including exposure to dampness and mild corrosion from moderate industrial environments. Used with fittings for gas meters, automotive accessories (such as air cleaners and oil filters), and in some electronic applications.
E	30	1200	Very severe service conditions, including elevated temperatures, where underlying metal diffusion and intermetallic formation processes are accelerated. Thicknesses of 30 to 125 μm (0.0012 to 0.005 in.) may be required if the coating is subjected to abrasion or is exposed to slowly corrosive liquids or to corrosive atmospheres or gases. Thicker coatings are used for water containers, threaded steel couplings of oil-drilling

(a) 10 μm (400 μin.) for steel substrates.

(b) 20 μm (800 μin.) for steel substrates

Applications. The largest use of tin electrodeposits occurs at steel mills that produce tinplate, primarily as food-preservation containers. A thin tin coating protects the steel inside a tin can, as long as an oxygen-free environment is maintained. The second largest use of tin electrodeposits occurs in the electronics industry, where coatings are applied to the surfaces that require good solderability and corrosion or tarnish resistance.

These include radio and television chassis, computer frames, integrated circuit chip leads, tags, connectors, lead frames, printed wiring boards, and copper wire. Electrodeposited tin is also used on food handling equipment, such as steel baking pans, sieves, can openers, and fasteners. In general, tin electrodeposits are used to protect surfaces and render them usable in applications for which they would otherwise be unsuited.

Types of Electrolytes

Tin can be deposited from either alkaline or acid solutions. Electrolyte compositions and process operating details are provided in Ref 1, 2, and 3, as well as in publications of the International Tin Research Institute. Table 2 gives the basic details of electrolyte composition and operating conditions for alkaline solutions, and Tables 3 and 4 provide this information for acid solutions. Tin ions in the alkaline electrolytes have a valence of +4, whereas those in the acid electrolytes have a valence of +2. Consequently, the alkaline systems require the passage of twice as much current to deposit one gram-molecule of tin at the cathode.

Table 2 Composition and operating conditions for stannate (alkaline) tin plating electrolytes

Values of composition are for electrolyte startup; operating limits for the electrolyte composition are approximately -10 to + 10% of startup values

Solution	Composition										Operating conditions			
	Potassium stannate		Sodium stannate		Potassium hydroxide		Sodium hydroxide		Tin metal[a]		Temperature		Cathode current density	
	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	°C	°F	A/dm^2	A/ft^2
A	105	14	. . .	. . .	15[b]	2[b]	. . .	. . .	40	5.3	66-88	150-190	3-10	30-100
B	210	28	. . .	. . .	22	3	. . .	. . .	80	10.6	77-88	170-190	0-16	0-160
C	420	56	. . .	. . .	22	3	. . .	. . .	160	21.2	77-88	170-190	0-40	0-400
D	. . .	. . .	105[c]	14	. . .	. . .	10[b]	1.3[b]	42	5.6	60-	140-	0.5-3	6-30

(a) As stannate.

(b) Free alkali may need to be higher for barrel plating.

(c) $Na_2SnO_3 \cdot 3H_2O$; solubility in water is 61.3 g/L (8.2 oz/gal) at 16 °C (60 °F) and 50 g/L (6.6 oz/gal) at 100 °C (212 °F)

Table 3 Composition and operating conditions for sulfate (acidic) tin plating electrolyte

Constituent	Amount	Operating limits

	g/L	oz/gal	g/L	oz/gal
Stannous sulfate	80	10.6	60-100	8-13
Tin metal, as sulfate	40	5.3	30-50	4-6.5
Free sulfuric acid	50	6.7	40-70	5.3-9.3
Phenolsulfonic acid[(a)]	40	5.3	30-60	4-8
β-naphthol	1	0.13	1	0.13
Gelatin	2	0.27	2	0.27

Note: Temperature range for sulfate electrolytes is 21 to 38 °C (70 to 100 °F), and they do not require heating. Cooling can be considered if temperature rises to reduce adverse effects of heat on the electrolyte constituents. Cathode current density is 1 to 10

(a) Phenolsulfonic acid is most often used. Cresolsulfonic acid performs equally well and is a constituent of some proprietary solutions.

Table 4 Composition and operating conditions for fluoborate tin (acidic) plating electrolyte

Constituent or condition	Standard	High-speed	High throwing power
Electrolyte, g/L (oz/gal)			
Stannous fluoborate	200 (26.7)	300 (39.7)	75 (9.9)
Tin metal[(a)]	80 (10.8)	120 (16.1)	30 (4.0)
Free fluoboric acid	100 (13.4)	200 (26.8)	300 (40.2)
Free boric acid	25 (3.35)	25 (3.35)	25 (3.35)
Peptone[(b)]	5 (0.67)	5 (0.67)	5 (0.67)
β-naphthol	1 (0.13)	1 (0.13)	1 (0.13)
Hydroquinone	1 (0.13)	1 (0.13)	1 (0.13)
Temperature, °C (°F)	16-38[(c)] (60-100)[(c)]	16-38 (60-100)	16-38 (60-100)

Cathode current density, A/dm^2 (A/ft^2)	2-20 (20-200)	2-20 (20-200)	2-20 (20-200)

Note: The standard electrolyte composition is generally used for rack or still plating, the high-speed composition for applications like wire plating, and the high-throwing-power composition for barrel plating or applications where a great variance exists in cathode current density as a result of cathode configuration.

(a) As fluoborate.

(b) Dry basis.

(c) Electrolytes do not require heating. Cooling may be considered if temperature rises to reduce adverse effects of heat on the electrolyte constituents.

Alkaline electrolytes usually contain only a metal stannate and the applicable hydroxide to obtain satisfactory coatings. Unlined mild steel tanks are satisfactory. These can be heated by electrical immersion heaters, steam coils, or external gas burners. If steam coils are used, they should be supported 5 to 10 cm (2 to 4 in.) above the bottom of the tank to allow sediment to remain undisturbed. It is not necessary to filter still baths of this type, except at infrequent intervals. The electrical equipment is the same as that used in other plating operations. A rectifier for converting alternating current to direct current or a pulse-plating rectifier, which allows more precise control of electrical parameters, can be used. Factors such as operating temperature, solution constituent concentration, and operating current density all affect the efficiency and plating rate of the system and must be properly balanced and controlled.

Unusual operating conditions of the alkaline electrolytes involve:

- Tin anode control and electrochemical solution mode (discussed below)
- Cathodic deposition occurring from Sn^{+4}
- Solubility of the alkaline stannate in water

Ninety percent of the problems encountered in alkaline tin plating result from improper anode control. Conversely, operating the alkaline electrolytes is simple if one understands anode behavior, because there are no electrolyte constituents except the applicable stannate and hydroxide.

Tin anodes must be properly filmed, or polarized, in alkaline solutions to dissolve with the tin in the Sn^{+4} state. Once established, the anode film continues to provide the tin as Sn^{+4}. The anodes can be filmed either by subjecting them for about 1 min to a current density considerably above that normally used, or by lowering them slowly into the bath with the current already flowing.

Three reactions are possible at tin anodes in alkaline solutions:

$$Sn + 6OH^- \rightarrow Sn(OH)_6^{2-} + 4e^- \quad \textbf{(Eq 1)}$$

$$Sn + 4OH^- \rightarrow Sn(OH)_4^{2-} + 2e^- \quad \textbf{(Eq 2)}$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad \textbf{(Eq 3)}$$

Equation 1 represents the overall process occurring at the anodes when the film is intact and the tin is dissolving as stannate ion, with tin in the Sn^{+4} state. Film formation is confirmed by a sudden increase in the electrolyte cell voltage, a drop in the amperage passing through the cell, and the observation of a yellow-green film for pure tin anodes. High-speed anodes (containing 1% Al), used for tinplate production, turn darker. Because the anodes do not function at 100% efficiency when filmed, moderate gassing occurs as the result of the generation of oxygen, as in Eq 3.

Equation 2 is the process occurring if there is no film and the tin is dissolving as stannite ion, with tin in the Sn^{+2} state. The presence of stannite in the electrolyte produces unsatisfactory plating conditions, and the deposit becomes bulky, rough, porous, and nonadherent. The addition of hydrogen peroxide to the electrolyte oxidizes the Sn^{+2} to Sn^{+4}, returning it to a usable condition. If this remedy is required frequently, it indicates other problems that must be addressed. The concentration of caustic may be too high. This can be remedied with the addition of acetic acid.

Equation 3 shows the decomposition of hydroxyl ion with the formation of oxygen. While this is a normal reaction at the anode, it should not be permitted to become the dominant reaction, as occurs when the anode current density is too high. Under this condition, no tin dissolves and the anodes take on a brown or black oxide film. The anode current density should be reduced until the normal film color returns. If this is allowed to become thick enough, it is removable only by the action of strong mineral acids. Stannate baths normally appear colorless to straw colored, and clear to milky, depending on the quantity of colloidal material present. If an appreciable quantity of stannite builds up in the bath, it will appear light to dark gray, depending on the quantity of stannite that has formed. The gray color is caused by the precipitation of colloidal tin as a result of the disproportionation of stannite:

$$2Sn(OH)_4^{2-} \rightarrow Sn(OH)_6^{2-} + Sn + 2OH^-$$

This tin will codeposit with tin from the stannate ions, causing the rough spongy deposits mentioned above.

In the alkaline systems, two factors tend to restrict the usable current density range and limit the deposition rate. One factor is the solubility of the stannates in hydroxide solutions. With the sodium formula, the normal increase is not possible, because sodium stannate is one of the unusual salts that have a reverse temperature coefficient of solubility. An example of this process is given in Table 2. Less sodium stannate dissolves as the electrolyte temperature increases, which reduces the usable current density and the plating rate. Potassium stannate is more soluble with increasing temperature, but as the stannate increases, the potassium hydroxide must also increase. Stannate solubility decreases as the hydroxide content increases.

The second factor is that cathode efficiency decreases as current density increases. Eventually, a point is reached at which these factors become offset, and a further increase in current density does not increase the deposition rate. This limits the rate at which tin can be deposited.

In specialized applications, such as plating the inside of oil-well pipe, it is not possible to have an anode surface sufficient enough to avoid passivity. A higher current density can be used if insoluble anodes are utilized, but tin deposited on the cathode must then be replaced by the addition of chemicals. The addition of stannate to provide the tin cations also adds sodium or potassium hydroxide to the electrolyte. Although the resulting additional alkalinity can be neutralized by adding a calculated amount of an acetic acid, the sodium or potassium ion concentration continues to increase and the alkaline stannate solubility is reduced. This, in turn, reduces the available Sn^{+4} ion to a low enough concentration that the plating rate decreases rapidly, and the electrolyte must be discarded. A potassium-base composition has been developed, in which the necessary Sn^{+4} ions are added to the electrolyte as a soluble, colloidal, hydrated tin oxide (Ref 2). Because the potassium ion concentration builds up more slowly in this composition, electrolyte life is nearly indefinite. The throwing power of alkaline stannate solutions is quite high, allowing the coating of intricate shapes and interior parts of cathodes.

Acid Electrolytes. Several acid electrolytes are available for tin plating. Two of these--stannous sulfate and stannous fluoborate--are general systems that are adaptable to almost any application. Electrolytes such as halogen (a chloride-fluoride base system) and Ferrostan (a special sulfate-base system) have been developed for tin coating cold-rolled steel strip traveling at high speed for the production of tinplate. The acid electrolytes differ from alkaline electrolytes in many respects. A stannous salt that is dissolved in a water solution of the applicable acid does not produce a smooth, adherent deposit on a cathode. Therefore, a grain-refining addition agent (such as gelatin or peptone) must be used. Usually, such materials are not directly soluble in a water solution, and a wetting-agent type of material (such as β-naphthol) is also necessary.

Organic brighteners can be added if a bright-as-coated electrodeposit is desired. This produces a coating that looks the same as a reflowed tin coating. Over time, these brighteners will decompose in the bath and must be replenished. The composition of these organic brighteners has been the subject of considerable research over the years. The earliest substance studied, in the 1920s, was wood tar dispersed with a wetting agent. Other materials were studied in later years, especially pure compounds such as cresol sulfonic acid and various aromatic sulfonates. These were seen to have more of

a stabilizing effect, preventing the hydrolysis and precipitation of tin as tin(II) and tin(IV) salts. Later work has shown that a "cruder" material is more effective as a brightener. Such a material is obtained by the sulfonation of commercial cresylic acid. The implication here is that by-products of the sulfonation and not the cresol sulfonic acid itself are responsible for the brightening of the tin coating. Various proprietary brightening systems have been produced over the years. Very little of the development work on brightening agents has been published outside the patent literature. A comprehensive discussion of the topic is beyond the scope of this article. It is usually most convenient to purchase a packaged system from a plating supply house.

The organic materials will co-deposit with the tin, resulting in a higher than normal carbon content in the electrodeposit. This does not create a problem, unless the tin coating is to be soldered or reflowed. The supplier of the proprietary bath should be consulted for directions on controlling this problem.

To retard the oxidation of the stannous tin ions to the stannic form, either phenolsulfonic or cresolsulfonic acid is added to a sulfate-base system, and hydroquinone is added to a fluoboric acid-base system. Although the acid electrolytes can contain large amounts of stannic ions without affecting the operation of the system, only the stannous ions are deposited at the cathode. As a result, oxidation depletes the available stannous ions, which must be replaced by adding the corresponding stannous salt to the bath. To limit the oxidation of stannous ions, a sufficient anode area must be maintained, and the operating temperature must be kept as low as possible. In addition, one must avoid introducing oxygen into the solution, either by a filter leak or air agitation. Usually, an antioxidant is added to the solution.

In terms of operating characteristics, the basic differences between acid and alkaline electrolytes are related to the type of tin ion that is present in the electrolyte. In acid systems, the stannous ions must not be oxidized to the stannic form, and operation must occur at lower temperatures. The acid electrolytes require only half as much current to deposit one gram-molecule of tin. The tin dissolves directly from the metallic anodes, and the control of an anode film is not involved. Acid electrolytes are nearly 100% efficient, both anodically and cathodically, which avoids the necessity of regularly adding chemicals for tin. The problems of oxygen gas evolution at the anode surface and hydrogen gas at the cathode surface are reduced. Some particulate matter is produced as sludge from three sources: anode slime products, the precipitation of addition agents and their breakdown products, and basic tin compounds formed by oxidation. These materials must be removed during operation. In a still tank, the precipitates gradually settle, but agitated solutions require continuous filtration.

Acid-resistant equipment must be used. Lead-lined plating tanks were formerly used, but stoneware, rubber- or plastic-lined steel, or plastic tanks are now more common. Filtration equipment should be available, because solid particles of precipitated matter in the solution will cause deposit porosity and roughness. With still baths, suspended matter can be allowed to settle without filtration, but with agitated baths, continuous filtration is advisable. Cathode bar movement is often recommended.

The stannous sulfate electrolyte is most popular because of its general ease of operation. The rate of deposition is somewhat limited by optimum metal concentration in the electrolyte. A still bath is operated at a cathode current density of 1 to 2 A/dm^2 (10 to 20 A/ft^2). Current densities of up to 10 A/dm^2 (100 A/ft^2) are possible with suitable electrolyte agitation. Higher current densities will result in burned deposits. The anode surface area must be increased when higher current densities are used, otherwise the anodes will become passive. Addition agent control is not quantitative in nature, but deficiencies are easily recognized by the experienced plater. An electrolyte can be prepared from readily available chemicals, or a proprietary system can be purchased from suppliers. Most commercial bright acid tin processes and the more recent matte acid tin systems are based on the stannous sulfate solution. Precise information on operation and control should be obtained directly from the specific supplier.

The stannous fluoborate electrolyte is a good general-purpose electrolyte. It can operate at higher current densities because of the conductivity provided by the fluoboric acid. Cathode current densities of 20 A/dm^2 (200 A/ft^2) and higher are possible with suitable solution agitation. The need to increase anode surface area at high current densities and the control of the addition agents parallel the requirements associated with using stannous sulfate. Table 4 gives standard, high-speed, and high-throwing-power electrolyte compositions, because each meets a specific need. The solution conductivity that is lost because of the lower metal content in the high-throwing-power bath is compensated for by the higher concentration of fluoboric acid. The lower total metal in the solution reduces the variance in deposit thickness that is usually associated with varying areas of cathode current density. Boric acid is listed as a constituent of the fluoborate solutions because of its presence in the stannous fluoborate and fluoboric acid used to prepare the solutions. It is not a necessary ingredient in the electrolyte.

References cited in this section

1. F.A. Lowenheim, Ed., *Modern Electroplating,* 3rd ed., Wiley-Interscience, 1974
2. S. Hirsch, Tin-Lead, Lead, and Tin Plating, *Metal Finishing Guidebook and Directory Issue,* Vol 91 (No. 1A), Jan 1993, p 269-280
3. J.W. Price, *Tin and Tin Alloy Plating,* Electrochemical Publications Ltd., Ayr, Scotland, 1983

Lead Plating

Revised by George B. Rynne, Novamax Technology

Introduction

LEAD has been deposited from a variety of electrolytes, including fluoborates, fluosilicates, sulfamates, and methane sulfonic acid baths. Fluoborate baths are the most widely used because of the availability of lead fluoborate and the simplicity of bath preparation, operation, and stability. Fluoborate baths provide finer grained, denser lead deposits. Fluosilicate baths, although less costly to use for large operations, are difficult to prepare for small-scale plating. They are not suitable for plating directly on steel and are subject to decomposition, which produces silica and lead fluoride. Use of sulfamate baths is almost nonexistent in the United States, because neither lead silicofluoride nor lead sulfamate is available commercially. These salts must be prepared by the plater using litharge (PbO) and the corresponding fluosilicic or sulfamic acids. Sulfamate baths are subject to decomposition, which produces lead sulfate.

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Applications

The appearance and properties of lead limit its commercial use in electroplating largely to corrosion protection and bearing applications-two fields in which the physical and chemical properties of lead render it unique among the commercially plated metals. Lead has not been extensively electroplated because its low melting point of 325 °C (620 °F) facilitates application by hot dipping. Electrodeposited lead has been used for the protection of metals from corrosive liquids such as dilute sulfuric acid; the lining of brine refrigerating tanks, chemical apparatus, and metal gas shells; and barrel plating of nuts and bolts, storage battery parts, and equipment used in the viscose industry.

Electroplated lead has been used for corrosion protection of electrical fuse boxes installed in industrial plants or where sulfur-bearing atmospheres are present. Lead is also codeposited with tin for wire plating, automotive crankshaft bearings, and printed circuits.

Nonporous lead deposits with thicknesses of 0.01 to 0.025 mm (0.4 to 1 mil) give good protection against corrosion, although the coating may be subject to breaking during abrasion due to the soft nature of lead. Better mechanical properties and improved durability are obtained with coating deposits with thicknesses greater than 0.025 mm (1 mil). Depositing more than 0.08 mm (3 mils) of lead is relatively easy, in that a deposit of about 0.1 mm (4 mils) can be produced in about 1 h at 2 A/dm^2 (19 A/ft^2) (Ref 1).

Reference cited in this section

1. H. Silman, G. Isserlis, and A.F. Averill, *Protective and Decorative Coatings for Metals,* Finishing Publications Ltd., 1978, p 443-448

Process Sequence

Low-Carbon Steel. Lead can be plated directly on steel from the fluoborate bath using the following cycle:

- Degrease with solvent (optional)
- Alkali clean (anodic)
- Water rinse
- Dip in 10% fluoboric acid (*Caution: Hydrochloric or sulfuric acid should not be used because they can precipitate insoluble lead sulfate or chloride on the work in the event of poor rinsing*)
- Water rinse
- Lead plate
- Rinse

Lead can be plated on steel from fluosilicate and sulfamate baths using the following cycle:

- Degrease with solvent (optional)
- Alkali clean (anodic)
- Rinse
- Dip in 5 to 25% hydrochloric acid
- Rinse thoroughly
- Dip in 30 to 75 g/L (4 to 10 oz/gal) sodium cyanide
- Rinse
- Copper cyanide strike
- Rinse thoroughly
- Dip in 10% fluoboric acid (see caution above)
- Rinse
- Lead plate
- Rinse

Copper. Lead can be plated directly on copper from fluoborate, fluosilicate, or sulfamate baths using the following cycle:

- Alkali clean (anodic or cathodic/anodic)
- Rinse
- Dip in 10% fluoboric acid (see caution above)
- Rinse
- Lead plate
- Rinse

Fluoborate Baths

Lead fluoborate baths are prepared by adding the required amount of lead fluoborate concentrate and fluoboric acid to water followed by peptone as the preferred addition agent.

Until methane sulfonic acid (MSA) baths became widely used in the past few years, fluoroborate baths were the most important bath for lead plating. Good lead deposits up to 1.5 mm (60 mils) in thickness can be achieved with a fluoroborate bath of the following composition:

Basic lead carbonate, $2PbCO_3 \cdot Pb(OH_2)$	300 g/L (40 oz/gal)

Hydrofluoric acid (50% HF)	480 g/L (64 oz/gal)
Boric acid, H_3BO_3	212 g/L (28 oz/gal)
Glue	0.2 g/L (0.03 oz/gal)

A bath of half the above concentration is suitable for thinner deposits at low current densities, but the lead concentration should be kept high if smooth deposits and good throwing power are required (Ref 1). More detailed information on fluoroborate formulations and performance for lead plating is covered in Ref 2, 3, 4, and 5.

Many different types of glue and gelatin additives are available, but no one type is manufactured specifically for lead plating. Depending on the method of manufacture, each can exhibit different levels of solubility and impurities that may be of concern to the plater.

Glue and gelatin addition agents must be swelled and dissolved in water by the plater just prior to addition to the bath. The resultant colloidal solution has a limited shelf-life and is prone to bacterial degradation on standing. Glue and hydroquinone are relatively expensive. Often, it is a by-product of an industrial process and can contain organic and inorganic impurities detrimental to the lead plating process. No grade is manufactured and sold specifically for lead plating.

Concentrates of lead fluoborate and fluoboric acid contain free boric acid to ensure bath stability. An anode bag filled with boric acid in each corner of the plating tank is recommended to maintain a stable level of boric acid in the bath solution. The concentration of boric acid in the bath is not critical and can vary from 1 g/L (0.13 oz/gal) to saturation. The water used in the bath preparation must be low in sulfate and chloride, as these lead salts are insoluble.

Table 1 provides the compositions and operating conditions of high-speed and high-throwing-power fluoborate plating baths. The high-speed bath is useful for plating of wire and strip where high current densities are used. The high-throwing-power formulation is used in applications such as barrel plating of small parts or where thickness distribution on intricate or irregularly shaped parts is important. The high-throwing-power bath should be operated at a lower current density because of the lower lead content of the bath.

Table 1 Compositions and operating conditions of lead fluoborate baths

Anode composition, pure lead; anode/cathode ratio, 2:1

Bath	**Bath composition**							**Temperature**		**Cathode current density[(a)]**	
	Lead		**Fluorobic acid (min)**		**Peptone solution, vol%**	**Free boric acid**					
	g/L	**oz/gal**	**g/L**	**oz/gal**		**g/L**	**oz/gal**	**°C**	**°F**	**A/dm^2**	**A/ft^2**
High-speed	225	30	100	13.4	1.7	1 to saturation	0.13 to saturation	20-41	68-105	5	50
High-throwing-	15	2	400	54	1.7	. . .	. . .	24-71	75-	1	10

(a) Values given are minimums. Current density should be increased as high as possible without burning the deposit; this is influenced by the degree of agitation.

Fluoborate baths rank among the most highly conductive plating electrolytes and thus require low voltage for the amperage used.

Maintenance and Control. The very high solubility of lead fluoborate in solution with fluoboric acid and water accounts for its almost universal use for lead plating. In the high-speed bath formulation of Table 1, neither the lead nor acid content is critical, and the bath can be operated over a wide range of lead and acid concentrations.

The high-throwing-power bath formulation of Table 1 must be operated fairly close to the guidelines given. Lowering the lead concentration improves the throwing power characteristics; however, a reduction in lead concentration must be followed by a corresponding decrease in the cathode current density. On the other hand, an increase in lead content above the optimum permits the use of higher current densities, with a corresponding decrease in throwing power.

Sludge may form in the fluoborate bath as a result of the use of impure lead anodes that contain bismuth or antimony or as a result of the drag-in of sulfates. Fluoborate baths should be constantly filtered through dynel or polypropylene filter media to remove any sludge that may form. Anodes must be bagged in dynel or polypropylene cloth. Absence of gas bubbles at the cathode or anode while plating indicates all electric energy is theoretically being used to transfer lead from the anode to the workpiece; in other words, the process is operating at 100% anode and cathode efficiency. The plating bath concentration therefore remains unchanged except for changes due to evaporation and dilution from placing wet parts in the bath in combination with dragout when the parts are removed from the bath.

Methods are available for analyzing lead and fluoboric acid concentrations. Additive concentration can be adequately evaluated through the use of the Hull cell. Low concentration of additive results in loss of throwing power, coarse-grained deposits, and treeing. (*Treeing* is the formation of irregular projections on a cathode during electrodeposition, especially at edges and other high-current-density areas).

References cited in this section

1. H. Silman, G. Isserlis, and A.F. Averill, *Protective and Decorative Coatings for Metals,* Finishing Publications Ltd., 1978, p 443-448
2. S. Hirsch, Tin-Lead, Lead and Tin Plating, *Metal Finishing Guidebook and Directory,* Elsevier Science, 1992, p 262-278
3. F.A. Lowenheim, *Modern Electroplating,* 2nd ed., John Wiley & Sons, 1963, p 242-249
4. A. Graham, *Electroplating Engineering Handbook,* 3rd ed., Van Nostrand Reinhold, 1971, p 238, 246, 266
5. *The Canning Handbook,* 23rd ed., Canning, 1982, p 742-746

Fluosilicate Baths

Fluosilicic acid is formed by the action of hydrofluoric acid on silicon dioxide. The lead fluosilicate ($PbSiF_6$) electrolyte is formed when fluosilicic acid is treated with litharge. No great excess of silicic acid can be held in solution; therefore, the fluosilicate solution is less stable than the fluoborate solution. Table 2 lists compositions and operating conditions for two lead fluosilicate baths.

Table 2 Compositions and operating conditions of lead fluosilicate baths

Temperature, 35-41 °C (95-105 °F); cathode current density, 0.5-8 A/dm^2 (5-80 A/ft^2); anode current density, 0.5-3 A/dm^2 (5-30 A/ft^2); anode composition, pure lead

Bath	Lead		Animal glue		Peptone equivalent		Total fluosilicate	
	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal
1	10	1.3	0.19	0.025	5	0.67	150	20

2	180	24	5.6	0.75	150	20.1	140	18.75

Although at low current densities it is possible to secure smooth deposits of lead from the fluosilicate bath without additive agents, higher current densities are likely to produce treeing, especially in heavy deposits. Therefore, an additive agent, such as peptone glue or other colloidal materials or reducing agents, is always used. The use of excess glue in lead plating baths, however, may result in dark deposits. Maintenance and control procedures for the fluosilicate baths are similar to those described for the fluoborate baths.

Sulfamate Baths

Sulfamate baths consist essentially of lead sulfamate with sufficient sulfamic acid to obtain a pH of about 1.5. Sulfamic acid is stable and nonhygroscopic, and is considered a strong acid. Compositions and operating conditions of two typical sulfamate baths are given in Table 3.

Table 3 Compositions and operating conditions of lead sulfamate baths

pH, 1.5; temperature, 24-49 °C (75-120 °F); cathode current density, 0.5-4 A/dm^2 (5-40 A/ft^2); anode current density, 0.5-4 A/dm^2 (5-40 A/ft^2); anode/cathode ratio, 1:1; anode composition, pure lead

Bath	Lead		Animal glue		Peptone equivalent		Free sulfamic acid	
	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal
1	140	18.75	5.6	0.75	150	20.1	. . .	. . .

Because the acid and the salt used in the solutions in Table 3 are highly soluble in water, sulfamate baths can be prepared either by adding constituents singly or as formulated salts to water. Solutions are usually formulated to concentrations that allow bath operation over a wide range of current densities. Lead concentration can vary from 112 to 165 g/L (15 to 22 oz/gal), while the pH is held at about 1.5. As in other lead plating solutions, additive agents (peptone gelatin or other colloids, alkyl or alkyl aryl polyethylene glycols) are required to produce smooth, fine-grained deposits.

Spongy deposits are obtained if the lead concentration is too low, the current density is too high, or the concentration of additive agent is too low. At low pH or high temperature, sulfamate ions hydrolyze to ammonium bisulfate to form insoluble lead sulfate. Ordinarily, this hydrolysis presents no problem, provided the bath is correctly operated.

Maintenance and Control. Sulfamate baths do not require much attention other than maintenance of the correct proportion of additive agents to produce the desired deposit quality. Additive agent content is evaluated by the use of the Hull cell. The pH is easily adjusted with sulfamic acid or ammonia and can be measured with a glass electrode. Lead concentration can be determined with sufficient accuracy by hydrometer readings or an occasional gravimetric analysis.

Methane Sulfonic Acid Baths

Methane sulfonic acid (MSA) baths consist essentially of MSA-lead concentrate mixed with MSA to arrive at a total acid concentration of 300 mL/L. The overall system is stable and is considered to be a strong acid. Compositions and operating conditions for two MSA baths are given in Table 4.

Table 4 Compositions and operating conditions of lead methane sulfonic acid (MSA) baths

Temperature, 45 °C (110 °F); anode composition, pure lead; anode/cathode ratio, 1:1

Bank	Lead		MSA, mL/L	Additive, vol%	Cathode current density	
	g/L	oz/gal			A/dm^2	A/ft^2
Rack/barrel	30	4	300	4	0.5-5	5-50
High-current	100	13.3	300	4	0.5-20	5-200

The materials used to formulate MSA baths are highly soluble liquids. The baths listed in Table 4 are metal concentrations and, as such, are sensitive to current density. A lead concentration of 30 g/L (4 oz/gal) supports a maximum current density of 5 A/dm^2 (50 A/ft^2); an increase in the lead concentration to 100 g/L (13.3 oz/gal) allows a corresponding increase in the maximum current density to 20 A/dm^2 (200 A/ft^2). The use of a proprietary additive (4% of bath composition) is required to produce the smooth, fine-grained deposits usually provided by colloidal agents in fluoborate systems.

The principal advantage of MSA baths, in addition to their overall chemical stability, is the absence of the fluoride and borate ions present in other lead plating baths. These ions are heavily regulated or prohibited in many states because of their deleterious effects on fruit-bearing trees when released to the environment. An additional advantage of MSA baths is that when they are applied to 60Pb-40Sn solder alloys, these eutectic alloys can be plated over an extremely broad range of current densities. MSA baths are easily operated and controlled, but they are more expensive to make up.

Maintenance and Control. The MSA system is extremely stable and requires little or no maintenance other than control of the metal, acid, and additive concentrations within relatively broad ranges. Of these, it is of greatest importance to control the acid concentration in actual production situations. Additive concentration is evaluated using the Hull cell; metal and acid concentrations can be evaluated through simple titrations. Deionized water must be used for rinsing the part prior to immersion in the plating bath because MSA is sensitive to chloride ions in the makeup water.

Anodes

Lead of satisfactory purity for anodes may be obtained either as corroding lead or chemical lead. Chemical lead anodes generally are preferred. Impurities in the anodes such as antimony, bismuth, copper, and silver cause the formation of anode slime or sludge and can cause rough deposits if they enter the plating solution. These impurities can also cause anode polarization if present in the anode, especially at higher anode current densities. Small amount of tin and zinc are not harmful. Anode efficiency in acid baths is virtually 100%.

Anodes should be bagged in dynel or polypropylene cloth to prevent sludge from entering the plating bath. These bags should be leached in hot water to remove any sizing agents used in their manufacture before use in the plating bath. Nylon and cotton materials deteriorate rapidly and should not be used in any of the baths.

Equipment Requirements

Fluoborate and fluosilicate baths attack equipment made of titanium, neoprene, glass, or other silicated material; thus, these materials should not be used in these solutions. Anode hooks should be made of Monel metal.

Tanks or tank linings should be made of rubber, polypropylene, or other plastic materials inert to the solution. Pumps and filters of type 316 stainless steel or Hastelloy C are satisfactory for intermittent use; for continuous use, however, equipment should be made from or lined with graphite, rubber, polypropylene, or other inert plastic. Filter aids used for the fluoborate solution should be made of cellulose rather than asbestos or diatomaceous earth.

Stripping of Lead

Table 5 identifies solutions and operating conditions for stripping lead from steel. Method C, at about 16 °C (60 °F), strips 25 μm (1 mil) of lead in 6 or 7 min with very slight etching of the steel. With Method B, voltage increases suddenly when the lead coating has been removed; at room temperature and 9.3 A/dm^2 (92 A/ft^2), the voltage may be about 2.7 V during stripping, but increases to 4.6 V when stripping is complete.

Table 5 Solutions and operating conditions for stripping lead from steel

Method A	
Sodium hydroxide	100 g/L (13.4 oz/gal)
Sodium metasilicate	75 g/L (10 oz/gal)
Rochelle salt	50 g/L (6.7 oz/gal)
Temperature	82 °C (180 °F)
Anode current density	1.9-3.7 A/dm^2 (18.5-37 A/ft^2)
Method B	
Sodium nitrite	500 g/L (67 oz/gal)
pH	6-10
Temperature	20-82 °C (68-180 °F)
Anode current density	1.9-18.5 A/dm^2 (18.5-185 A/ft^2)
Method C[(a)]	
Acetic acid (glacial)	10-85 vol%
Hydrogen peroxide (30%)	5 vol%
Method D[(a)(b)]	
Fluoboric acid (48-50%)	4 parts
Hydrogen peroxide (30%)	1 part
Water	2 parts

Temperature	20-25 °C (68-77 °F)

(a) Formulations should be made up fresh daily.

(b) Alternate method for stripping lead or lead-tin deposits. Work must be removed as soon as the lead is stripped; otherwise, the base metal will be attacked.

With the solutions used in Method A or B, a stain occasionally remains on the steel after stripping. The stain can be removed by immersion for 30 s in the solution used in Method C, leaving the steel completely clean and unetched (unless the nitrate solution of Method B was used at less than about 2 V).

Silver Plating

Alan Blair, AT&T Bell Laboratories

ELECTROPLATED SILVER--which was developed primarily for use on holloware, flatware, and tableware--has proven its usefulness in both decorative and functional applications in both engineering and electrical/electronic applications. Decorative applications of silver plating still predominate; however, silver has been successfully substituted for gold in some functional uses in electronics. Its greatest success has been the virtually complete replacement of gold on metallic leadframes, the devices that support the majority of silicon chips. Here the development of new silicon-to-silver bonding techniques and ultimate encapsulation of the silver allow for the replacement of a much more expensive precious metal without loss of performance. In electrical contact applications, where the long-term integrity of the surface is of paramount importance, silver has been less successful as a gold substitute due to its tendency to form oxides and sulfides on its surface and the resultant rise in contact resistance. Silver has been employed as a bearing surface for many decades. It is particularly useful where the load-bearing surfaces are not well lubricated (e.g, in kerosene fuel pumps on gas turbine engines.)

Solution Formulations. The first patent concerning electroplating was filed in 1840 and reported a process for plating silver from a cyanide solution. To this day, silver is plated almost exclusively with cyanide-based solutions, despite the considerable research effort that has been expended on evaluating less toxic alternatives. A formulation for such a solution is given in Table 1. This type of electrolyte would be used for plating decorative or functional deposits of silver in a conventional way (i.e., on a rack or in a barrel). It is possible to produce fully bright deposits that require no further buffing or polishing. This is achieved by including a brightening agent in the solution formula, (one of several sulfur-bearing organic compounds, or selenium or antimony added as soluble salts). Antimony containing silver deposits are harder than pure silver. A typical antimony content might be 0.1 to 0.2% by weight. However, it should be noted that antimony content will vary with the current density employed during deposition; lower current densities will produce a deposit with higher antimony content.

Table 1 Plating solutions for silver

Component/Parameter	Rack	Barrel
Silver as $KAg(CN)_2$, g/L (oz/gal)	15-40 (2.0-2.5)	5-20 (0.7-2.5)
Potassium cyanide (free), g/L (oz/gal)	12-120 (1.6-16)	25-75 (3.3-10)
Potassium carbonate (min), g/L (oz/gal)	15 (2.0)	15 (2.0)

Temperature, °C (°F)	20-30 (70-85)	15-25 (60-80)
Current density, A/dm^2 (A/ft^2)	0.5-4.0 (5-40)	0.1-0.7 (1-7.5)

Anodes of pure silver are readily soluble in the excess or "free"cyanide of these solutions. Carbonate is a natural byproduct of atmospheric oxidation of cyanide, but this adds to the solution conductivity, and some carbonate is included when preparing a new solution. Silver metal concentration is normally maintained by anode dissolution, but occasional small additions of the metal salt may be needed. This is facilitated by adding either silver cyanide (80% silver) or potassium silver cyanide (54% silver, sometimes referred to as the double salt). Additions of the former will lower the free cyanide concentration, whereas additions of the double salt will not.

Silver is usually more noble than the metal over which it is being plated, and because of this it has a tendency to form "immersion deposits." These are poorly adherent films of silver that form due to a chemical reaction between the base metal substrate and the silver ions in solution before true electrodeposition can commence. In order to avoid this phenomenon a silver strike should always be used. (A *strike* is a low-concentration bath operated at high cathode current density.) The following gives a typical silver strike solution formulation.

Component/Parameter	**Value**
Silver, as $KAg(CN)_2$, g/L (oz/gal)	1.0-2.0 (0.13-0.27)
Potassium cyanide (free), g/L (oz/gal)	80-100 (10-13)
Potassium carbonate (minimum), g/L (oz/gal)	15 (2.0)
Temperature, °C (°F)	15-25 (60-80)
Current density, A/dm^2 (A/ft^2)	0.5-1.0 (5-10)

Stainless steel anodes should always be used in a silver strike solution to avoid an increase in silver metal concentration.

High-speed, selective plating of leadframes or similar electronic components requires the use of extremely high current densities and short plating times. Typical thicknesses range from 1.5 to 5.0 μm deposited in less than 2 s. Under these conditions, solutions containing free cyanide decompose very rapidly, the cyanide polymerizes and codeposits through electrophoresis, and the deposits cease to provide the desired properties. Solutions that use phosphate or nitrate salts as conducting media and use insoluble platinum or platinized titanium or niobium anodes have been developed to meet this requirement. Silver is present as potassium silver cyanide, and its concentration must be maintained by making periodic additions of this double salt. Careful attention must be paid to buffering because of the tendency to produce low pH values at the insoluble anodes. If this occurs, an insoluble silver salt will rapidly coat the anode and plating will cease. A typical formula is shown below.

Component/Parameter	Value
Silver, as $KAg(CN)_2$,g/L (oz/gal)	40-75 (5-10)
Conducting/buffering salts,g/L (oz/gal)	60-120 (8-16)
pH	8.0-9.5
Temperature, °C (°F)	60-70 (140-160)
Current density, $A/dm^2 (A/ft^2)$	30-380 (275-3500)

Noncyanide formulas that have been reported include those based on simple salts such as nitrate, fluoborate, and fluosilicate; inorganic complexes such as iodide, thiocyanate, thiosulfate, pyrophosphate, and trimetaphosphate; and organic complexes such as succinimide, lactate, and thiourea. A succinimide solution and a thiosulfate/metabisulfite solution have been commercialized, but the volumes used are very small compared with the cyanide solutions.

Specifications. Federal specification QQ-S-365D gives general requirements for silver plating. Using this specification it is possible to define the type of finish needed: matte (type I), semibright (type II), or bright (type III), and with chromate film for added tarnish resistance (grade A), or with no film (grade B). A minimum thickness of 13 μm (0.0005 in.) is required for functional coatings.

ASTM B 700 specifies electrodeposited coatings of silver for engineering uses and defines purity (types 1, 2, and 3: 99.9, 99.0, and 98.0%, respectively); degree of brightness or mechanical polish (grades A, B, and C: matte, plated bright, and mechanically polished, respectively); and absence or presence of a chromate film (class N or S). Thickness must be specified by the purchaser.

The aerospace industry refers to four aerospace material specifications: AMS 2410G, AMS 2411D, and AMS 2412F, each of which applies to specific undercoats and bake temperatures; and AMS 2413C, which defines requirements for silver and rhodium plating on microwave devices.

International standard ISO 4521 defines silver coatings on metallic and nonmetallic substrates. Thicknesses are not specified but preferred thicknesses are quoted.

Users of silver plating for decorative purposes will find guidance in "Guides for the Jewelry Industry," originally issued by the Federal Trade Commission.

Gold Plating

Alfred M. Weisberg, Technic Inc.

Introduction

GOLD PLATING is similar to other metal plating in most chemical and electrochemical ways. Gold differs from other metals primarily in that it is much more expensive. Within recent memory, the price of gold metal has gone from $35 per ounce to $850 per ounce and at the time of this writing is characteristically unstable at about $375 per ounce. Thus the cost of a gallon of gold plating solution is quite high.

This price level and the daily variability of its price have required chemists and engineers to severely limit the concentration of gold in the plating solution. Nickel, alkaline copper, and silver are typically plated from solutions that contain 37 g of metal per liter of plating bath. Acid copper is plated from a solution that contains 60 g of metal per liter,

and a chromium solution can contain over 240 g of metal per liter. Gold, because of its price and the cost of the dragout losses, is rarely plated from a solution that contains more than 1 troy ounce per gallon (8.2 g/L). Some gold baths used for striking, decorative use, and barrel plating use as little as 0.8 or 0.4 g/L of gold.

These very low metal concentrations, or "starved" solutions, present problems to the gold plater that are quite different from those of other metal plating solutions. With a starved solution, every control parameter in the plating process becomes more critical. Gold concentration, electrolyte concentration, pH, impurity level, and additive level must all be monitored and controlled. Temperature, current density, agitation, and the current efficiency must be accurately known and controlled beyond the degree necessary for copper, nickel, or even silver plating. If any factor changes, even 2 to 3%, the cathode gold deposition efficiency changes. If the efficiency decreases, items being plated under standard conditions will be underplated and the specified thickness will not be attained. Similarly, if the cathode efficiency increases, the plate will be too thick and result in increased cost because of using excess gold.

The engineer and plater of gold must tread the narrow line between not depositing enough gold and giving away too much gold. In addition, those concerned with gold plating must not only keep the chemistry of the process and the peculiarities of electrodeposition in mind, as do other platers, but also be aware of the market price of gold. The plater must be an economist in order to realize when the operating conditions of the solution should be altered or the entire process changed to reflect the changes in the price of gold. Economics also determines the total consumption of gold. In the recent past, when the price of gold vaulted above $500 per troy ounce, many electronics companies replaced some of the total thickness of gold with undercoats of palladium or palladium-nickel alloys. Others abandoned gold completely. Economics is a more important factor in the plating and metallurgy of gold than in the plating of nonprecious metals.

General Description

Gold electroplating was invented in 1840. During the first 100 years electrodeposited gold was used primarily for its aesthetic appeal as a decorative finish. Because decorative appeal is a matter of fashion and personal whim, hundreds of different formulations are recorded in the literature. Each was the favorite color and finish of a master plater. In their time and place, each was good. Today, however, many factors have changed, especially the price, and the old formulas should be used for historical reference only.

With the development of electronics and radar during World War II, gold had to become a functional utilitarian coating. Low voltages, milliamp currents, dry circuits, and microwave frequencies required the very best low resistance surfaces for contacts, connectors, and waveguides. The stability of the contact resistance was of paramount importance. Nontarnishing and low-resistance 24K gold surfaces were the logical choice for connectors. Later, as the demands on the gold surface increased, it was found necessary to change the metallurgy of the gold deposit. Initially, wear resistance was increased by hardening the deposit to 150 to 250 HK. Later, wear resistance was increased by altering the crystal orientation of the gold deposit from the (100) plane to the slip plane, (111). Both of these results were achieved by the addition of controlled amounts of metallic and nonmetallic additives.

At virtually the same time, transistors required high-purity gold that could be doped with antimony or indium to give n- or p-type junctions. The printed circuit industry required gold electroplates that could be produced from solutions of lower pH (actually on the acid side) and from solutions that contained no free cyanide. The alkalinity of free cyanide lifted the resist and sometimes even lifted the laminate itself. It was rediscovered that potassium gold cyanide was stable at acidic pH. Under these conditions of mild acidity, hard, bright, and even solderable coatings could be achieved. This led to the development of perhaps another 100 formulations that could meet all of the requirements mentioned above as well as the different purities and hardnesses of the military gold plating standard MIL-G-45204 with its various modifications. The multiplicity of gold electroplating formulations was further augmented by the addition of baths for high-speed deposition that were used for continuous strip, stripe, or spot plating. Some of these plated at up to 215 A/dm^2 (2000 A/ft^2). Recently, numerous formulations have been developed to allow immersion and/or electroless gold plating. As additional requirements develop, there will be a continuing introduction of new gold plating formulations to meet these needs. All of the many formulations work, and each one has its own special advantages, but care must be taken to pick the best one for a particular application.

Decorative Plating

The traditional gold electroplating solution (Table 1) for decorative use required:

- A source of gold

- A complexing agent for the gold
- A conducting salt to help carry the current and broaden the conditions of operation
- An alloying metal or metals for color and/or hardness

The source of gold was historically gold cyanide. The complexing agent was sodium or potassium cyanide (Table 1). The conducting salts were cyanides, phosphates, carbonates, hydroxides, and occasionally but rarely citrates, tartrates, and so forth.

Table 1 Typical flash formulations for decorative gold plating

Component or parameter	Type of jewelry plating						
	English (24K)	**Hard (18K)**	**Hamilton[a]**	**White**	**Rose**	**Green**	**Barrel flash**
Gold as potassium gold cyanide, g/L (oz/gal)	2 (0.3)	1.6 (0.2)	1.25 (0.15)	0.4 (0.05)	4.1 (0.5)	2 (0.3)	0.8 (0.1)
Free potassium cyanide, g/L (oz/gal)	7.5 (1)	7.5 (1)	7.5 (1)	15 (2)	3.75 (0.5)	7.5 (1)	7.5 (1)
Dipotassium phosphate, g/L (oz/gal)	15-30 (2-4)	15-30 (2-4)	15-30 (2-4)	15-30 (2-4)	. . .	15-30 (2-4)	60-90 (8-12)
Sodium hydroxide, g/L (oz/gal)	. . .	. . .	. . .	. . .	15 (2)	. . .	. . .
Sodium carbonate, g/L (oz/gal)	. . .	. . .	. . .	. . .	30 (4)	. . .	. . .
Nickel as potassium nickel cyanide,g/L (oz/gal)	. . .	0.15-1.5 (0.02-0.2)	0.3 (0.04)	1.1 (0.15)	. . .	. . .	0.3 (0.04)
Copper as potassium copper cyanide, g/L (oz/gal)	. . .	. . .	1.5 (0.2)	. . .	. . .	. . .	. . .
Silver as potassium silver cyanide, ppm	. . .	. . .	. . .	. . .	. . .	200	. . .
Temperature, °C (°F)	60-70 (140-158)	60-70 (140-158)	65-70 (150-158)	. . .	65-82 (150-180)	54-65 (130-150)	49-60 (120-140)
Current density, A/dm^2 (A/ft^2)	1-4 (10-40)	1-4 (10-40)	1-3 (10-30)	. . .	2-5.5 (20-55)	1-2 (10-20)	0.5-10 (5-10)

(a) *Hamilton* is a term that has been applied to white, pink, green, and brown golds. It is practically meaningless today, but is still widely used.

If any four numbers are randomly assigned to the concentrations of the four constituents of the gold electroplating solution, plating conditions can be found that will yield a satisfactory deposit. The four numbers chosen would determine

the necessary temperature of operation, the degree of agitation, the current density for producing a good deposit, and the time of plating needed for different thicknesses. The fact that any four numbers could be used explains why hundreds of formulations appear in the literature. Given the proper operation conditions, any of the formulas will work, and at one time or another each cited formula was optimum and economic for a given plant and a given plater. Variations in the price of gold, the size of the item to be plated, the necessary rate of production, the desired deposit thickness, and the desired color resulted in almost every plater designing the "best bath."

Today, most jewelry is flash plated or strike plated from a hot-cyanide alloy (color) bath. The deposit is usually applied over a bright nickel deposit. Occasionally, the gold is flash plated over a palladium deposit over a bright acid-copper deposit, where nickel-free deposits are desired. (The European Common Market is concerned about nickel dermatitis from costume jewelry, snap fasteners, and other items that contact the skin.) Occasionally, the flash gold deposit is applied over a karat gold or rolled-gold plated item. This is done to give an even color to jewelry items made of several different findings. (Some jewelry is flashed from an acid bath directly over stainless steel for hypoallergenic jewelry.)

Typical flash formulations are given in Table 1. Although broad ranges are given for the decorative flash baths, it is absolutely essential that each parameter be closely and tightly controlled within its range if consistency of color is desired. The time of plating is quite short, usually 5 to 30 s. For minimum porosity and subtle color matches, even a 30 s plate may be duplex plated from two different solutions. For flash barrel plating the gold concentration can be as low as 0.8 g/L, the free cyanide is 7.5 g/L, the dipotassium phosphate should be 75 g/L or above, and nickel, as a brightener, should be added at 2 g/L or higher as potassium nickel cyanide.

The deposit is generally 0.05 to 0.1 μm (2 to 4 μin.) and *cannot*be marketed as gold electroplate. If the jewelry is to be marketed as gold electroplate the deposit must be 0.175 μm (7 μin.). If the jewelry is to be marketed as heavy gold electroplate the deposit must be 2.5 μm (100 μin.). Most deposits in this range are plated from an acid gold formulation (Table 2) or from a sulfite gold bath (Table 3).

Table 2 Acid gold color plating baths for heavy deposits

Component or parameter	1N Color[(a)]	2N Color[(a)]	Yellow 24K	Yellow 22K
Gold, g/L (oz/gal)	0.4-0.8 (0.05-0.1)	0.4-0.8 (0.05-0.1)	0.4-0.8 (0.05-0.1)	0.4-0.8 (0.05-0.1)
Conducting salt[(b)], g/L (oz/gal)	120 (16)	120 (16)	120 (16)	120 (16)
Nickel as chelate, g/L (oz/gal)	11 (1.5)	3.7-6 (0.5-0.8)	. . .	200 ppm
Cobalt as chelate, ppm	. . .	. . .	250	1000
pH	4-4.5	4-4.5	4.4-4.8	4.5
Temperature, °C (°F)	50-60 (120-140)	38-50 (100-120)	26-32 (80-90)	32-38 (90-100)
Current density, A/dm^2 (A/ft^2)	1-2 (9-19)	1-2 (9-19)	1-2 (9-19)	1-2 (9-19)
Agitation	Yes	Yes	Yes	Yes

(a) European color standards.

(b) The conducting salt can be a phosphate or an organic acid such as citric or malic.

Table 3 Sulfite gold decorative plating baths

Component or parameter	24K	Flash green	Pink	Heavy plating
Gold as sulfite, g/L (oz/gal)	1.25-2 (0.17-0.27)	1.25-2 (0.17-0.27)	1.25-2 (0.17-0.27)	8-12 (1.0-1.6)
Conducting sulfite salt, g/L (oz/gal)	90 (12)	90 (12)	90 (12)	45-75 (6-10)
Nickel as chelate, g/L (oz/gal)	. . .	1.1 (0.15)	0.5 (0.07)	. . .
Copper as chelate, g/L (oz/gal)	. . .	. . .	0.5 (0.07)	. . .
Cadmium as chelate, ppm	. . .	760	. . .	. . .
Brightener, often arsenic, ppm	20	20	20	20
Current density, A/dm^2 (A/ft^2)	3-5 (28-46)	3-5 (28-46)	3-5 (28-46)	0.1-0.4 (1-4)
Temperature, °C (°F)	50-65 (120-150)	50-65 (120-150)	50-65 (120-150)	50-60 (120-140)
Time, s	10-20	15-30	10-20	[a]

(a) 12.5 min at 0.3 A/dm^2 (3 A/ft^2) gives 100 μin.

As with cyanide gold plating, to achieve consistent good color control it is necessary to regulate each chemical and physical variable within its range given in Table 2. It is also necessary to analyze for metallic impurities and control their concentrations. Drag-in of metallic impurities can have a disastrous effect on color control.

Sulfite gold plating solutions (Table 3) have several unique and advantageous characteristics. First, they contain no cyanide, so the normal safety precautions used when working with or handling cyanide are not necessary when using sulfite gold. In addition, of course, there is no cyanide to destroy in the dragout, rinse stream or old solutions shipped for recovery. The second unique property is exceptional microthrowing power; the bath will actually build brightness during plating. The deposit is essentially featureless with exceptionally fine crystal structure.

Industrial Gold Plating

The printed circuit industry of the late 1950s led to the rediscovery of the stability of potassium gold cyanide on the acid side (below a pH of 7). This was first hinted at in a Ruolz French patent of addition of 1840-45. The stability was described in the English edition of *Cyanogen Compounds* by H.E. Williams in the 1890s. Finally, the Lukens patent of 1938 made use of low-pH gold cyanide plating to ensure good adhesion on stainless steel. Lukens referred to this bath, made up with sodium gold cyanide, sodium cyanide, and hydrochloric acid as *acid gold plating.*

The alkaline gold plating solutions in use in the early 1950s caused lifting of printed circuit resists, especially the wax-based resists introduced in an attempt to speed board preparation. The pH of the gold solutions was progressively lowered

to minimize this effect. In one case, an accident resulted in too low a drop in the pH. It was not noticed at first because the bath continued to plate and there was no lifting of the resist. However, a drop in cathode current efficiency and a decrease in the thickness of the gold deposit alerted the operator. On investigation it was found that the pH had fallen to 4.0.

Separately, it was discovered by Duva that at a pH of 3.5 to 5, it was possible to add small amounts of cobalt, nickel, iron, and other metals to harden the gold deposit and cause it to plate bright. The purity of the deposit was still over 98% gold, but the hardness could be as high as 230 HK. Later, it was also noticed that the crystal structure of the surface could be plated to yield a (111) crystal plane, which greatly increased the wear resistance of the contact surface. Depending on the added metal or metals, the chemical form of the addition, and the pH of the electrolyte, deposits of various hardnesses and other characteristics could be made (Table 4).

Table 4 Acid gold industrial plating baths

Component or parameter	**Bright, hard acid**	**Weak acid**
Regular baths		
Gold as potassium gold cyanide g/L (oz/gal)	4-16 (0.5-2)	4-8 (0.5-1)
Potassium citrate, citric acid, g/L (oz/gal)	180 (24)	. . .
Mono- and dipotassium phosphate, g/L (oz/gal)	. . .	180 (24)
Brightener	(a)	. . .
pH	3.5-5.0	5.5-7.0
Temperature, °C (°F)	20-50 (68-122)	65-74 (150-165)
Current density, A/dm^2 (A/ft^2)	1-10 (9-90)	0.1-0.5 (1-5)
Current efficiency, %	30-40	85-100
High-speed baths		
Gold as potassium gold cyanide, g/L (oz/gal)	4-24 (0.5-3)	8-32 (1-4)
Citrates, g/L (oz/gal)	90 (12)	. . .
Phosphates/citrates, g/L (oz/gal)	. . .	90 (12)
Brighteners	(a)	(a)
Temperature, °C (°F)	49-60 (120-140)	71-82 (160-180)

Current density[b], A/dm^2 (A/ft^2)	10-200 (93-1860)	5-50 (46-460)
Current efficiency, %	40-50	50-60

(a) As required.

(b) Values given are typical; they depend on agitation and the individual machine.

At the same time that the above developments took place, the semiconductor industry developed a need for high-purity golds at increased thicknesses. This led to a series of formulations by Ehrheart that plated gold from mild acid solutions. Raising the pH resulted in better covering power and higher current efficiency. At first the hardness and brightness of the acid golds was lost, but it was found that by modifying the neutral electrolytes, these properties could be partially restored (Table 4). So many different solutions were developed that a standard was needed. The most recent MIL-G-45204C (1984) and ASTM B 488-86, the military specification defines the purity, hardness, and thickness of the deposit. Purity is described as:

- Type I: 99.7% gold min
- Type II: 99.0% gold min
- Type III: 99.9% gold min

Hardness is specified as:

- A, 90 HK max
- B, 91-129 HK max
- C, 130-200 HK max
- D, 201 + HK

Thickness is specified as:

- Class 00, 0.5 μm (20 μin.)
- Class 0, 0.75 μm (30 μin.)
- Class 1, 1.25 μm (50 μin.)
- Class 2, 2.5 μm (100 μin.)
- Class 3, 5.0 μm (200 μin.)
- Class 4, 7.5 μm (300 μin.)
- Class 5, 12.5 μm (500 μin.)
- Class 6, 37.5 μm (1500 μin.)

Type I purity cannot have hardness D, and Type II purity cannot have hardness A. Type III purity can only be hardness A.

Strike Plating. Gold is a noble metal and deposits at a very low applied potential. These characteristics can cause nonadherence of the gold deposit if the substrate is either passive or not perfectly clean. Poor adhesion can be prevented by using a gold strike bath. A *strike* is generally a solution with very low metal concentration that is operated at high voltage and high current density for a very short period of time. For rack plating, the strike plating time is less than 1 min at a current density of 1 to 3 A/dm^2 (9 to 28 A/ft^2). A gold strike generally is not needed when plating from an acid gold solution unless the gold concentration is greater than 8 g/L or the substrate is passive.

Noncyanide Gold Plating Solutions. Sulfite gold industrial baths are used for their unique physical properties in addition to the desirable property of being noncyanide. As discussed above, sulfite golds have exceptional microthrowing power, which makes them the only gold formulations that build brightness. Furthermore, they have the best infrared reflectivity of any gold plating solution. The following table shows the composition and operating parameters of sulfite gold industrial baths:

Component or parameter	Value
Gold as sodium gold sulfite, g/L (oz/gal)	4-16 (0.5-2)
Sodium sulfite and sulfate, g/L (oz/gal)	90 (12)
pH	8.5-10.0
Temperature, °C (°F)	50-60 (122-140)
Brightener	As required
Current density, A/dm^2 (A/ft^2)	0.1-0.4 (1-4)
Current efficiency, %	100

Electroplating Calculations. Factors to use with gold electroplating calculations are:

- The price of gold, as given in newspapers and on the radio, is expressed in dollars per troy ounce (1 troy ounce = 31.1 g).
- A deposit of gold that is 1 µm thick = 19.58 g/m^2 (1.82 g/ft^2).
- At 100% cathode current efficiency, 7.35 g of gold can be electrodeposited in 1 ampere-hour, or 0.123 g in 1 ampere-minute.
- At 100% cathode current efficiency, 160.5 ampere-minutes are required for a gold deposit that is 1 µm thick and covers 1 m^2.

Time, temperature, and amperage can be accurately measured and controlled in gold electroplating. The largest errors that can affect gold calculations are the inaccuracies in the current density and the current efficiency. Current density is determined by calculating the area measurement, which is not always an easy task. Outside surface areas may be correctly calculated, but inside surfaces and holes, such as solder cups, must be calculated and then their effective plating area must be estimated.

Current efficiency is determined by current density, metal concentration, electrolyte concentration, and impurity content. The impurities that change the current efficiency are the metallic impurities, the organic impurities from masking materials and resists, and airborne dust. Current efficiency can be measured with a weighed coupon plated in the laboratory using a sample of the solution.

In practice, a good way to measure the efficiency of a solution is to estimate the required amperage and time based on theory, increase the amount by, say, 10%, and then plate a load under these conditions. The thickness of the gold on the

plated work can be measured by microsection, x-ray diffraction, beta-ray backscatter, or other means. The thickness actually measured should be used to correct the estimated efficiency and to modify the plating conditions. It is best to measure the thickness periodically, because the cathode current efficiency of a gold bath will change not only with the variability of all the chemical constituents but also with the age of the bath. Periodic monitoring of the thickness ensures consistent quality control.

Dragout

Minimizing the dragout of gold solutions is of both economic and environmental concern. It is an economic advantage to decrease the cost of gold loss, and it is an environmental advantage to reduce the amount of processing needed to purify the waste stream before discharge.

Many factors affect dragout:

- The thickness of the gold plated
- The shape of the part to be plated
- The number of holes or other solution-trapping structures
- The speed of removing the plated part from the plating tank
- Provisions for air jets or wiper blades to return the drippings to the plating tank

In some cases the dragout is from 30 to 50% of the gold actually deposited. Typically, however, it is 10 to 20%. It is far better to limit the dragout than to expend effort in processing the cyanide and recovering the gold from the dragout.

Minimizing the dragout can be done with simple procedures such as training the operator to remove the rack slowly and to "nudge" or shake the withdrawn rack over the gold tank so droplets return to the tank. Barrels should be allowed to drip over the gold tank and should be rotated one-half turn or more before being dipped into the dragout recovery tank. Continuous plating machines should have an air knife or a synthetic sponge to remove excess gold solution.

All gold-plated work should be rinsed in a stagnant gold recovery tank that is treated frequently to recover the dragged-out gold. The gold can be recovered by passing the dragout solution through an appropriate ion exchange resin, or it may be recovered by plating out, in which the dragout is circulated and continuously electroplated on a carbon or wire-mesh cathode. The gold-plated cathode should periodically be sent to a refiner.

Platinum-Group Metals Plating

Ch.J. Raub, Forschungsinstitut für Edelmetalle und Metallchemie

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Introduction

THE SIX PLATINUM-GROUP METALS (PGMs), listed in order of their atomic numbers, are ruthenium, rhodium, palladium, osmium, iridium, and platinum. The PGMs are among the scarcest of metallic elements, and thus their cost is high. Their most exceptional trait in the metallic form is their excellent corrosion resistance. The electroplating of PGMs from aqueous electrolytes for engineering applications is limited principally to palladium and, to a much lesser extent, to platinum, rhodium, and thin layers of ruthenium. There are practically no electrolytes on the market for the deposition of osmium or iridium. While solution formulations have been published for these last two metals, they have not proven themselves in practical use for any significant applications, and thus will be discussed only briefly in this article.

Detailed information about the general availability, properties, and applications of PGMs is provided in *Properties and Selection: Nonferrous Alloys and Special-Purpose Materials,* Volume 2 of *ASM Handbook.* Good overview coverage of plating of these metals is available in Ref 1, 2, and 3.

Acknowledgement

The section on anode materials was prepared by Ronald J. Morrissey, Technic, Inc.

References

1. F.H. Reid, Platinum Metal Plating-A Process and Application Survey, *Trans. Inst. Met. Finish.,* Vol 48, 1970, p 112-123
2. F.H. Reid, Electrodeposition of Platinum-Group Metals, *Met. Rev.,* Vol 8, 1963, p 167-211
3. Ch.J. Raub, Electrodeposition of Platinum-Group Metals, *GMELIN Handbook of Inorganic Chemistry,* Platinum Supplement, Vol A1, 1982

Ruthenium Plating

Ruthenium in the solid form is hard and brittle; furthermore, it oxidizes rather easily. These factors limit its use, even as its low price relative to the other PGMs provides impetus for its application. Despite extensive research work on electroplating of ruthenium, it has obtained a small market share in only two areas: for decorative applications such as eyeglass frames and for layers on electrical contacts used in sealed atmospheres.

All ruthenium plating electrolytes are based on solutions of simple ruthenium salts or ruthenium nitrosyl derivatives. Typical examples are ruthenium sulfate, ruthenium phosphate, ruthenium sulfamate, or ruthenium chloride (Ref 4). These electrolytes are all essentially based on those described in Ref 5 and 6. They work in a wide range of current densities from 1 to 10 A/dm^2 (9 to 93 A/ft^2) at temperatures between 50 and 90 °C (120 and 195 °F), and at current efficiencies of 50 to 90%. Compositions and operating conditions for two ruthenium plating solutions are given in Table 1.

Table 1 Ruthenium electroplating solutions

Constituent or condition	Amount or value
General-purpose solution	
Ruthenium (as sulfamate or nitrosyl sulfamate), g/L (oz/gal)	5.3 (0.7)
Sulfamic acid, g/L (oz/gal)	8 (1.1)
Anodes	Platinum
Temperature, °C (°F)	
Sulfamate solution	27-60 (80-140)
Nitrosyl sulfamate solution	21-88 (70-190)
Current density, A/dm^2 (A/ft^2)	1-3 (10-30)
Current efficiency, %	20
Time to plate thickness of 0.003 mm (0.0001 in.)	30-40 min at 2 A/dm^2 (20 A/ft^2)
Flash-plating solution for decorative deposits	

Ruthenium (as nitroso salt), g/L (oz/gal)	2.0 (0.3)
Sulfuric acid, g/L (oz/gal)	20 (2.7)
Current density, A/dm^2 (A/ft^2)	2-3 (20-30)
Temperature, °C (°F)	50-80 (120-180)

Note: Both solutions require a flash-plated undercoat of gold or palladium. Source: Ref 7

The preparation of the electrolyte constituents is rather critical. Deposits are hard and highly stressed, making it difficult to obtain crack-free layers at higher thicknesses. For electrical contact applications, a layer of gold flash plated on top of the ruthenium is recommended to ensure excellent wear and good contact resistant on a long-term basis (Ref 8, and 9). Smooth and bright deposits can be obtained from cyanide melts (Ref 10, 11). Microhardness of such layers is between 600 and 900 HK.

References cited in this section

4. F.H. Reid and J.C. Blake, *Trans. Inst. Met. Finish.,* Vol 38, 1961, p 45-51
5. H.C. Angus, *Trans. Inst. Met. Finish.,* Vol 43, 1965, p 135-142
6. T.A. Palumbo, *Plat. Surf. Finish.,* Vol 66, 1979, p 42-44
7. A.M. Weisberg, Ruthenium Plating, *Met. Finish.,* Vol 90 (No. 1A), 1992, p 257
8. R.G. Baker and T.A. Palumbo, *Plat. Surf. Finish.,* Vol 69, 1982, p 66-68
9. A.F. Bogenschütz, J.L. Jostan, and W. Mussinger, *Galvanotechnik,* Vol 67, 1976, p 98-105
10. R.N. Rhoda, *Plating,* Vol 49, 1962, p 69-71
11. G.S. Reddy and P. Taimsalu, *Trans. Inst. Met. Finish.,* Vol 47, 1969, p 187-193

Rhodium Plating

Rhodium in its solid form is hard (microhardness about 800 to 1000 HV) and tough. It is nearly as tarnish resistant as platinum and palladium. However, because of its rare occurrence in PGM ores and market speculation, it is much more expensive, limiting its engineering use. Like silver, it has one of the highest reflectivities of all metals, making it ideal for use as a counterpoint to cut diamonds in jewelry and as a nontarnishing reflective coating for mirrors. Its excellent wear resistance and its superb contact resistance prompt its frequent use for rotating electrical contacts.

The electrolytes for deposition of rhodium from aqueous solutions are similar to those for ruthenium insofar as they are either based on simple rhodium salts or on special rhodium complexes (Ref 12, and 13). Because, in most cases, only layer thicknesses of 1 μm or less are specified, most commercial electrolytes have been developed to produce layers in this thickness range. The deposits have a high concentration of nonmetallic impurities (e.g., up to 1000 ppm H and/or O) (Ref 14), which causes high hardnesses and internal stresses, which easily lead to cracks. This thin and highly porous layer of rhodium, coupled with the high electrochemical nobility of the metal, limits its use as a corrosion protection layer. Therefore, an electroplated base coating must be used. Silver and silver-tin alloys (with varying concentrations of tin) have exhibited excellent field service behavior and are now applied for decorative as well as engineering purposes. Nickel is not recommended for use as a base coating. For decorative use the color (better reflectivity) is most important. It changes from electrolyte to electrolyte, many of which are commercial solutions. Deposition conditions must be carefully controlled for best results.

The complex rhodium salts of solutions cited in the literature are based on sulfate, phosphate, sulfate-phosphate, sulfate-sulfite, sulfamate, chloride, nitrate, fluoroborate, or perchlorate systems. Properties of the layers are strongly influenced by the chemistry of their salts as well as by impurities present (Ref 15). Three solutions for decorative rhodium plating are given in Table 2.

Table 2 Solutions for decorative rhodium plating

Solution type	Rhodium		Phosphoric acid (concentrate) fluid		Sulfuric acid (concentrate) fluid		Current density		Voltage, V	Temperature		Anodes
	g/L	oz/gal	mL/L	oz/gal	mL/L	oz/gal	A/dm^2	A/ft^2		°C	°F	
Phosphate	2[a]	0.3[a]	40-80	5-10	. . .	. . .	2-16	20-160	4-8	40-50	105-120	Platinum or platinum-coated[b]
Phosphate-sulfate	2[c]	0.3[c]	. . .	. . .	40-80	5-10	2-11	20-110	3-6	40-50	105-120	Platinum or platinum-coated[b]
Sulfate	1.3-2[c]	0.17-0.3[c]	. . .	. . .	40-80	5-10	2-11	20-110	3-6	40-50	105-120	Platinum or platinum-

(a) Rhodium as metal, from phosphate complex syrup.

(b) Platinum-coated products are also known as platinized titanium.

(c) Rhodium, as metal, from sulfate complex syrup

A typical, widely used production bath is based on rhodium sulfate (Ref 15). With use of proper additives, especially sulfur-containing compounds, crack-free layers may be obtained in thicknesses of about 10 μm and microhardnesses of 800 to 1000 HV (Ref 15). The deposition temperature of such baths is about 50 °C (120 °F), the current density is between 1 and 10 A/dm^2 (9 to 93 A/ft^2), and current efficiency is approximately 80%. Insoluble anodes are normally used.

For electronic applications where undercoatings are undesirable, special low-stress compositions have been developed. One electrolyte contains selenic acid and another contains magnesium sulfamate (Table 3). Deposit thickness obtained from these solutions range from 25 to 200 μm (1 to 8 mils), respectively. The low-stress sulfamate solution is used for barrel plating of rhodium on small electronic parts. Operating conditions for various plating thicknesses using this solution are given in Table 4.

Table 3 Solutions for electroplating low-stress rhodium deposits for engineering applications

Solution	Selenic acid process	Magnesium sulfamate process
Rhodium (sulfate complex)	10 g/L (1.3 oz/gal)	2-10 g/L (0.3-1.3 oz/gal)
Sulfuric acid (concentrated)	15-200 mL/L (2-26 fluid oz/gal)	5-50 mL/L (0.7-7 fluid oz/gal)
Selenic acid	0.1-1.0 g/L (0.01-0.1 oz/gal)	. . .

Magnesium sulfamate	. . .	10-100 g/L (1.3-13 oz/gal)
Magnesium sulfate	. . .	0-50 g/L (0-7 oz/gal)
Current density	1-2 A/dm^2 (10-20 A/ft^2)	0.4-2 A/dm^2 (4-22 A/ft^2)
Temperature	50-75 °C (120-165 °F)	20-50 °C (68-120 °F)

Table 4 Plating parameters for producing low-stress deposits from a rhodium sulfamate solution

Required thickness		**Thickness of plate**		**Apparent current density**[(a)]		**Calculated current density**[(a)]		**Plating time**
µm	**mil**	**µm**	**mil**	**A/dm^2**	**A/ft^2**	**A/dm^2**	**A/ft^2**	
1	0.04	0.5-1.5	0.02-0.06	0.55	5.5	1.6-2.2	16-22	35 min
2.5	0.1	1.75-3.25	0.07-0.127	0.55	5.5	1.6-2.2	16-22	$1\frac{1}{4}$ h

(a) Calculated current density is an estimate of the amount of current being used by those parts that are making electrical contact and are not being shielded by other parts in the rotating load in the barrel. Calculated current density is considered to be about three times the apparent current density, that is, the actual current used for the load divided by the surface of that load.

Rhodium also can be electroplated from fused-salt electrolytes. This deposition process is interesting because the requirements are that the coatings must be highly ductile for high-temperature use (e.g., coatings on molybdenum for combustion engine parts or glass-making equipment). For fused-salt electrolysis, a variety of mixtures have been tested, ranging from cyanide to chloride melts (Ref 16).

Thickness class designations for engineering applications of electroplated rhodium are given in Table 5.

Table 5 Thickness classifications for rhodium plating for engineering use

Specification	**Class**	**Minimum thickness**	
		µm	**mil**
ASTM B 634-78	0.2	0.2	0.008
	0.5	0.5	0.02
	1	1	0.04

	2	2	0.08
	4	4	0.16
	5	6.25	0.25
MIL-R-46085A	1	0.05	0.002
	2	0.3	0.01
	3	0.5	0.02
	4	2.5	0.10
	5	6.4	0.25

Source: Ref 17

References cited in this section

12. G.R. Smith, C.B. Kenahan, R.L. Andrews, and D. Schlain, *Plating,* Vol 56, 1969, p 804-808
13. W.B. Harding, *Plating,* Vol 64, 1977, p 48-56
14. Ch. J. Raub, unpublished research
15. F. Simon, Degussa-Demetron, Information Sheet, and article in *GMELIN Handbook of Inorganic Chemistry,* Platinum Supplement, Vol Al, 1982
16. R.N. Rhoda, *Plating,* Vol 49, 1962, p 69-71
17. L.J. Durney, Ed., *Electroplating Engineering Handbook,* 4th ed., Van Nostrand Reinhold, 1984, p 276

Palladium Plating

Palladium has been electroplated since before the turn of the 20th century. However, it stirred little interest until the 1960s and 1970s, when the price of gold peaked, prompting a search for alternatives. Palladium plating is currently used for jewelry and electrical contacts; however, the decorative applications of palladium are limited due to the dark color of the metal. Three typical palladium plating solutions are listed in Table 6.

Table 6 Palladium electroplating solutions

Constituent or condition	**Amount or value**
Solution A	
Palladium (as tetraamino-palladous nitrate, g/L (oz/gal)	10-25 (1-3)[(a)]
pH	8-10

Temperature, °C (°F)	40-60 (100-140)
Current density, A/dm^2 (A/ft^2)	0.5-2.2 (5-20)[(b)]
Cathode efficiency, %	90-95
Anodes	Insoluble; palladium, platinum, or platinized titanium
Tank lining	Glass or plastic
Solution B	
Palladium (as diamino-palladous nitrite), g/L (oz/gal)	10 (1)
Ammonium sulfamate, g/L (oz/gal)	110 (15)
Ammonium hydroxide	To pH
pH	7.5-8.5
Temperature	Room
Current density, A/dm^2 (A/ft^2)	0.5-2.2 (5-20)[(b)]
Cathode efficiency, %	70
Anodes	Insoluble; platinum or platinized titanium
Tank lining	Glass or plastic
Solution C	
Palladium (as palladous chloride), g/L (oz/gal)	50 (7)
Ammonium chloride, g/L (oz/gal)	30 (4)
Hydrochloric acid	To pH
pH	0.1-0.5
Temperature, °C (°F)	40-50 (100-120)

Current density, A/dm^2 (A/ft^2)	0.5-1.1 (5-10)
Anodes	Soluble palladium
Tank lining	Rubber, plastic, or glass

Source: Ref 18

(a) Normally 10-15 g/L (1-2 oz/gal).

(b) Normally 0.5 A/dm^2 (5 A/ft^2).

Palladium alloys such as palladium-nickel, palladium-iron, and, to a lesser extent, palladium-cobalt are also electroplated. The plating solutions for palladium alloys are generally based on the same or similar complexes as the ones for palladium alone. The main application at present for these alloy electrodeposits is for electrical connectors (Ref 19, 20, 21, 22). A solution composition for depositing palladium-nickel is given in Table 7.

Table 7 Palladium-nickel electroplating solutions

Constituent or condition	**Amount or value**
Palladium as $Pd(NH_3)_2(NO_2)_2$, g/L (oz/gal)	6 (0.8)[a]
Nickel sulfamate concentrate, mL/L (fluid oz/gal)	20 (2.6)[b]
Ammonium sulfamate, g/L (oz/gal)	90 (12)
Ammonium hydroxide	To pH
pH	8-9
Temperature, °C (°F)	20-40 (70-100)
Current density, A/dm^2 (A/ft^2)	0.5-1.0 (5-9)
Anodes	Platinized

Note: Formulation is for plating an alloy of about 75 wt% Pd. A strike of gold or silver is recommended for most base metals prior to plating.

Source: Ref 23

(a) Palladium metal, 3 g/L (0.4 oz/gal).

(b) Nickel metal, 3 g/L (0.4 oz/gal).

The properties of palladium electrodeposits are generally similar to those of gold, but it has higher receptivity and hardness. Soldering, crimping, and wire wrapping present no serious problems. The sliding and wear behavior of palladium are similar to those of hard gold. Palladium coatings may be slightly less porous than gold coatings, and they resist tarnish and corrosion. On the other hand, the chemical properties of palladium are quite different from those of gold, which may explain why an effective agent for stripping palladium and palladium alloy electrodeposits has not yet been developed.

In service, palladium and palladium alloys tend to exhibit what is called a *brown powder effect,* in which a "brown polymer" catalytically forms on the contact surface upon exposure to organic compounds in the environment. This effect can be minimized by application of flash plating a layer of fine gold on top of the palladium surface. The biggest challenge when electrodepositing palladium is avoiding hydrogen embrittlement. Palladium in electrodeposition may dissolve fairly large amounts of hydrogen, and this expands the palladium lattice, especially if the so-called β-Pd/H phase is formed. However, this hydrogen diffuses out of the palladium during storage at room temperature, and the lattice contracts again. This expansion/contraction generates stresses in the deposit that cause cracks and pores. Furthermore, palladium promotes diffusion of atomic hydrogen, which may cause secondary reactions (e.g., hydrogen embrittlement of underlying steel bases or blister) if the base material does not take up the diffused hydrogen.

Electrolytes have been developed that effectively solve the problem of hydrogen embrittlement. The most economical are based on palladium chloride. In these solutions, the palladium ion is complexed by ammonia or amines. Other systems using other complexes have also been developed (Ref 19, 20, 21, 22, 24). Currently, no electrolyte for the deposition of palladium-silver or palladium-copper alloys is available. The influence of organic and inorganic impurities on palladium-nickel deposits has been studied extensively (Ref 19).

Thickness class designations for engineering applications of electroplated palladium are given in Table 8.

Table 8 Thickness classifications for palladium plating for engineering use

Specification	Class	Minimum thickness	
		µm	mil
ASTM B 679-80	5.0	5.0	0.20
	2.5	2.5	0.10
	1.2	1.2	0.05
	0.6	0.6	0.02
	0.3	0.3	0.01
	F	0.025	0.0010

MIL-P-45209	. . .	1.3[a]	0.05[a]

Source: Ref 17

(a) Unless otherwise specified.

References cited in this section

17. L.J. Durney, Ed., *Electroplating Engineering Handbook,* 4th ed., Van Nostrand Reinhold, 1984, p 276
18. N.V. Parthasaradhy, *Practical Electroplating Handbook,* Prentice Hall, 1989, p 202-205
19. Ch.J. Raub, *Platinum Met. Rev.,* Vol 28, 1992, p 158-166
20. F.H. Reid, *Plating,* Vol 52, 1965, p 531-539
21. M. Antler, *Platinum Met. Rev.,* Vol 26, 1982, p 106-117
22. H. Grossmann, M. Huck, and G. Schaudt, *Galvanotechnik,* Vol 71, 1980, p 484-488
23. R.J. Morrissey, Palladium and Palladium-Nickel Plating, *Metal Finishing,* Vol 90 (No. 1A), 1992, p 247-248
24. German Society for Electroplating and Surface Technology, Precious Metals Working Group, Electroplating of Palladium and Palladium Alloys, *Galvanotechnik,* Vol 84, 1993, p 2247-2938

Osmium Plating

Currently, no practical applications exist for electrodeposited osmium, primarily because the metal oxidizes readily at room temperature, forming poisonous and volatile osmium tetroxide. The metal itself is hard and brittle and has few industrial uses. For a review of the existing literature on electrodeposition of osmium, see Ref 25, 26, and 27.

References cited in this section

25. J.M. Nutley, *Trans. Inst. Met. Finish.,* Vol 50, 1972, p 58-62
26. L. Greenspan, *Plating,* Vol 59, 1972, p 137-139
27. J.W. Crosby, *Trans. Inst. Met. Finish.,* Vol 54, 1976, p 75-79

Iridium Electroplating

The electroplating of iridium has up to now not found any widespread application. Essentially, no electrolytes are available that can deposit iridium from aqueous electrolytes at reasonable thicknesses and with satisfactory properties.

Known electrolytes are mostly based on the chloro-iridic acid. The bath is highly acidic and works at a temperature of about 80 °C (176 °F) and at a current density of 0.15 A/dm^2 (1.4 A/ft^2). The microhardness of deposits is 900 DPN, and their total reflectivity is about 61% that of silver. At thicknesses of more than 1 μm, the layers are cracked. The current efficiency of these processes approaches 50%. At low current densities, the plating rate is close to 1 μm/h (Ref 28, 29, 30, 31).

Iridium has been deposited from fused salts. The solution was prepared by passing alternating current between two electrodes suspended in the melt, which was a eutectic of NaCN or KCN/NaCN, with melting points of 564 and 500 °C (1050 and 930 °F), respectively (Ref 32). However, these electrolytes have not proven to be usable in commercial practice.

References cited in this section

28. F.H. Reid, *Met. Rev.*, Vol 8, 1963, p 167, 211
29. C.J. Tyrell, *Trans. Inst. Met. Finish.*, Vol 43, 1965, p 161-166
30. F.H. Reid, *Trans. Inst. Met. Finish.*, Vol 48, 1970, p 115-123
31. G.A. Conn, *Plating*, Vol 52, 1965, p 1256-1261
32. R.N. Rhoda, *Plating*, Vol 49, 1962, p 69-71

Platinum Plating

The electrodeposition of platinum from aqueous electrolytes is of limited engineering value. The metal is very expensive, and the currently available plating solutions are not capable of consistently producing ductile and pore-free deposits at thicknesses above a few microns. Today, most of the deposits produced are less than 1 μm thick and are used primarily for decorative applications.

The main challenge when electroplating platinum from aqueous electrolytes is to obtain a clean, ductile platinum coating with a minimum of nonmetallic impurities, which act as hardeners and embrittle the platinum. This is rather difficult because platinum compounds tend to hydrolyze even at rather low pH levels. Therefore, close control of plating parameters is very important.

The three most common electrolytes used today are platinum chloride, diamino-dinitroplatinum (platinum "P" salt), and alkali hydroxy platinate. The current efficiency of the highly acidic baths is close to 90%, but the electrolytes are difficult to handle. Two platinum plating solutions are listed in Table 9.

Table 9 Platinum electroplating solutions

Constituent or condition	Amount or value
Solution A	
Platinum (as sulfatodinitrito-platinous acid), g/L (oz/gal)	5 (0.7)
Sulfuric acid	To pH
pH	1.5-2.0
Temperature, °C (°F)	Room to 40 (100)
Current density, A/dm^2 (A/ft^2)	5-20 (5-20)
Anode	Platinum or platinized titanium
Cathode efficiency	10-20%
Solution B	
Platinum (as diaminodinitrito salt), g/L (oz/gal)	10 (1.3)
Ammonium nitrate or phosphate, g/L (oz/gal)	100 (13.4)

Sodium nitrite, g/L (oz/gal)	10 (1.3)
Ammonium hydroxide (28% solution), mL/L (fluid oz/gal)	50 (6.4)
Temperature, °C (°F)	90-100 (190-210)
Current density, A/dm^2 (A/ft^2)	3-10 (30-100)[(a)]
Anode	Platinum (insoluble)
Tank lining	Glass or plastic
Cathode efficiency	Low[(b)]

Source: Ref 18

(a) Normally 4 A/dm^2 (40 A/ft^2).

(b) 10% at 6 A/dm^2 (60 A/ft^2).

A commercial process gaining more and more importance for engineering applications in the chemical, electronics, and glass industries is the electrodeposition of platinum from salt melts, because the process forms highly dense and ductile platinum layers. The platinum compound can be formed by electrolytic dissolution with alternating current in a NaCN/KCN fused-salt mixture, melting at 500 °C (930 °F). For deposition, a cyanide/cyanate mixture operating at about 450 °C (840 °F) is recommended.

For decorative platinum deposits, the use of a flash-plated base coat is recommended. Suitable layers include palladium-iron, silver, and copper-tin systems. Detailed information on platinum electroplating is available in Ref 33, 34, 35, 36, 37, and 38.

References cited in this section

18. N.V. Parthasaradhy, *Practical Electroplating Handbook,* Prentice Hall, 1989, p 202-205

33. F.H. Reid, *Trans. Inst. Met. Finish.,* Vol 48, 1970, p 115-123

34. F.H. Reid, *Met. Rev.,* Vol 8, 1963, p 167-211

35. K. Wundt, *Oberfl. Surf.,* Vol 25, 1984, p 207-212

36. R.N. Rhoda, *Plating,* Vol 49, 1962, p 69-71

37. H.H. Beyer and F. Simon, *Metall.,* Vol 34, 1980, p 1016-1018

38. C. Hood, *Plat. Met. Rev.,* Vol 20, 1976, p 48-52

Anodes for PGM Plating

In most aqueous or oxygen-bearing environments, the platinum-group metals are coated with a very thin layer of the appropriate metal oxide. This film is referred to as a *passive layer,* and it serves to prevent the underlying metal from corroding. Thus, anodes fabricated from PGMs are insoluble (inert) in most environments. The anode processes are mainly

$$2H_2O \rightarrow O_2 + 4H^+ + 4E^-$$

in acid solutions, or

$$4OH^- \rightarrow O_2 + 2H_2O + 4E^-$$

in alkaline solutions.

There are exceptions to this rule. The platinum metals are soluble in hot halogen acids (HF, HCl, HBr) and will dissolve anodically under these conditions. Similarly, oxidizing ligands such as nitrate and nitrite tend to dissolve PGMs, particularly in the presence of halogen acids. Plating solutions based on such systems are highly corrosive, and it is usually necessary to protect the work to be plated by prestriking with gold. Platinum-group metal anodes are also soluble in molten cyanide systems, from which PGMs can be deposited to very heavy thicknesses. Molten cyanide systems operate under an argon atmosphere at temperatures of about 600 °C (1100 °F), and for these reasons are not widely used. They are useful for heavy deposition because the high temperature provides some degree of stress-relief annealing during the plating operation.

Because anodes fabricated from PGMs are inert in most aqueous environments, they are useful not only for the electrodeposition of PGMs but also for plating of other metals, such as gold. Platinum is the metal of choice for such applications and is available in the form of wire mesh, or plated onto anodizable metals such as titanium, or clad onto passive-prone metals such as niobium or tantalum. In the plated and clad configurations, the required mechanical strength is provided by the substrate, and the actual amount of platinum used is quite small.

Reference 39 is a good general resource of information about anode selection and general plating practices.

Reference cited in this section

39. F.A. Lowenheim, Ed., *Modern Electroplating,* 3rd ed., Wiley, 1974

Copper Alloy Plating

Henry Strow, Oxyphen Products

Introduction

COPPER ALLOYS are widely used as electroplated coatings, and they can be used with practically any substrate material that is suitable for electroplating. While alloys such as copper-gold and copper-gold-nickel are commonly electroplated, these are usually considered as part of gold plating technology. The most frequently electroplated copper alloys are brass (principally alloys of copper and zinc) and bronze (principally alloys of copper and tin). Brass and bronze are both available in a wide variety of useful compositions that range in content practically from 100% Cu to 100% Zn or Sn.

The history of brass and bronze plating dates back at least as far as the 1840s. Early work that was commercially exploited occurred in Russia, France, and England. All of the early copper alloy plating solutions were cyanide based and used batteries for power. Progress was slow, with much of the work being of an academic nature. A major advance was made in 1938 when patents on a high-speed copper plating process by DuPont were extended to a high-speed process for plating of both yellow and white brass (alloys containing about 70 to 80% Cu). The solution was cyanide based with a relatively high hydroxide content.

Brass Plating

Decorative Applications. The largest use of brass plating is for decorative applications. Copper-zinc alloys that contain more than 60% Cu have distinct colors, depending on the composition. The 60Cu-40Zn alloys are pale yellow, sometimes with a brown cast. Alloys with compositions from 70Cu-30Zn to 80Cu-20Zn are yellow, with only slight color

variations over this range. The 85Cu-15Zn alloys are darker and resemble gold. The 90Cu-10Zn alloys are darker still, with a reddish, bronze-like cast. With proper control of plating parameters, the variation of the alloy composition of brass plate can be kept within 1%, and consistency in color can be achieved. Plated alloys have the same color as wrought alloys of the same composition and surface treatment. Brass darkens with age due to the formation of copper oxide on the surface, so the appearance of old samples will not match that of newly plated items.

Yellow brass plate (normally a 75Cu-25Zn alloy) is frequently flash plated over bright nickel plating to maintain its bright appearance; the surface is subsequently lacquered to preserve the finish. (*Flash plating* is the electrodeposition of a thin layer of material; plating times are usually under 1 min.) This type of flash plating is accomplished in both rack plating and barrel plating operations. Heavy brass plate can be buffed to a bright finish or oxidized to a dark finish; dark finishes can be *relieved* (selectively buffed) for an antique appearance. Brass plated items can also be burnished in tumbling barrels to give a uniform bright finish. Cosmetic cases are frequently plated with an 85Cu-15Zn alloy to impart a golden appearance; the alloy can be applied as a flash plate or as a heavier plate that is subsequently burnished. Builders hardware plated with a 90Cu-10Zn alloy called *architectural bronze* uses these same techniques.

Engineering applications for brass plating are also important. Brass plate on sheet steel and wire performs a lubricating function in deep drawing and wire drawing operations. Brass plating is used to promote adhesion of rubber bonded to steel. For example, the wire in steel-belted radial tires is plated with a brass alloy containing between 63 and 70% Cu (to secure the best adhesion, it is important that composition limits of the alloy be kept within 1%). After plating, the wire is drawn from 1.2 mm (0.049 in.) to approximately 0.15 mm (0.006 in.) without a break in the coating. The wire bonds to rubber so that blistering of the tires does not occur. Brass is also plated on sheet steel from which parts are stamped.

Equipment. Brass plating can be done in all the standard plating equipment, including barrel, rack, and continuous wire and strip machines. Steel is a suitable material for tanks, coils, and filters. However, rubber- or plastic-lined tanks with stainless or titanium coils are preferred because the iron in the steel can form ferrocyanides that precipitate as zinc ferrocyanide, resulting in the formation of a gray-colored sludge.

Surface Preparation. Brass can be plated on most metallic surfaces (e.g., zinc castings, steel, nickel, and aluminum) after only standard preplating procedures. Direct brass plating of zinc castings requires the use of relatively heavy coatings to prevent diffusion of the brass into the zinc and a resulting loss of color; an intermediate layer of plate is often used for this purpose. One method of brass plating uses this diffusion interaction to produce brass by plating separate layers of copper and zinc of appropriate thickness and then heating the plate to create the alloy by diffusion.

Plate thickness can be varied as required from very thin flash deposits for decorative purposes to deposits over 0.02 mm (0.001 in.) thick. The heavier plates are needed to withstand buffing, bright dipping antiquing, and other post-treatments that require heavier plate to maintain coverage.

Solution Composition and Operating Conditions. The majority of currently used brass plating solution are based on cyanide complexes. No other material brings the deposition potential of copper and zinc so close together. Solutions using a pyrophosphate base have been used commercially with limited success. Brass solutions using polyhydroxy aliphatic chemicals have also been used commercially with limited success. Formulas for low-pH brass plating solutions are given in Table 1.

Table 1 Low-pH brass plating conditions

Constituent or condition	Standard brass solution	High-copper brass solution
Makeup		
Sodium cyanide, g/L (oz/gal)	50 (6.7)	75 (10.0)
Copper cyanide, g/L (oz/gal)	35 (4.7)	45 (6.0)

Zinc cyanide, g/L (oz/gal)	10 (1.3)	7.5 (1.0)
Sodium carbonate, g/L (oz/gal)	10 (1.3)	10 (1.3)
Sodium bicarbonate, g/L (oz/gal)	7.5 (1.0)	7.5 (1.0)
Ammonia (aqua), %	0.5	0.1
Analysis		
"Total" sodium cyanide, g/L (oz/gal)	22 (2.9)	33 (4.4)
Copper (as metal), g/L (oz/gal)	23 (3.1)	22 (2.9)
Zinc (as metal), g/L (oz/gal)	6 (0.8)	4.2 (0.6)
pH	9.8-10.2	9.8-10.5
Operating conditions		
Temperature, °C (°F)	24-35 (75-95)	27-45 (80-113)
Current density, A/dm^2 (A/ft^2)	≤ 3 (≤ 28)	≤ 2.5 (≤ 23)
Sodium cyanide to zinc		
Ratio	3.5:1	7.0:1
Range	3-5:1	6-9:1

The formulas for standard brass plating solution can be varied to suit various uses while maintaining the ratios of components. The solution listed in Table 1 is well suited for barrel plating, where high efficiency is needed and good conductivity enables the use of maximum current. (Barrel plating is carried out at a voltage of 6 to 14 V.) Where flash plating is used, the solution should be operated with the cyanide constituents at approximately half the amounts shown in Table 1. This reduced cyanide concentration allows the use of a wider range of current densities and results in excellent covering power. The plating efficiency at the reduced cyanide concentration is lower, but this is not a significant factor in flash plating. For rack plating, the optimum cyanide concentration is about two-thirds of that shown in Table 1; this level provides improved efficiency (compared to flash plating) while still allowing use of a wide range of current densities.

Formulas for high-alkalinity brass plating solutions are given in Table 2. The solutions listed in Table 2 may be varied to meet specific applications. The functions of the solution constituents are somewhat different than in the low-pH solutions. In the high-alkalinity solutions, the hydroxide and cyanide can work together so that a higher hydroxide content increases the zinc content of the deposit; thus, the ratio of cyanide to zinc is not applicable. The high-alkalinity solutions have high efficiencies and can be used at high current densities; the use of additives is needed to secure uniform color at low current densities. Thus they are difficult to use in barrel plating operations.

Table 2 High-alkalinity brass plating solutions

Constituent or condition	Original (potassium)	High-speed strip plating	Modern
Makeup			
Sodium cyanide, g/L (oz/gal)	. . .	120 (16.1)	125 (16.8)
Potassium cyanide, g/L (oz/gal)	125 (16.8)	. . .	. . .
Copper cyanide, g/L (oz/gal)	44 (5.9)	100 (13.4)	75 (10.1)
Zinc cyanide, g/L (oz/gal)	17.3 (2.3)	. . .	5 (0.7)
Sodium hydroxide, g/L (oz/gal)	. . .	11 (1.5)	45 (6.0)
Potassium hydroxide, g/L (oz/gal)	30 (4.0)	. . .	. . .
Analysis			
Copper (as metal), g/L (oz/gal)	31 (4.2)	70 (9.4)	50 (6.7)
Zinc (as metal), g/L (oz/gal)	9.6 (1.3)	7 (0.9)	3 (0.4)
"Total" cyanide, g/L (oz/gal)	80 (10.7)	50 (6.7)	53 (7.1)
Sodium hydroxide, g/L (oz/gal)	. . .	11 (1.5)	45 (6.0)
Potassium hydroxide, g/L (oz/gal)	30 (4.0)	. . .	. . .
Operating conditions			
Temperature, °C (°F)	45 (113)	80 (176)	70 (158)
Current density, A/dm^2 (A/ft^2)	1-4 (9-37)	3-16 (28-149)	1-8 (9-74)

The copper cyanide content of the plating solution serves as a source of copper for the plating deposit, but also is a major factor in plating efficiency. Cyanide is necessary to form the complexes that enable the copper and zinc to plate together to form brass. The ratio of cyanide to zinc in a conventional brass solution is the major determinant of the resulting composition of the plated alloy. The zinc can form a complex with either cyanide or hydroxide, depending on the hydroxide content of the solution. Cyanide is also necessary for solubility of the anodes. While zinc is usually added as cyanide, a very pure grade of zinc oxide can also be used.

The carbonate content of a brass solution is usually regarded as an impurity. It is formed by breakdown of the cyanide. Small amounts (15-20 g/L) are necessary in low-pH solutions to buffer the solution. Without carbonate, the solution is unstable and will give inconsistent plating. Hydroxide acts as a stabilizer in the solutions in which it is present, and thus carbonate is not essential in these solutions. The carbonate in the low-pH solutions exists as an equilibrium between carbonate and bicarbonate, making the use of both necessary to secure the proper pH. Carbonates in sodium baths can be frozen out; potassium baths can be treated with barium cyanide or barium hydroxide to precipitate the carbonate. It should be noted, however, that the use of barium cyanide or barium hydroxide creates insoluble sludges that are poisonous and cannot be destroyed, so that a hazardous waste is created. The use of calcium salts is recommended.

Hydroxide is used in the high-speed solutions to complex the zinc and increase efficiency. Increasing the hydroxide content increases the zinc content in the plated alloy.

Ammonia is a very important constituent in the low-pH brass plating solutions. Ammonia serves as a brightener and improves the appearance of plating accomplished at both high and low current densities. Ammonia is formed during plating by the decomposition of cyanide and is usually stable at temperatures up to 30 °C (86 °F). Higher temperatures (and the high hydroxide content of high-speed solutions) drive off ammonia faster than it is formed, making regular additions necessary to maintain color. Amines may be used to secure the benefit of ammonia at higher temperatures. An excess of ammonia causes the alloy to become richer in zinc; large excesses may result in white plate. Additions of ammonia do not change the pH level of the solution.

The temperature of the plating solution should be controlled to give constant alloy composition. A rise in temperature increases the copper content of the plate and also increases the plating efficiency.

Impurities in the solution affect the quality of the plating. Soluble oils and soaps will cause a brown smutty plate; they can be removed by carbon filtration. Tin is not usually troublesome but can cause dullness and white plate in recesses. Treatment is by dummy plating. Iron is not troublesome because it forms ferrocyanides, which precipitate out of the solution (but, as noted above, may result in the formation of sludge). Lead is by far the most troublesome impurity. As little as 10 ppm Pb will result in red recesses in the plate, especially in barrel-plated parts. Higher amounts of lead will cause dullness, black areas, and blistering. The source of lead is usually the anodes, although lead pipe and other lead-containing objects in the solution can cause contamination.

Anodes for brass plating may be forged, cast, extruded, or rolled, and differences in performance are minimal. Balls or nuggets (chopped rod) are frequently used with steel or titanium baskets; these furnish a uniform high current area, which is especially good for barrel plating where a relatively high current is used. Brass anodes should be used at low current densities because high current densities will cause polarization. The anodes should be of high purity and contain less than 0.02% Pb and less than 0.1% Fe or other metals. The optimum composition of yellow brass anodes is 70% Cu and 30% Zn. Use of anodes with higher copper contents will necessitate frequent additions of zinc to the solution. Deposition of brass with higher copper content requires the use of 85Cu-15Zn or 90Cu-10Zn anodes; the composition of the anodes should approximate that of the alloy being plated. Anodes of the composition types mentioned above are readily available. Steel anodes can be used in place of some of the brass anodes in order to lower the metal concentration in the solution.

Solution Analysis. Analysis and close control of the plating solution are essential for maintaining control of the alloy composition and color of the plated deposit. Analysis of copper and zinc content can be done by several methods, ranging from simple titrations to x-ray fluorescence. The results of these methods are generally accurate and reproducible.

Analysis of cyanide content is not so simple. Many methods analyze the "free" cyanide content, which is applicable to copper cyanide solutions but of dubious value when zinc is present, as in brass plating solutions. A simple and reproducible method is that used to determine the total cyanide content in zinc cyanide plating solutions: The cyanide is titrated with silver nitrate using a small amount of hydroxide in the sample being analyzed. This makes all of the cyanide in the brass solution available except that which is combined with the copper. A meaningful number is the ratio of this "total" cyanide to the zinc content of the solution. Another method for analyzing cyanide content involves distilling the cyanide from an acidified sample. This method is used to determine the cyanide content of waste solutions. Its results include cyanide present in the solution as ferrocyanide, so this method may indicate relatively high cyanide contents.

The pH level can be determined by meters, pH papers, or colorimetric comparison with suitable indicators. Hydroxide content can be determined by titration with acid using a high pH indicator. Carbonate content is easily determined by standard methods involving precipitation of the carbonate, separation, and titration.

Ammonia content can be determined by using a specific ion electrode, but is more commonly determined by using a plating cell and checking the effects of ammonia additions. For the standard Hull cell, a total current of 1 A for 10 min. can be used. The plating cell panel will also indicate the effect of impurities and additions determined by analysis. For high-speed solutions, a current of 2 A for 10 min. is recommended. Effects at various current densities can also be determined by reading the panels. For flash plating, a Hull cell preplated with bright nickel and a total current of 1A for 1 min is preferred.

Bronze Plating

Applications of bronze plating are varied. Alloys containing from 10 to 15% Sn are attractive and are used for decorative wares. These alloys have gold color that is browner than true gold; equivalent copper-zinc alloys are pinker in color.

Bronze plating is used on builders hardware, locks, and hinges to provide an attractive appearance and excellent corrosion resistance. Bronze-plated steel or cast iron bushings replace solid bronze bushings for many uses. Bronze plating is used where improved lubricity and wear resistance against steel are desired. Its good corrosion resistance makes it desirable as an undercoat on steel for bright nickel and chromium plate. Speculum alloys (45Sn-65Cu) are similar in appearance to silver and are used almost entirely for decorative purposes.

Solution Composition and Operating Conditions. Copper-tin alloys are plated from a simple system containing copper as a cyanide complex and tin as a stannate complex. A typical formula is given in Table 3. Because there are no interrelated complexes in the bronze plating solution, the alloy composition is controlled by the relative amounts of copper and tin in the solution (i.e., raising the tin content of the solution produces a higher tin content in the bronze plate). Alloys with very high tin contents, such as speculum, can be produced by simply increasing the tin content of the solution. Additives can be used to produce a bright plate. These additives usually contain lead, which acts as a brightener in bronze plating solutions.

Table 3 Composition and operating conditions for a typical bronze plating solution

Composition of plated deposit, 88Cu-12Sn

Constituent or condition	Amount
Makeup	
Potassium cyanide, g/L (oz/gal)	64 (8.6)
Copper cyanide, g/L (oz/gal)	29 (3.9)
Potassium stannate, g/L (oz/gal)	35 (4.7)
Potassium hydroxide, g/L (oz/gal)	10 (1.3)
Rochelle salt, g/L (oz/gal)	4.5 (6.0)
Analysis	
"Free cyanide," g/L (oz/gal)	22 (2.9)
Copper (as metal), g/L (oz/gal)	20 (2.7)

Tin (as metal), g/L (oz/gal)	14 (1.9)
Hydroxide, g/L (oz/gal)	10 (1.3)
Operating conditions	
Temperature, °C (°F)	65 (149)

The temperature of the solution is an important plating variable. Temperatures below 40 °C (105 °F) generally produce poor deposits that are almost always higher in copper content. Higher temperatures create higher efficiencies and allow the use of a wide range of current densities. Normal temperatures are from 60 to 80 °C (140 to 175 °F). Barrel plating solutions usually use lower temperatures.

Equipment requirements for bronze plating are similar to those for brass plating; however, the tanks should be built to withstand the higher temperatures that are generally used for bronze plating.

Anodes. The choice of anodes for bronze plating is complicated by a number of factors. The tin in bronze plating solutions is present as stannate, and when bronze alloy anodes are used, the tin dissolves as stannite; thus bronze anodes are not suitable for use. Dual anodes of copper and tin, where each type of anode has a separate current source, have been used. To eliminate the need for separate current sources, it is customary to use oxygen-free copper anodes and to add stannate tin as stannic oxide, potassium stannate, or a slurry of stannate oxide to replace the tin being plated. The presence of stannite is indicated by a dark color in the solution. The stannite is oxidized to stannate by the use of hydrogen peroxide, which must be added slowly and with constant stirring to prevent reaction with cyanide. Other impurities are not of major concern in bronze plating solutions.

Waste Water Treatment

The treatment of waste water from brass and bronze plating operations is relatively simple. Normal procedures for eliminating cyanide (i.e., treating the waste water with chlorine and adjusting pH to precipitate the metals) are all that is required. The metallic limits and allowance for chemicals in the final discharge are fixed by federal, state, and local regulations. Waste water treatment systems are usually designed by engineers who are conversant with local regulations and can make sure the equipment meets the necessary requirements.

Tin Alloy Plating

Reginald K. Asher, Sr., Motorola Semiconductor Product Sector

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Introduction

ELECTRODEPOSITION of tin alloys is used to protect steel against corrosion or wear, to impart resistance to etching, and to facilitate soldering. Four types of tin alloys are available in commercial processes.

Tin-lead is the most commonly used of these processes because of its simplicity and low cost. It is especially popular in the electronics industry because of its excellent solderability, resistance to tin whisker growth, and resistance to tin pest (formation of a gray powder on the surface, also called *tin disease*). These properties make it a valuable coating for integrated-circuit leads, surface-mount (small outline transistor) components, and circuit board connections.

Tin-bismuth processes have been developed in recent years as a substitute for tin-lead. Bismuth as an alloying agent prevents the whiskering and tin pest that can occur in tin coatings.

Tin-nickel is used for corrosion-resistant coatings, especially in seawater environments. It has an attractive chromelike appearance and high lubricity when plated over bright nickel.

Tin-zinc provides outstanding corrosion protection, comparable to cadmium, and is a possible replacement for cadmium at a lower cost.

Acknowledgement

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Tin-Lead Plating

Tin-lead plating is a relatively simple process because the standard electrode potentials of tin and lead differ by only 10 mV. Tin-lead alloys have been deposited from electrolytes such as sulfonates, fluosilicates, pyrophosphates, chlorides, fluoborates, and, infrequently, phenosulfonates or benzenesulfonates. Of these, fluoborate and sulfonates (methane sulfonic acid, or MSA, also known as nonfluoborates, or NF) are available commercially. Tin-lead plating has traditionally been done with fluoborate solutions, but MSA solutions have become popular in the electronics industry because they are less corrosive to plating equipment, more uniform in deposition, easier to control, and more acceptable environmentally.

Fluoborate and methane sulfonate solutions plate tin from the stannous valance state. The term *stannous valence state* refers to the valence of tin in solution. In the case of fluoborate and MSA solutions, the tin is in the +2 valence state as Sn^{+2}. Tin will plate only from the +2 state in acid solution. Alkaline stannate solutions plate tin from the +4 valence state. In fluoborate and MSA solutions, the stannous tin requires only two electrons to reduce it to metal:

$$Sn^{+2} + 2e \rightarrow Sn^{0} \text{ (metal)} \qquad \textbf{(Eq 1)}$$

Stannous fluoborate, along with lead fluoborate, fluoboric acid, and an addition agent, comprises the plating solution. The ingredients of the nonfluoborate MSA solution are stannous methane sulfonate with lead methane sulfonate, MSA, grain refiners (wetting agents), antioxidants, and fungicides. These components, as well as various addition agents, are available in commercial quantities. The solution operates at 100% cathode and anode efficiency.

Uses of Tin-Lead. Electrodeposition of tin-lead alloys was first patented in 1920, when these alloys were used to protect the interiors of torpedo air flasks against corrosion. When air was pumped into a flask under pressure, moisture in the air condensed and corroded the flask, weakening it. Lead coatings had been used to protect the interior against corrosion, but tin-lead alloy was found to be more corrosion resistant.

Today, tin-lead deposits are used as corrosion-resistant protective coatings for steel. The deposits usually contain 4 to 15% Sn, but the composition varies with the application. Automotive crankshaft bearings are plated with tin-lead or tin-lead-copper alloys containing 7 to 10% Sn, whereas an alloy containing 55 to 65% Sn is plated onto printed circuit boards. Tin-lead plating on circuit boards acts as an etch-resistant coating and facilitates soldering of board components after they have been inserted into the board. Copper alloys and alloy 42 (42Ni-58Fe) substrates are ordinarily plated with 80% Sn/20% Pb ± 10% MSA solutions in the manufacture of electronic components such as integrated circuits and surface mounts for postsoldering requirements. The shelf life, storage, and thickness of this composition have been proven by some Taguchi fractional multivariable experiments.

MSA Plating Solutions for Tin-Lead

In the electronics industry, MSA solutions are replacing fluoborate solutions for tin-lead plating of contacts on integrated circuits, surface-mount devices, radio-frequency components, and similar devices. The tin-lead MSA solution is well-established worldwide for rack, vibratory bowl, barrel, reel-to-reel, and especially high-speed cut-strip plating. Rack plating of components is being replaced where possible by semiautomated cut-strip lines.

Advantages. The MSA process is preferred over fluoborate solution for several reasons. First, it produces a better-quality, more uniform finish. For a typical specification of a coating thickness of 7 to 20 μm (300 to 800 μin.) with a composition of 80% Sn + 20% Pb ± 10%, it can maintain 6-sigma reliability (fewer than 3.4 rejects per million). MSA solutions are faster and have higher throwing power than fluoborate solutions, and they are able to produce a finer grain size. A recently developed, patented process is able to produce a semibright solderable finish. Because of low levels of occluded codeposited organic substances (<500 ppm C), coatings are suitable for soldering as-plated or after standard

thermal excursions. Coatings produced from MSA solutions have excellent storage life and pass the bake and steam age solderability requirements of MIL-883, Method 2003.7. They also pass MIL-38510 requirements for surface finish on electronic components.

Second, the MSA process is environmentally more acceptable. MSA is less corrosive than fluoborate solutions, and because there is no boron or fluorine in the solution, it is more acceptable for wastewater treatment and water reuse. The electrolyte is safer to handle, and the MSA activator (10 to 20 vol%) can be recycled. The latter consideration offsets the higher initial cost and higher operating cost of MSA.

Third, the MSA process is easily automated. Cut strips of electronic components are loaded into high-speed plating equipment by magazine or cassette for easy handling. Deposition rates are two to five times higher than for fluoborate solutions, ranging from 5.4 to 21.5 A/dm^2 (50 to 200 A/ft^2). Table 1 lists deposition rates for a high-speed solution. There are high-speed fluoborate baths operating at from 500 to 1000 A/ft^2.

Table 1 Time required to plate 2.54 μm (100 μin) of 80Sn-from high-speed methane sulfonic acid (MSA) solution

Total metal content		Time required at indicated current density, min				
g/L	**oz/gal**	**10.8 A/dm^2 (100 A/ft^2)**	**13.5 A/dm^2 (125 A/ft^2)**	**16.1 A/dm^2 (150 A/ft^2)**	**18.8 A/dm^2 (175 A/ft^2)**	**21.5 A/dm^2 (200 A/ft^2)**
20	2.7	0.78	0.72	0.65	0.59	0.56
30	4.0	0.70	0.64	0.56	0.52	0.47
40	5.3	0.62	0.63	0.44	0.40	0.37
50	6.7	0.55	0.47	0.40	0.36	0.33
60	8.0	0.54	0.46	0.38	0.34	0.30
70	9.3	0.53	0.46	0.37	0.33	0.28
80	10.7	0.52	0.45	0.36	0.32	0.27
90	12.0	0.51	0.43	0.35	0.31	0.26
100	13.4	0.50	0.42	0.34	0.29	0.25

Source: Ref 1

Experimental modified MSA tin-lead plating solutions are being evaluated for semiautomatic plating of leaded-glass sealed integrated-circuit packages, with excellent results.

A minimum of 2% Pb in a tin deposit is reported to prevent whiskering, eliminating the need for reflow as required by MIL-38510 for integrated-circuit devices. The electrolyte will accommodate any tin-lead composition.

Automation. Commercially available automated process lines for electronic devices are loaded manually or from a magazine or cassette. The process operations include deflashing, deoxidation, activation, tin-lead plating, neutralization (if necessary), final rinse, hot deionized water rinse, hot air dry, and automatic reloading into the magazine or cassette. Rinses are pressure spray, with air knives to remove the maximum water for recovery and reuse.

At the time of this writing, equipment for electronic components is limited to strips 23 cm (9 in.) long and 6.4 cm (2.5 in.) wide. A contact rail 3 mm (0.12 in.) wide for light strips and 5 mm (0.20 in.) wide for heavy strips is necessary for gripping the top edge of the strip.

Substrates. The MSA process is generally used for electronic solderable leads on integrated circuits, surface-mount devices, radio-frequency components, and similar devices. The materials used are typically copper or alloy 42 (42Ni-58Fe). Silicon and zirconium copper alloys require special, proprietary preparations for plating.

Properties of the Coated Surface. The deposit usually has a smooth matte finish. Some newly developed solutions give a semibright finish with dense deposits and excellent solderability.

Health and Safety Considerations. Local exhaust is required for fumes from the electrolyte. This is generally provided in the commercial equipment. Chemical goggles, a face shield, rubber gloves, and an acid-resistant apron should be worn when handling the electrolyte. Ordinarily, exhaust fans eliminate the problem of lead fumes in the air (Ref 2), and there should be no problem with meeting Occupational Safety and Health Administration requirements OSHA Standard 1910.1025.

Parameters. Any desired tin-lead alloy composition can be plated from an MSA solution. The composition of the deposit depends on the amount of stannous tin and lead in the solution, the type and amount of addition agent, the current density, and the tin-lead content of the anodes (usually 85Sn-15Pb for high-speed plating). Solution temperature and degree of agitation affect composition, especially in high-speed solutions.

Multivariable fractional factorial experiments have shown that the 80Sn-20Pb (80/20) coating has a slightly higher solderability quality than 90/10 or 60/40 compositions, and much better than rack 100% Sn.

Solution Components. Concentrated solutions of stannous and lead nonfluoborates, MSA, and additives are available commercially, so alloy plating solutions are made by mixing and diluting concentrates. Additives are wetting agents, antioxidants, and fungicides.

80Sn-20Pb high-speed MSA solution (Ref 3) is used for high-speed automated plating of leads for electronic components, including dual-inline-pin and surface-mount integrated circuits, radio-frequency components, and similar devices where highly consistent coating thickness, surface finish, and solderability are required, along with high production rates. The solution composition is:

- Stannous tin: 52±7 g/L (7.0±1.0 oz/gal)
- Lead: 13.0±1.9 g/L (1.73±0.25 oz/gal)
- Free MSA: 255±15 g/L (34.0±2.0 oz/gal)
- Mixed nonionic surfactant: 5 to 10 g/L
- Antioxidant: 0.5 to 1.5 g/L

The operating conditions are:

- Temperature: 21±2.8 °C (70±5 °F)
- Current density: 10.8±5.4 A/dm^2 (100±50 A/ft^2) with less than 1% current ripple on the plating rectifiers
- Agitation: very rapid, mechanical pump and hydraulic pressure
- Anodes: 85Sn-15Pb
- Filtration: continuous through polypropylene or acrylic filter cartridges

80Sn-20Pb MSA solution (Ref 4) is used for barrel plating of electronic components and applications requiring higher throwing power than the high-speed solution. The solution composition is:

- Stannous tin: 14±2 g/L (1.9±0.3 oz/gal)
- Lead: 2.0 to 4.0 g/L (0.27 to 0.54 oz/gal), 3.4 g/L (0.45 oz/gal) optimum
- Free MSA: 165±32 g/L (22.0±4.3 oz/gal)
- Proprietary additive: 5 to 10%

The operating conditions are:

- Temperature: 21±2.8 °C (70±5 °F)
- Current density: 0.32 to 0.64 A/dm^2 (3 to 6 A/ft^2)
- Agitation: mechanical (sparger)
- Anodes: 80Sn-20Pb
- Filtration: continuous through polypropylene or acrylic filter cartridges

Table 2 is a troubleshooting guide to MSA plating solutions.

Table 2 Troubleshooting guide for tin alloy plating with methane sulfonic acid (MSA) solutions

Problem	Possible cause	Solution
Burn (dark, rough deposit) at high current density	Low metal content	Analyze metal content and adjust if necessary.
	Current density too high	Lower rectifier settings.
	Temperature of plating solution too high	Check and adjust to 19-21 °C (66-70 °F).
	Lack of solution circulation	Check to be sure all circulating pumps are operating.
	Excessive copper in plating solution	Analyze and remove contamination by dummy plating.
	Additive low	Analyze and adjust.
Dark, nonuniform deposit at low density	Low acid content of the plating solution	Analyze and adjust.
	Plating current density too low	Check and adjust current setting.
	Poor cleaning or inadequate activation	Check parts going out of descale/activator. Adjust to proper operating conditions if necessary.
Poor throwing power or plating distribution	Metal content too high	Analyze and adjust.

distribution	Plating current density too low	Check and adjust current setting.
Pitting	Organic contamination	Check for carbon and treat if necessary.
	Oil or grease in solution	Check and dump if positive.
	Poor cleaning	Check/analyze descale and activation for proper operating conditions.
	Insufficient solution agitation	Check circulating pump.
Rough deposits	Particles (anode sludge, dirt) in solution	Check filter for proper operating condition. Replace cartridge.
	Excessive current setting	Check and adjust.
	Insufficient solution agitation	Check circulation.
Alloy composition in deposit out of specification	Incorrect bath composition	Analysis and adjust
Poor solderability	Low thickness	Check and adjust.
	Organic contamination in the bath	Analyze for carbon and treat if necessary.
	Copper contamination in the bath	Check and do low-current dummy plating if necessary.
	Incorrect alloy composition	Check and adjust.
	Insufficient/poor cleaning of base metal	Check parts going out of descale. Check descale and activator for proper operating conditions.
Excessive foaming	Air being drawn into filter	Check for line leaks.
	Imbalance of system circulation	Set discharge line flow. Close down on drain back valves.
	Excessive additive concentration	Analyze and dilute if necessary.
	Air blow offset too high	Reduce air wipe flows.

Poor adhesion	Poor pretreatment	Adjust to proper operating range. Makeup new when necessary.
	Poor rinsing	Check and adjust rinse flow.
	Excessive additive	Analyze and adjust.
Staining or discoloration	Air blower nozzle offset	Check and reset.
	Poor/insufficient rinse	Check and adjust flows.
	Air wipe blocked or offset	Check and reset.
	Insufficient additive	Analyze and adjust.

References cited in this section

1. Techni-Solder NF Acid process information sheet, Technic, Inc., Cranston, RI
2. Techni-Solder NF Acid material safety data sheet, Technic, Inc., Cranston, RI, 1991
3. Techni-Solder NF 80/20 Alloy High Speed Matte product data sheet, Technic, Inc., Cranston, RI
4. Techni-Solder NF 1957 product data sheet, Technic, Inc., Cranston, RI

Fluoborate Plating Solutions for Tin-Lead

Any desired tin-lead alloy composition can be plated from a fluoborate solution. The composition of the deposit depends on the amount of stannous tin and lead in the solution, the type and amount of addition agent, the current density, and the tin-lead content of the anodes. Bath temperature and degree of agitation also affect the composition, especially in high-speed solutions.

Solution Components. Concentrated solutions of stannous and lead fluoborates and fluoboric acid are available commercially, so alloy plating solutions are made by mixing and diluting concentrates. Some compositions of concentrates are given in Table 3. The fluoborates of tin and lead contain free or excess fluoboric and boric acids for stability, and fluoboric acid contains free boric acid for the same reason.

Table 3 Composition of fluoborate alloy plating solution concentrates

Constituent	**Amount**		
	wt%	**g/L**	**oz/gal**
Lead fluoborate			
Lead fluoborate, $Pb(BF_4)_2$	51.0	893	119
Lead, Pb[(a)]	27.7	485	65

Fluoboric acid, free HBF_4	0.6	10.5	1.4
Boric acid, free H_3BO_3	1.0	18	2.4
Stannous (tin) fluoborate			
Stannous fluoborate, $Sn(BF_4)_2$	51.0	816	109.0
Tin, $Sn^{-2(a)}$	20.7	331	44.3
Fluoboric acid, free HBF_4	1.8	29	3.9
Boric acid, free H_3BO_3	1.0	16	2.1
Fluoboric acid			
Fluoboric acid, HBF_4	49	671	89.9
Boric acid, free H_3BO_3	0.6	8.3	1.1
Hydrofluoric acid, free HF	None	. . .	. . .

(a) Equivalent

The reason that excess boric and fluoboric acids provide stability in the fluoborate concentrates can best be shown by the reactions described below, with lead fluoborate used as an example, although the same is true for all other fluoborate concentrates. In the absence of boric acid, the metal fluoride will form. To stabilize the lead fluoborate, the following reaction takes place:

$$4PbF_2 + 2H_3BO_3 \rightarrow Pb(BF_4)_2 + 3Pb(OH)_2 \qquad \textbf{(Eq 2)}$$

The reaction is incomplete unless fluoboric acid is added to produce the result:

$$3Pb(OH)_2 + 6HBF_4 \rightarrow 3Pb(BF_4)_2 + 3H_2O \qquad \textbf{(Eq 3)}$$

The overall reaction is then:

$$4PbF_2 + 2H_3BO_3 + 6HBF_4 \rightarrow 4Pb(BF_4)_2 + 6H_2O \qquad \textbf{(Eq 4)}$$

Commercially, fluoboric acid is made by reacting hydrofluoric acid with boric acid:

$$4HF + H_3BO_3 \rightarrow HBF_4 + 3H_2O \qquad \textbf{(Eq 5)}$$

When excess boric acid is added beyond the amount required to react stoichiometrically with the hydrofluoric acid present, the reaction is driven far to the right, thus stabilizing the fluoboric acid and preventing the formation of fluorides.

A tin-lead plating solution deficient in free boric acid can precipitate insoluble lead fluoride. To guard against this possibility, anode bags filled with boric acid should be hung in corners of the plating tank and immersed in solution. Bags should be refilled when the boric acid has dissolved.

Addition agents are important for the production of dense, fine-grain deposits and the improvement of throwing power in a tin-lead solution operation. Many organic addition agents have been used in tin-lead solutions, including bone glue, gelatin, peptone, aldehyde condensation products, glycols, sulfonated organic acids, beta-naphthol, hydroquinone, and resorcinol. Peptone is the addition agent most frequently used because of its commercial availability as a stabilized solution specifically prepared for tin-lead plating solutions.

Solution Compositions and Operating Conditions. Listed below are the tin-lead fluoboric bath compositions that are used most frequently.

7Sn-93Pb solution is used for bearings and corrosion protection of steel. The solution composition is:

- Stannous tin: 6.0 g/L (0.80 oz/gal)
- Lead: 88.0 g/L (11.8 oz/gal)
- Fluoboric acid: 100 g/L (13.4 oz/gal) min
- Boric acid: 25 g/L (3.4 oz/gal)
- Peptone, dry basis: 5 g/L (0.67 oz/gal)

The operating conditions are:

- Temperature: 18 to 38 °C (65 to 100 °F)
- Current density: 3.2 A/dm^2 (30 A/ft^2)
- Agitation: mild, mechanical
- Anodes: 7Sn-93Pb

60Sn-40Pb solution is used for printed circuit boards, barrel plating of small parts, and applications requiring high throwing power. The solution composition is:

- Stannous tin: 15 g/L (2 oz/gal)
- Lead: 10 g/L (1.3 oz/gal)
- Fluoboric acid: 400 g/L (53.4 oz/gal)
- Boric acid: 25 g/L (3.4 oz/gal)
- Peptone, dry basis: 5 g/L (0.7 oz/gal)

The operating conditions are:

- Temperature: 18 to 38 °C (65 to 100 °F)
- Current density: 2.1 A/dm^2 (20 A/ft^2)
- Agitation: mild, mechanical
- Anodes: 60Sn-40Pb

60Sn-40Pb high-speed solution is used for high-speed wire and strip plating, or for general plating where throwing power is not of prime importance. The solution composition is:

- Stannous tin: 52 g/L (7.0 oz/gal)
- Lead: 30 g/L (4.0 oz/gal)
- Fluoboric acid: 100 g/L (13.4 oz/gal) min
- Boric acid: 25 g/L (3.4 oz/gal)
- Peptone, dry basis: 5 g/L (0.7 oz/gal)

The operating conditions are:

- Temperature: 18 to 38 °C (65 to 100 °F)
- Current density: 3.2 A/dm^2 (30 A/ft^2)
- Agitation: mild, mechanical
- Anodes: 60Sn-40Pb

When this solution is used to deposit 60Sn-40Pb on wire or strip, current densities in excess of 32 A/dm^2 (300 A/ft^2) can be used if the wire or strip is moved continuously through the plating solution at a relatively high speed.

$HBF_4$60Sn-40Pb solution (Ref 5) provides high throwing power. The solution composition is:

- Fluoboric acid 48%: 350 mL/L
- Tin fluoborate 50%: 46.2 mL/L
- Lead fluoborate 50%: 25.2 mL/L
- Proprietary additive: 20 mL/L
- Boric acid: 26 g/L
- Tin-lead salt No. 1: 2 g/L

The optimum operating conditions are:

- Temperature: 21 °C (70 °F)
- Current density: 2.5 A/dm^2 (25 A/ft$^{2)}$
- Agitation: mechanical, slow to moderate
- Filtration: continuous through polypropylene or Dynel

Table 4 is a troubleshooting guide for this solution.

Table 4 Troubleshooting guide for $HBF_4$60Sn/40Pb high-throw bath

Problem	**Possible cause**	**Remedy**
Treeing	Low addition agent	Replenish.
Edge feathers	Too high a current density	Lower current density.
Grainy deposit	Organic contamination	Replenish addition agent. As a last resort, carbon treat.
Burning	Too high a current density	Lower amperage.

	Too low a metal content	Add stannous fluoborate or lead fluoborate.
	Low acid content	Add fluoboric acid.
Wrong alloy composition	Incorrect bath composition	Adjust bath composition.
	Wrong current density	Plate at 2.5-3 A/dm^2(25-30 A/ft^2).
	Insufficient addition agent	Replenish.
	Improper agitation	Use cathode rod agitation.
Poor throwing power	High pH	Add fluoboric acid.
	Too high an anode-to-cathode ratio	Remove some anodes.
	Low agitation agent	Replenish.
Precipitate in bath, roughness	Chloride or sulfate drag-in	Improve rinsing.
	Torn anode bags	Replace anode bags.
	Oxidation of tin from excessive agitation	Look for air leak in filter, if used.
Poor reflow	Insufficient deposit. Minimum should be 0.00025 in.	Do not reflow unless thickness is above minimum.
	Wrong alloy	Check reason for wrong alloy as described above.
	Organic contamination	Carbon treat.
	Metallic contamination	Dummy the bath.
	Copper substrate not active or clean	Check cleaning cycle.

Compositions of anodes and solutions for deposits up to 50% Sn are listed in Table 5. The composition of the anode should be the same as that desired in the deposit. If deposits do not have the desired composition, anode composition should be maintained as indicated and adjustments should be made to the solution formula.

Table 5 Composition of anode and fluoborate solution for deposits up to 50% Sn

Plated 3.2 A/dm^2(30 A/ft^2); compositions of all baths contains a minimum of 100 g/L (13.3 oz/gal) of free HBF_4, 25 g/L. (3.3 oz/gal) of free H_3BO_3, and 5.0 g/L (0.7 oz/gal) of peptone

Composition of deposit and anode, %		Composition of bath			
		Stannous tin		Lead	
Tin	Lead	g/L	oz/gal	g/L	oz/gal
5	95	4	0.5	85	11.3
7	93	6	0.8	88	11.8
10	90	8.5	1.1	90	12.0
15	85	13	1.7	80	10.7
25	75	22	2.9	65	8.7
40	60	35	4.8	44	5.8
50	50	45	6.0	35	4.7

Table 5 is based on an operating density of 3.2 A/dm^2 (30 A/ft^2). Higher or lower current densities may result in deposition of alloys of compositions differing from those given in the table. It is then necessary to make compensating corrections in solution composition. Deposition rates of tin-lead coatings can be controlled by current density. Table 6 shows that as the current density of a fluoborate solution is increased, the rate of 60Sn-40Pb deposition also increases.

Table 6 Rate of 60Sn-40Pb deposition from the fluoborate solution

100% cathode efficiency

Current density		Time in bath, min, at thickness of:			
A/dm^2	A/ft^2	25μm (0.0001 in.)	7.5μm (0.0003 in.)	12.5μm (0.0005 in.)	25μm (0.001 in.)
1.0	10	4.5	13.5	22.5	45
1.5	15	3.0	9.0	15.0	30
2.0	20	2.3	6.8	11.3	22.5
2.5	25	1.8	5.4	9.0	18
3.0	30	1.5	4.5	7.5	15

Temperature. Tin-lead fluoborate solutions operate efficiently in a temperature range of 18 to 38 °C (65 to 100 °F). Upper temperatures slightly increase tin in deposits, and lower temperatures can decrease tin.

Current densities below the specified amount for a particular solution formula can decrease the tin content of deposits. Higher current densities can increase tin content.

Agitation is an important factor in tin-lead plating. Optimum conditions exist when mild agitation is used. Use of a still bath results in nonuniform deposits because of local exhaustion of the solution at the cathode surface. Vigorous agitation may increase the stannic tin content of a solution, resulting in a decrease of tin in deposits. Cathode rod agitation or circulation through an outside pump provides suitable agitation for a tin-lead plating solution. Air agitation should not be used because it can oxidize stannous tin.

Boric acid is added to maintain solution stability. Approximately 25 g/L (3.4 oz/gal) of boric acid has been found desirable, but its concentration is not critical. An anode bag filled with boric acid may be hung in a corner of the tank to maintain the required concentration. Excess boric acid prevents fluoride precipitates, which can deplete lead from the solution. This is based on the following formula:

$$4HF + H_3BO_3 \rightleftharpoons HBF_4 + 3H_2O \qquad \textbf{(Eq 6)}$$

where $HBF_4$is the resultant fluoboric acid. The reaction is reversible if the stoicheiometric amount of boric acid (H_3BO_3)is used to react with the hydrofluoric acid (HF) present. As the amount of boric acid in the above reaction is increased, the reaction is driven far to the right so that the reaction becomes irreversible and no free hydrofluoric acid is regenerated. This is important because if free hydrofluoric acid were present, then insoluble fluorides, especially lead fluoride, would precipitate. Thus, all fluoborate concentrates and plating baths contain free boric acid. Although 25 g/L of boric acid is optimum (close to its solubility), any amount of free boric acid is acceptable to prevent the formation of fluorides.

Free fluoboric acid is maintained in the solution to provide the requisite acidity and to raise conductivity. In conjunction with peptone, it can prevent "treeing" and give a fine-grain deposit. Free fluoboric acid can be added in amounts ranging between 100 to 500 g/L (13.4 to 67 oz/gal), depending on the solution formula used.

Peptone is added to the plating bath to promote formation of fine-grain adherent deposits and prevent treeing. Peptone solution is available commercially, and proper amounts can be measured and poured directly into the plating bath. The bath can then be used immediately, after it is gently stirred to ensure complete mixing of peptone. During the operation of the plating bath, a loss of peptone can result because of dragout, chemical breakdown, and codeposition with the metal. As peptone is depleted, it must be replenished. Replenishment amounts should be determined by experience. As a guide, 1 L (2.1 pints) of peptone solution per 380 L (100 gal) of plating bath can be used per week. A Hull cell operated at 1 A for 10 min can be used to control the peptone content of a plating solution.

Tin-lead fluoborate solutions containing peptone should be filtered through activated carbon at least four times per year to ensure removal of organic breakdown products and avoid buildup of peptone from indiscriminate additions. The plating bath should be treated with about 4.5 kg. (10 lb) of activated carbon per 380 L (100 gal) of bath until, after filtration, the solution is water white. The bath should not be heated during carbon treatment, because stannous will be oxidized to stannic tin. Fresh peptone is added after carbon treatment. Because there is no simple analytical method for determining peptone concentration in this solution, carbon treatment and replenishment of peptone every 3 or 4 months ensures proper amounts of peptone in a solution.

Proprietary synthetic wetting agents can be purchased for grain refinement, as a substitute for peptone. Because these components are synthetic, they are less susceptible to algae and bacterial growth.

Metallic impurities are removed by low-current-density electrolysis, but in a tin-lead bath, low current density favors deposition of lead, which may unbalance the solution. Metallic impurities can be removed by dummying a bath at a current density of 0.2 A/dm^2 (2 A/ft^2) for at least 8 h. The solution should then be analyzed and brought up to specification with stannous or lead fluoborate. Iron, nickel, and other metals above hydrogen in the electromotive series are not removed by dummying, although copper is easily removed.

Filtration. A tin-lead fluoborate plating solution should be filtered constantly, to keep the bath clear. If constant filtration is not used, a bath can turn cloudy because of sulfates entering the solution and precipitating as lead sulfate.

Stannic salts can also precipitate out of the solution. Anode sludge or breakdown products from peptone solutions can contribute to a cloudy appearance as well. Polypropylene filter spools or cartridges can be used as filters, but they must first be leached in hot water (65 °C, or 150 °F) to remove organic agents used in their manufacture. The end of the return hose from the filter must be submerged in the bath to prevent aeration of the bath.

Anodes. Tin-lead alloy anodes of at least 99.9% purity must be used. The most objectionable anode impurities are arsenic, silver, bismuth, antimony, copper, iron, sulfur, nickel, and zinc. Extruded anodes are preferred over cast anodes, because cast anodes have a larger grain size and suffer from intergranular corrosion, which causes large pits or depressions to form on the anode surface. The finer grain size of extruded anodes provides uniform and efficient corrosion during plating. Tin-lead anodes should be left in an idle tin-lead fluoborate bath because they exercise a reducing effect on tin in solution, thus helping to maintain the bath in a stannous valence state. Tin-lead anodes should be bagged with acrylic or polypropylene cloth to contain any anode sludge that may form. Anode sludge suspended in solution can cause rough deposits.

Materials of construction for tin-lead plating equipment include:

- Steel lined with rubber or polypropylene or made entirely of polypropylene, used for tanks and pumps
- Monel metal, used for anode hooks
- Polypropylene, used for anode bags and filter spools
- Pure paper pulp (alpha cellulose), used for filter aid

The following materials should not be used in contact with fluoborate solutions: glass; quartz or other silicated materials; nylon; neoprene; or titanium. Equipment in contact with fluoborates should have the recommendation of the manufacturer for use in a fluoborate solution.

Lead disposal for fluoborate and MSA solutions is most commonly accomplished by diverting the lead-containing rinse water (or dilute concentrate) to a pH-controlled holding tank, filtering the solution, and then running it through an ion exchanger. The fluoborate rinse will have to be regenerated with MSA before going to a holding tank and then to electrowinning. The MSA rinse can go directly to electrowinning, where the lead is plated out on a reusable cathode. The water can then be carbon treated, ion exchanged, and reused for certain rinses.

Reference cited in this section

5. Techni HBF_4 60/40 High Throw PC product data sheet, Technic, Inc., Cranston, RI

Other Tin Plating

Tin-Bismuth Plating. A small amount of bismuth or antimony added to tin helps to eliminate whiskering and tin pest in tin coatings that are subjected to temperatures below 13.2 °C (55.8 °F). MIL-QQS-571 recommends 0.27% Sb to prevent tin pest. Several processes for tin-bismuth plating have been patented (Ref 6, 7, 8) and commercialized. Experimental processes using inert anodes, such as platinized titanium, have been used to produce printed circuit board prototypes with tin-bismuth coatings on parts. An MSA solution similar to that used for tin-lead plating has been developed, and solutions are being developed for commercial sales by chemical suppliers. Tin methane sulfonate and bismuth methane sulfonate are used in the solution. Plating is done at room temperature with mild agitation.

Tin-Zinc Plating. In most environments, tin-zinc alloys approach the corrosion resistance and solderability of cadmium. Because cadmium can release toxic fumes when heated, and because it is a strategic element and therefore relatively expensive and subject to availability concerns, tin-zinc coatings are often used as substitutes. Compositions ranging from 10Sn-90Zn to 85Sn-15Zn have been used. Electrolytes are made from a mixture of potassium stannate, zinc cyanide, potassium cyanide, and potassium hydroxide. The amount of potassium cyanide determined by analysis is higher than that added to the bath initially, because the analysis also detects the cyanide in zinc cyanide.

80Sn-20Zn solution is the most commonly used. The solution compositions are:

Still tank

- Stannous tin: 38 to 53 g/L (5.1 to 7.1 oz/gal)
- Zinc: 4.5 to 7.5 g/L (0.60 to 1.0 oz/gal)
- Potassium cyanide: 38 to 53 g/L (5.1 to 7.1 oz/gal)
- Free potassium hydroxide: 4.9 to 8.3 g/L (0.65 to 1.1 oz/gal)

Barrel

- Stannous tin: 32 to 40 g/L (4.3 to 5.3 oz/gal)
- Zinc: 6.8 to 10 g/L (0.91 to 1.3 oz/gal)
- Potassium cyanide: 41 to 60 g/L (5.5 to 8.0 oz/gal)
- Free potassium hydroxide: 8.3 to 11.3 g/L (1.1 to 1.51 oz/gal)

The operating conditions are:

- Temperature: 65 ± 2 °C (149 ± 4 °F)
- Anode current density: 1.5 to 2.5 A/dm^2 (14 to 23 A/ft^2)
- Cathode current density: 0.1 to 0.9 A/dm^2 (1 to 8 A/ft^2)
- Agitation: none for still tanks, or barrel agitation
- Anodes: 80Sn-20Zn
- Equipment: mild steel

Anodes must be filmed. (An oxide film is deposited on the anode by plating it at a high current density.) Unfilmed anodes cause formation of stannite (Cu_2FeSnS_4), which inhibits plating.

Temperature. Temperatures in the high end of the range increase the tin content and cause the cyanide to break down. Low temperatures decrease cathode efficiency and lower the percentage of tin.

Current densities at the low end of the range result in tin-rich deposits.

Electrolyte Concentrations. The proportions of zinc and tin in the deposit vary with the amounts in the solution. Higher concentrations of zinc in solution result in higher levels in the deposit, and likewise with tin. Higher levels of free potassium hydroxide increase the percentage of zinc in the deposit. Small changes in free cyanide content have little effect, because the solution contains more cyanide than is necessary. Excessively low levels of cyanide decrease tin content (Ref 9).

Tin-Nickel Plating. The intermetallic compound 65Sn-35Ni can be plated from several commercial electrolyte solutions. The finish has high lubricity and a bright, chromelike appearance with excellent corrosion resistance, especially in seawater environments. It is used more often for general industrial applications than for electronic components, because it is more difficult to solder than other tin-alloy coatings. The solution composition is:

- Nickel chloride: 250 g/L (33 oz/gal)
- Stannous chloride: 50 g/L (6.7 oz/gal)
- Ammonium chloride: 50 g/L (6.7 oz/gal)
- Starter (makeup and additives containing surfactants and grain refiners): 20% by volume

The operating conditions are:

- Temperature: 60 to 70 °C (140 to 160 °F), 66 °C (151 °F) optimum
- Current density: 0.1 to 3.2 A/dm^2 (1 to 30 A/ft^2), 1.6 A/dm^2 (15 A/ft^2) optimum

- Agitation: cathode rod, solution, or barrel. Still racks may be used at low current densities.
- Anodes: high-purity nickel in polypropylene bags
- Filtration: continuous through polypropylene or chlorinated polyvinyl chloride (CPVC) above 60 °C (140 °F)

Preparation. Metallic substrates should be cleaned. A common acid cleaning procedure is a 10 to 20% HCl bath immediately before plating. Steel substrates should be plated with an alkaline copper or acid nickel strike coating.

Equipment. All equipment in contact with the plating solution should be nonmetallic. Tanks and filters should be polypropylene or CPVC. Heaters should be fluorocarbon coated.

Handling Precautions. Gloves, protective clothing, and goggles should be worn when handling electrolyte solution or its components.

Environmental Considerations. Electrolyte solutions and their components should be treated according to procedures for fluoride- and cyanide-containing wastes. They should not be mixed with metal-bearing waste streams, because they contain metal chelators (Ref 10, 11).

Table 7 is a troubleshooting guide to tin-nickel plating solutions.

Table 7 Troubleshooting guide for tin-nickel plating solutions

Problem	**Possible cause**	**Remedy**
Powdery gray deposit	Current density too high	Use a lower current density.
	Nickel content too low	Analyze nickel content, add nickel chloride if necessary.
Dull or black deposit	Tin content too low	Analyze tin content, add stannous chloride if necessary (starter concentrate must be added at the same time as stannous chloride).
Brittle or milky deposit	Low replenisher	Add replenisher.
	Metallic contamination	Remove metal by electrolyzing solution.
Dark or black deposits in low-current-density plating areas	Copper contamination	Eliminate source of contamination, remove copper by electrolyzing.
Dark deposit with standard current density or burn with high current density	Organic contamination	Filter solution through activated carbon. Never add hydrogen peroxide, potassium permanganate, or other oxidizing agents.
Incorrect alloy composition	Incorrect solution composition	Analyze tin and nickel contents of bath and adjust.
Nickel content increases during operation	Excess anode area	Decrease anode area.

Source: Ref 10

References cited in this section

6. T.I. Murphy and B.R. Reynolds, "Low Temperature Tin-Bismuth Electroplating System," International Patent Application PCT/US92/08485, April 1993
7. H.P. Wilson, "Bismuth Composition, Method of Electroplating a Tin Bismuth Alloy and Electroplating Bath Therefor," U.S. Patent 4,331,518, May 1982
8. H.P. Wilson, "Electrodeposited Eutectic Tin-Bismuth Alloy on a Conductive Substrate," U.S. Patent 5,039,576, Aug 1991
9. F.A. Lowenheim, Ed., *Modern Electroplating,* 3rd ed., Wiley, 1974, p 531-533
10. Nicostan product data sheet, LeaRonal, Freeport, NY
11. Techni Tin-Nickel product data sheet, Technic, Inc., Cranston, RI

Zinc Alloy Plating

Nabil Zaki, Frederick Gumm Chemical Company, Inc.

Introduction

ZINC ALLOY PLATING has found significant use since about 1980 in Japan and Europe, and more recently in the United States. The driving force behind the development of this technology was the quest for higher-performance coatings, especially in the automotive industry. Another driver was the urgent need to find an adequate replacement for cadmium plating; cadmium is highly toxic and has been banned in many industrial countries.

The use of zinc alloys provides several advantages. Electrochemically, alloys have different corrosion potentials from their alloying elements. Alloys of zinc, for example, can be designed to maintain anodic protection to steel, but remain less electrochemically active than pure zinc. Thus, a zinc alloy coating can still be sacrificial to steel components, but corrodes much more slowly than zinc when exposed to a corrosive environment.

Several zinc alloy processes are currently in commercial use. The choice of a particular process depends on the end-product requirements and conditions of use. Available alloys are zinc-iron, zinc-cobalt, zinc-nickel, and tin-zinc. As in unalloyed zinc plating, chromate conversion coating post-treatments are used to improve the overall corrosion resistance of the alloy, and especially to retard the bulky "white rusting" characteristic of unalloyed zinc. Specialty chromating processes designed to work with these alloys are used for this purpose. See the article "Zinc Plating" in this Volume for more information.

Zinc-Iron Plating

Zinc-iron plating produces alloys containing 15 to 25% Fe as-plated. Advantages of this alloy are good weldability and ductility. It is electroplated on steel coil and strip for auto bodies. Strip for the manufacture of automotive components is also plated in baths that produce 1% Fe in the alloy deposit; a special feature of this alloy is its suitability for deep black chromating.

The corrosion resistance of zinc-iron is generally lower than that of the other zinc alloys, especially after exposure to high temperatures such as those encountered by under-the-hood automotive components. A typical zinc-iron solution composition used in strip line plating is:

Constituent	Content	
	g/L	oz/gal
Ferric sulfate	200-300	27-40
Zinc sulfate	200-300	27-40
Sodium sulfate	20-40	2.7-5.3
Sodium acetate	10-30	1.3-4
Organic additive	1-5	0.1-0.66

Zinc-Cobalt Plating

Zinc-cobalt coatings contain 0.6 to 2% Co. Zinc-cobalt alloys find extensive use for relatively inexpensive components in applications that require improved abrasion resistance and corrosion protection. Typically, an 8 μm film with 1% cobalt will last up to 500 h in a neutral salt spray test before red rust if the proper chromate is applied. Some reduction in corrosion resistance is experienced after exposure to high temperature, but not as much as with zinc-iron alloys. A unique attribute of zinc-cobalt is its corrosion resistance to sulfur dioxide in accelerated corrosion tests. This suggests that these coatings may be suitable for use in sulfur-containing corrosive environments.

There are two types of zinc-cobalt plating baths; acid and alkaline. Alkaline baths are preferred for tubes and other configurations with internal unplated areas. Exposure to acidic electrolyte reduces the corrosion resistance of such parts. Available chromates include clear, yellow, iridescent and black.

Typical zinc-cobalt bath compositions and process parameters are given in Table 1.

Table 1 Compositions and process parameters for zinc-cobalt plating solutions

Constituent or parameter	Amount or value
Acid baths	
Zinc chloride, g/L (oz/gal)	80-90 (10-12)
Potassium chloride, g/L (oz/gal)	150-200 (20-27)
Ammonium chloride[(a)], g/L (oz/gal)	50-70 (7-9)
Boric acid[(a)], g/L (oz/gal)	20-30 (3-4)
Cobalt chloride, g/L (oz/gal)	1-20 (0.1-2.7)

Organic additive, g/L (oz/gal)	5-20 (0.66-2.7)
pH	5.0-6.0
Temperature, °C (°F)	20-40 (70-100)
Anodes	Zinc
Alkaline baths	
Zinc oxide, g/L (oz/gal)	10-20 (1.3-2.7)
Sodium hydroxide, g/L (oz/gal)	80-150 (10-20)
Cobalt salt complex, g/L (oz/gal)	1.0-2.0 (0.1-0.3)
Organic additive, g/L (oz/gal)	5-10 (0.66-1.3)
Temperature, °C (°F)	25-40 (77-100)
Anodes	Zinc

(a) Used only in some compositions

Zinc-Nickel Plating

Zinc-nickel alloys produce the highest corrosion resistance of electroplated zinc alloys. These alloys contain from 5 to 15% Ni. Corrosion resistance improves with nickel content up to 15 to 18%. Beyond this range the alloy becomes more noble than steel and loses its sacrificial protection property. An alloy containing 10 to 13 wt% Ni is electroplated on steel strip and coil as an alternative to zinc-iron or electrogalvanizing. An advantage of this composition is the formability of the steel after coiling. For components, chromatizing is required; however, best results are achieved on alloys containing 5 to 10% Ni. For alloys in this range of nickel content, corrosion resistance to neutral salt spray reaches 1000 h or more before red rust. An advantage of zinc-nickel alloys is their retention of 60 to 80% of their corrosion resistance after forming and after heat treatment of plated components. This attribute makes these alloys suitable for automotive applications such as fasteners, brake and fuel lines, and other under-the-hood components.

Zinc-nickel alloys plated from alkaline baths have shown potential as substitutes for cadmium coatings in aircraft and military applications. Available chromates are clear, iridescent, bronze, and black. Typical zinc-nickel bath compositions and process parameters are given in Table 2. Alkaline formulations are preferred for their ease of operation and because they provide more uniform alloy composition and better overall corrosion resistance, especially on tubing and on internal configurations of parts.

Table 2 Compositions and process parameters for zinc-nickel plating solutions

Constituent or parameter	Amount or value

Acid baths	
Zinc chloride, g/L (oz/gal)	120-130 (16-17)
Nickel chloride, g/L (oz/gal)	110-130 (15-17)
Potassium chloride, g/L (oz/gal)	200-250 (27-33)
Ammonium chloride[(a)], g/L (oz/gal)	100-200 (13-27)
Organic additives, g/L (oz/gal)[(a)]	5-10 (0.66-1.3)
pH	5-6
Anodes	Zinc and nickel connected to two separate rectifiers
Alkaline baths	
Sodium hydroxide, g/L (oz/gal)	100-130 (13-17)
Zinc, g/L (oz/gal)	6-15 (0.8-2.0)
Nickel, g/L (oz/gal)	0.5-1.5 (0.07-0.20)
Organic additives, g/L (oz/gal)	2-5 (0.25-0.66)
Anodes	Zinc and steel, one rectifier
Temperature, °C (°F)	20-35 (70-95)

(a) Used only in some compositions

Tin-Zinc Plating

Tin-zinc alloys contain 70 to 90% Sn and 10 to 30% Zn. Cyanide, acid, and neutral commercial baths are available. Tin-zinc baths are expensive to operate because they require the use of special cast tin-zinc anodes. Tin-zinc alloys exhibit excellent solderability, ductility, and corrosion resistance.

Chromate posttreatments are limited to yellow or clear. The tin-zinc deposit is semibright as-plated and is used primarily as a functional coating. Tin-zinc is finding increasing application in the automotive and electronic industries and as a substitute for cadmium plating.

Additional information about tin-zinc coatings is contained in the article "Tin Alloy Plating" in this Volume.

Corrosion Protection

Corrosion rates for zinc alloy coatings as demonstrated by the neutral salt spray test are:

Coating[a]	Hours to red rust
Zinc	200-250
Zinc-iron (1% Fe)	350
Zinc-cobalt (0.8% Co)	500
Zinc-nickel (8% Ni)	1000
Tin-zinc (70% Sn)	1000

(a) Coating thickness, 8 μm; iridescent yellow chromate post-treatment

Nickel Alloy Plating

S. Alec Watson, Nickel Development Institute

Introduction

NICKEL ALLOYS electroplated for engineering applications include nickel-iron, nickel-cobalt, nickel-manganese, and zinc-nickel. Zinc-nickel plating is covered elsewhere in this Volume; see the article "Zinc Alloy Plating." Iron is a cheap metal, and solutions for plating nickel-iron alloys were developed mainly in order to reduce the cost of the metal used to form a layer of given thickness, but they were also developed for special magnetic purposes. Cobalt and manganese are used to increase the hardness and strength of nickel plating. Additionally, nickel-manganese alloys have improved resistance to sulfur embrittlement when heated. Alloy layers 20 to 30 μm thick of nickel with about 15% Mo exhibit higher hardness and resistance to corrosion than pure nickel but at the expense of a reduction in ductility to around 1% (Ref 1). Coatings of nickel-tungsten show very high resistance to corrosion, but they are believed not to be true alloys (Ref 2) and have not been used in practice. This article will discuss the alloys nickel-iron, nickel-cobalt, and nickel-manganese that are of practical interest, plus a few paragraphs on nickel-chromium binary and ternary alloys.

References

1. E. Chassaing, K. Vu Quang, M.E. Baumgärtner, M. Funk, and Ch.J. Raub, High Temperature Ni-Mo Electrodeposited Alloys--Structure and Properties, *Plating and Surface Finishing,* Vol 77 (No. 8), Aug 1990, p 60-65
2. G. Raucher, V. Rogoll, M.E. Baumgärtner, and Ch.J. Raub, Investigation of the Dissolution Behaviour of Electrodeposited Ni-W Layers in Concentrated Hydrogen Chloride Solution, *Transactions of the Institute of Metal Finishing,* Vol 71 (Part 3), Aug 1993, p 95-98

Nickel-Iron

Bright nickel-iron plating was strongly promoted as a substitute for bright nickel plating in the period from 1970 to the early 1980s when the relative price of nickel was high (Ref 3, 4, 5, 6).

Advantages. The main advantage of the alloy is the significant saving in the cost of metal, because up to 35% of the nickel is replaced by iron. An additional advantage is that iron entering the plating solution through chemical dissolution of steel substrates, which is highly detrimental in straight nickel plating solutions, is readily dissolved and subsequently plated out. This feature is particularly relevant during plating onto tubular steel parts. Ductility is usually higher for the alloy coatings than for bright nickel, which may be advantageous if the plated parts are subject to deformation.

Disadvantages. The organic addition agents are more expensive than those needed for bright nickel, substantially negating the saving on metal. The addition agent system is also more complex so that electrolyte control is more difficult. At equal thickness, nickel-iron plating is less resistant to corrosion than nickel, and the higher the iron content, the lower its resistance. The corrosion product is rust-colored, and there is no international standard for the alloy coatings.

Process Description. Preferred solutions for plating bright nickel-iron are slightly more dilute than nickel plating solutions in order to obtain a high-iron alloy without using a high iron concentration in the solution. A typical solution is given in Table 1 (Ref 4). Addition agents include stabilizers for the ferrous iron, organic brighteners, leveling agents, and wetting agents. Total iron includes ferrous and ferric ions, and it is important to control the ratio, with ferric usually below 20%. Solution temperature is typically 54 to 60 °C (130 to 140 °F), and solution pH must be kept low at 2.8 to 3.6. The solution is preferably used with air agitation rather than cathode-rod movement, because higher plating rates can be used, a higher iron content can be obtained in the deposits, and iron content can be altered at will by increasing or reducing the rate of air bubbling.

Table 1 Typical nickel-iron solution composition

Constituent	Amount, g/L (oz/gal)
Ni^{+2}	56 (7.46)
Iron (total)	4 (0.53)
$NiSO_4 \cdot 6H_2O$	150 (20.00)
$NiCl_2 \cdot 6H_2O$	90 (12.00)
$FeSO_4 \cdot 7H_2O$	20 (2.67)
H_3BO_3	45 (6.00)
Stabilizer[(a)]	15 (2.00)

(a) Concentration will vary between 10-25 g/L (1.3-3.3 oz/gal), depending on the type of stabilizer used.

Properties of the alloy deposits that are of interest include ductility, deposit hardness, internal stress, and magnetic properties.

Ductility depends on iron content, brightener concentration, solution temperature, and pH.

Deposit hardness varies with iron content. With iron content increasing from zero to about 10%, microhardness rises from 490 to 560 HK, then falls to around 510 HK with 49% Fe for coatings plated at standard conditions of 4 A/dm^2 (40 A/ft^2), 60 °C (140 °F), pH 3.5, and air agitation. Changes in solution pH and brightener concentration also influence deposit hardness, enabling values exceeding 700 HV to be achieved.

Internal stress is tensile, in contrast to that of most bright nickel deposits. It is influenced by iron content and, more sharply, by solution pH. Increasing iron content from 10.8 to 27.6% raises stress from 93 to 154 MN/m^2 (13,500 to 22,400 psi). Increasing pH from 2.8 to 4.5 raises stress from 17.5 to 230 MN/m^2 (2500 to 33,600 psi) (Ref 4).

Magnetic properties of nickel-iron are not important in the application of bright decorative coatings. Similar alloys are, however, deposited for magnetic applications from solutions not containing brightening additions (Ref 7). The alloys with 18 to 25% Fe are soft magnetic materials with low coercive force, low remanence, and high maximum permeabilities (Ref 8). They can be used as coatings or as electroformed parts (i.e., freestanding electrodeposited shapes detached from the substrate after being deposited).

References cited in this section

3. R.J. Clauss, R.A. Tremmell, and R.W. Klein, Decorative Nickel-Iron Alloy Electrodeposits: Present Status and Future Possibilities, *Transactions of the Institute of Metal Finishing,* Vol 53 (No. 1), Spring Conference 1975, p 22-27
4. R.A. Tremmell, Decorative Nickel-Iron Coatings: An Acceptable and Economic Alternative to Bright Nickel--No. I, *Plating and Surface Finishing,* Vol 68, Jan 1981, p 22-26
5. R.A. Tremmell, Decorative Nickel-Iron Coatings: An Acceptable and Economic Alternative to Bright Nickel-No. II, *Plating and Surface Finishing,* Vol 68, Feb 1981, p 30-33
6. J.S. Hadley and J. O'Grady, Corrosion Studies on Nickel-Iron Electrodeposits, *Transactions of the Institute of Metal Finishing,* Vol 59 (No. 3), Autumn 1981, p 89-92
7. P.J. Boden, D.E. Eastham, and M.E. Henstock, Recent Developments in the Electrodeposition of Permalloy Films, *Transactions of the Institute of Metal Finishing,* Vol 50 (No. 3), Summer 1972, p 117-118
8. H.H. Law, C.A. Holden, C.A. Mattoe, J. Sapjeta, Y. Degani, and T.H. Tiefel, Prototype Manufacture of Miniature Nickel/Iron Alloy Magnetic Sleeves for Optical Switching, *Plating and Surface Finishing,* Vol 79 (No. 8), Aug 1992, p 50-54

Nickel-Cobalt

Some of the earliest solutions for bright nickel plating contained cobalt, formate, and formaldehyde additions, but with the development of modern bright nickel solutions based on organic addition agents only, the cobalt-containing solutions have fallen into disuse. Today, the cobalt additions are used when it is necessary to increase the hardness and strength of nickel plating, especially in electroforming applications.

Advantages. Compared with nickel itself, nickel-cobalt alloys are harder and stronger. In contrast to nickel hardened with conventional organic addition agents such as naphthalene 1:3:6 trisulfonic acid, nickel-cobalt alloys can be heated to high temperatures without embrittlement by sulfur incorporated from addition agents.

Disadvantages. Compared with nickel alone, the need to maintain the level of cobalt ions in solution introduces an additional maintenance requirement. Also, deposit internal stress is moved in the tensile direction, and there is a practical limit to the level of cobalt that can be used. Hence the maximum hardness of about 400 HV is less than the 600 HV that can be attained using conventional organic additives.

Process Description. Most of the published data about nickel-cobalt plating were determined using the 600 g/L nickel sulfamate solution of the Ni-Speed process (Ref 9, 10, 11). The initial charge of cobalt is added to the base solution as cobalt sulfamate. Replenishment during operation of the solution is usually made by metered additions of cobalt sulfamate. It can, however, be achieved by dividing the anodic current between a nickel anode and a cobalt anode, so that the percentage of total current passing to the cobalt is the same as the percentage of cobalt required in the alloy deposited at the cathode. Good control of solution cobalt content by analysis is needed.

Processing Variables and Properties of the Alloy from 600 g/L Nickel Sulfamate Solution. With solution composition and pH standardized, the cobalt content and the properties of the alloys depend on solution temperature and deposition current density. The properties are modified by subsequent heat treatment (Ref 12, 13, 14) and by simultaneous use of sulfur-free organic addition agents (Ref 15). The main results of various studies were drawn together in 1989 (Ref 16).

Alloy Hardness. The relationship between cobalt content and deposit hardness is shown in Fig. 1. The broken curve shows microhardness versus cobalt content in the deposits formed at 5.4 A/dm^2 (50 A/ft^2), and the solid curve shows microhardness versus cobalt content in the solution. A peak hardness of about 520 HV is attained with 6 g/L Co in the solution, which gives an alloy containing about 34% Co. At peak hardness, internal tensile stress is too high for electroforming applications, although the alloy can be used as a coating on a solid substrate. For electroforming purposes, the limit of tolerable deposit stress is reached with alloys containing about 15% Co that have hardnesses around 350 to 400 HV.

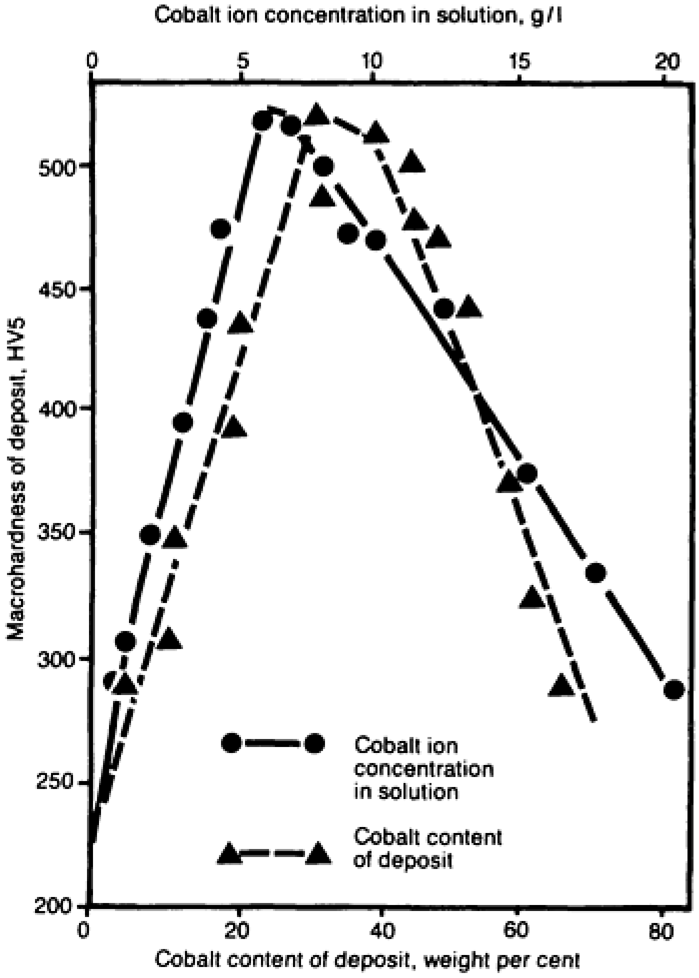

Fig. 1 Relationship between deposit hardness and cobalt concentration in the sulfamate solution and in the deposit

Alloy hardness depends on both the cobalt content of the solution and the deposition current density. Figure 2 shows hardness plotted against current density for different concentrations of cobalt in a solution operated at 60 °C(140 °F), pH 4.0. Deposit stress also depends on deposition current density, and moving left to right along any one of the curves, deposit stress changes from compressive through zero to tensile. The superimposed dotted line is a zero-stress contour linking the combinations of cobalt ion concentration and current density for zero-stress alloys. The corresponding value of deposit hardness can be read from the graph for each combination. The overall relationship is that the higher the cobalt ion concentration, the lower the current density that can be used for zero-stress alloys, but the higher the hardness of the alloy.

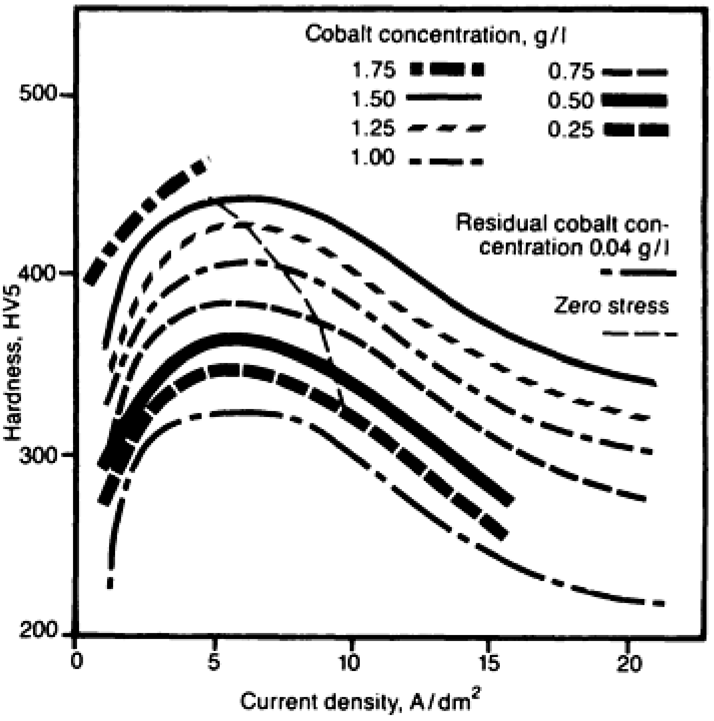

Fig. 2 Relationship between current density and alloy deposit hardness for various cobalt concentrations in solution with superimposed zero stress contour

Effect of Heat. Heating at temperatures up to 300 °C (570 °F) has little effect on the mechanical properties of the alloys. At higher temperatures deposit hardness falls, but nickel-cobalt alloys still retain greater hardness than that of nickel deposits similarly heat treated (Fig. 3).

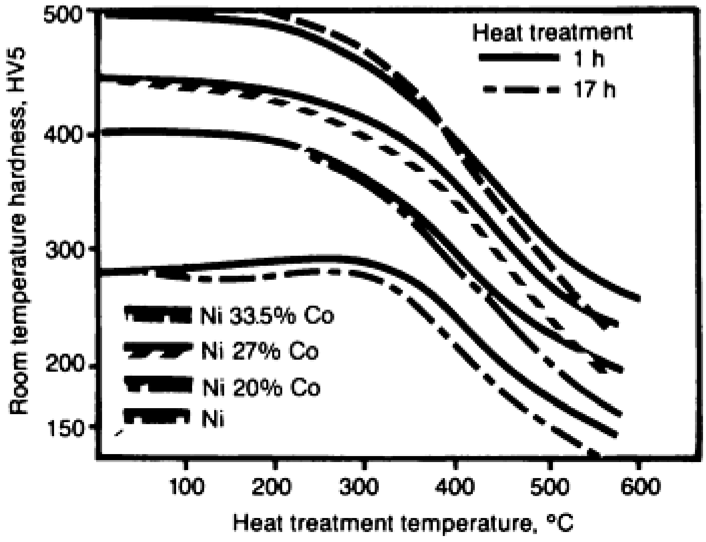

Fig. 3 Room-temperature hardness of electroformed nickel and nickel-cobalt alloys after heating

Tensile strength, 1034 MN/m^2 (150,000 psi) for a 15% Co alloy and 745 MN/m^2 (108,000 psi) for a 10% Co alloy (Ref 14), falls progressively as heat-treatment temperature is increased above 300 °C (570 °F) (Fig. 4). The effect is similar with proof stress, 677 MN/m^2 (98,000 psi) for an as-deposited 15% Co alloy and 531 MN/m^2 (77,000 psi) for a 10% Co alloy (Ref 14).

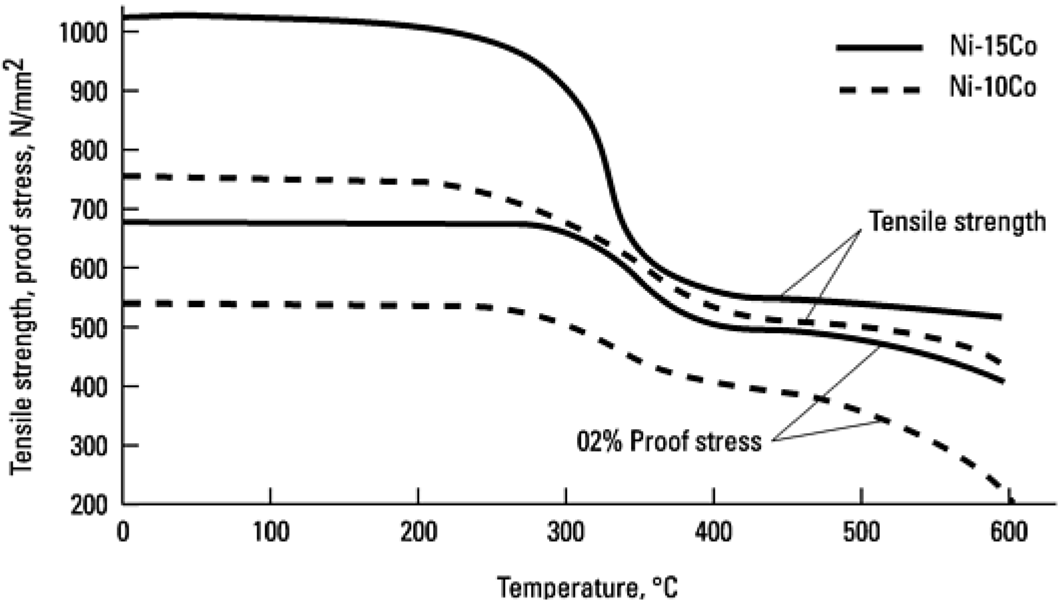

Fig. 4 Effect of heat treatment on the mechanical properties of Ni-10Co and Ni-15Co alloys

Deposit ductility increases on heating above about 300 °C (570 °F), from a value of 5% elongation as-deposited to about 40% after heating at 600 °C (1100 °F) for both 10% and 15% Co alloys (Fig. 5).

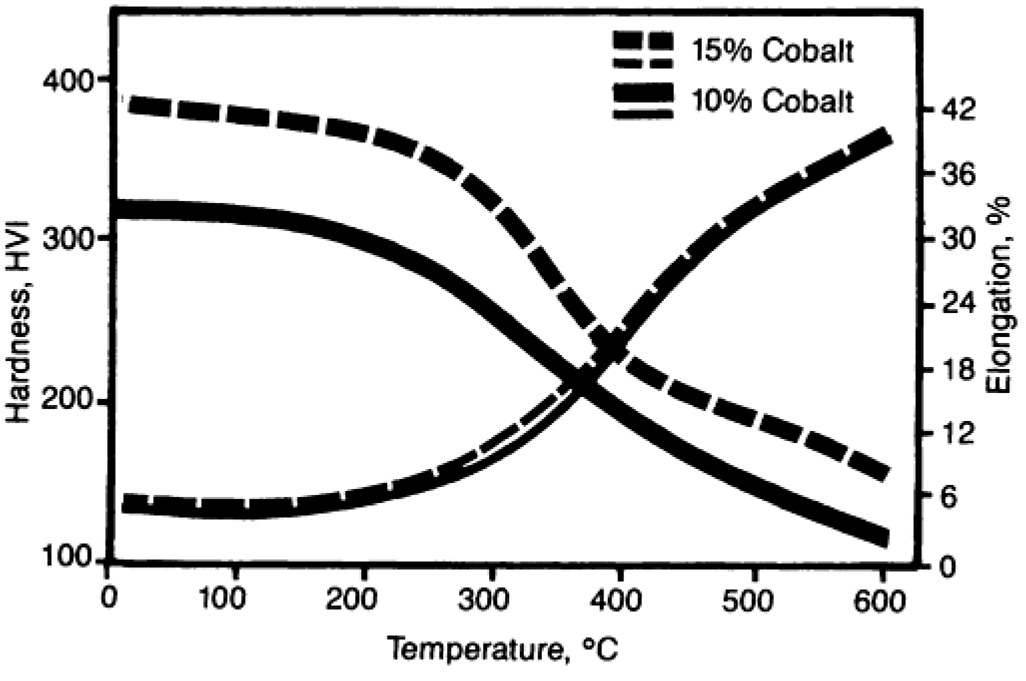

Fig. 5 Hardness and elongation of Ni-10Co and Ni-15Co alloys after heating to various temperatures

Properties of Alloys from Other Nickel Solutions. The above data apply to alloys from a 600 g/L nickel sulfamate solution. A Ni-14Co alloy deposited from a 450 g/L solution without chloride or organic additions, operated at 52 °C (126 °F), pH 4.0, and cathodic current density 2.5 A/dm^2 (23 A/ft^2) has a hardness of 350 to 400 HV, ductility less than 5%, and internal tensile stress of 50 to 60 MN/m^2 (7000 to 9000 psi) (Ref 17).

Measurements of the effects of heat treatment at 204 °C (400 °F) on alloys containing 53 to 55% Co indicate a small increase in yield strength, from 1062 MN/m^2 (154,000 psi) to 1124 MN/m^2 (163,000 psi), and a substantial increase in elongation, from 10 to 16% (Ref 18). Heat treatment at 260 °C (500 °F) or more reduces yield strength, as with alloys from the 600 g/L nickel sulfamate solution. Prior heat treatment of the 53 to 55% Co alloys at 204 °C (500 °F), 371 °C (700 °F), or 427 °C (800 °F) improves subsequent mechanical properties measured at a test temperature of 260 °C (500 °F). Thus pretreatment for 4 h at 427 °C (800 °F) increases yield strength from 372 to 448 MN/m^2 (54,000 to 65,000 psi) and elongation from 28 to 32%.

Alloys deposited from a sulfosalicylate-based solution exhibit a maximum hardness value above 700 HV (Ref 19). To date, this solution has not been used industrially.

References cited in this section

9. R.J. Kendrick, High Speed Nickel Plating from Sulphamate Solutions, *Transactions of the Institute of Metal Finishing,* Vol 41 (Advance Copy, International Conference), 1964; also Inco Publication 2782
10. R.J. Kendrick and S.A. Watson, Plating with Nickel Sulphamate, *Electrochimica Metallorum,* Symposium on Sulfamic Acid and Its Electrometallurgical Applications (Milan), 25-27 May 1966; also Inco Publication 4055
11. "The Ni-Speed Electrodeposition Process: Operating Conditions," Inco Publication 2902a
12. K.C. Belt, J.A. Crossley, and S.A. Watson, Nickel-Cobalt Alloy Deposits from a Concentrated Sulphamate Electrolyte, *Transactions of the Institute of Metal Finishing,* Vol 48 (No. 4), Autumn 1970, p 132-139
13. W.R. Wearmouth and K.C. Belt, The Mechanical Properties and Electroforming Applications of Nickel-Cobalt Electrodeposits, *Transactions of the Institute of Metal Finishing,* Vol 52 (No. 3), Summer 1974, p 114-118
14. W.R. Wearmouth, Application of New Developments in Electroforming Technology in the Toolmaking Industry, *Plastics and Rubber: Processing,* Vol 2 (No. 4), Dec 1977, p 131-138
15. W.R. Wearmouth and R.C.E. Bishop, Hard Smooth Stress-Free Electroformed Nickel for Video Discs, *Transactions of the Institute of Metal Finishing,* Vol 62 (No. 3), Autumn 1984, p 104
16. S.A. Watson, Additions to Sulphamate Nickel Solutions, Nickel Development Institute Technical Series, Publication 10053, 1989, p 1-7
17. W. Metzger and L. Läser, Electrolytic Manufacture of Line Gratings, *Galvanotechnik,* Vol 77 (No. 12), Dec 1986, p 2985-2986
18. R.J. Walter, Tensile Properties of Electrodeposited Nickel-Cobalt, *Plating and Surface Finishing,* Vol 73 (No. 10), Oct 1986, p 48-53
19. J. Vitec, J. Neuman, and P. Nejedly, Some Properties of Nickel-Cobalt Alloys Electrodeposited from Sulphosalicylate Solutions, *Transactions of the Institute of Metal Finishing,* Vol 69 (No. 3), Aug 1991, p 86-89

Nickel-Manganese

Embrittlement of nickel by incorporated sulfur when heated above 200 °C (390 °F) can arise by formation of brittle grain boundary films. In electrodeposits, the sulfur incorporation can result from the use of organic addition agents put into the solution in order to control internal stress in the plating. In these circumstances, manganese ions can be added to the solution so as to allow deposition of a nickel-manganese alloy resistant to sulfur embrittlement.

Manganese ions are also added in the absence of sulfur-bearing addition agents in the solution in order to produce nickel-manganese alloys that are stronger than plain nickel. There are both actual and potential applications of nickel-manganese alloy deposition in electroforming.

Advantages. The ability to neutralize the harmful effect of sulfur is not shared by iron or cobalt. Harder, stronger nickel alloys can be attained with manganese than with cobalt.

Disadvantages. Manganese does not codeposit as readily as iron or cobalt with nickel, and so nickel-manganese alloys contain much less manganese for a given concentration in solution of the second metal. Nickel-manganese alloys containing a useful amount of manganese tend to have high tensile internal stress and to be brittle.

Process Variables and Properties of the Alloys from Solutions with Stress Reducer. The percentage of manganese in the alloy at a fixed level of manganese in solution rises as deposition current density is increased, whether the solution is Watts-type, conventional sulfamate, or 600 g/L nickel sulfamate Ni-Speed (Ref 20). Manganese content rises from 0.02 to 0.03% at 4.3 A/dm^2 (40 A/ft^2) to 0.17 to 0.22% at 12.9 A/dm^2 (120 A/ft^2). These data were obtained in a solution that contained 15 g/L Mn and 0.25 g/L soluble saccharin to control deposit stress. Although sulfur uptake in the deposit also rises with increasing current density, by a half in the Watts and Ni-Speed solutions, the ratio of manganese content to sulfur content rises much more, from 1.1 to 6.2. Measurements of deposit ductility after heat treatment at various temperatures show that a higher ratio is required to avoid embrittlement for higher temperatures: 1.1 for 200 °C (390 °F) and 5.1 for 500 °C (930 °F) (Ref 20).

Alloy Hardness. As-deposited hardness of alloys plated with 15 g/L Mn and 0.25 g/L saccharin rises with an increase in percentage manganese in the alloy, from 287 HV at 0.02% Mn to 420 HV at 0.27% Mn when the base solution is Watts, and from 338 HV at 0.04% Mn to 445 HV at 0.23% Mn when the base solution is conventional sulfamate (Ref 21). Heat treatment for 22 h at 200 °C (390 °F) increases room-temperature hardness about 10% for all alloys with 0.1% Mn or more. Similar periods of heat treatment at 300 °C (570 °F) drastically reduce hardness to about 170 HV for all alloys irrespective of manganese content. Further increase in temperature to 400 °C (750 °F) or 500 °C (930 °F) has little further effect.

Internal stress in deposits from the 15 g/L Mn plus 0.25 g/L saccharin system is compressive for alloys deposited at up to 10.8 A/dm^2 (100 A/ft^2), whether the base solution is Watts, conventional sulfamate, or 600 g/L nickel sulfamate. Values lie in the range of 43 to 62 MN/m^2 (6200 to 9000 psi) for Watts, 62 to 91 MN/m^2 (9000 to 13,200 psi) for 600 g/L nickel sulfamate, and 94 to 100 MN/m^2 (13,600 to 14,500 psi) for conventional sulfamate (Ref 20). At the highest current density, 12.9 A/dm^2 (120 A/ft^2), the Watts deposit remains in its compressive range while the conventional and 600 g/L nickel sulfamate deposits show small tensile stress values, respectively 17 MN/m^2 (2500 psi) and 36 MN/m^2 (5200 psi). These low-stress deposits produced at 12.9 A/dm^2 (120 A/ft^2), with hardness values 420 to 443 HV, are harder than any low-stress alloys produced with the nickel-cobalt system.

Properties of Alloys from Solutions without Stress Reducer. Alloys deposited from straight nickel plating solutions with only manganese additions can have tensile strengths exceeding 1000 MN/m^2 (145,000 psi) and yield strengths up to 800 to 950 MN/m^2 (116,000 to 138,000 psi) (Ref 22). However, ductility is low when more than a small percentage of manganese is alloyed with the nickel, deposit internal stress is tensile, and the alloys may crack during formation. Nonetheless, such alloys have been used as rigid electroforms (Ref 23). Heat treatment of the alloys increases ductility and relieves stress, the values depending on heat-treatment temperature and manganese content, and deposit properties can be further modified using pulse plating during deposition of the alloys (Ref 22).

References cited in this section

20. W.R. Wearmouth and K.C. Belt, Electroforming with Heat-Resistant Sulfur-Hardened Nickel, *Plating and Surface Finishing,* Vol 66, Oct 1979, p 53-57
21. W.R. Wearmouth, Nickel Alloy Electrodeposits for Non-Decorative Applications, *Transactions of the Institute of Metal Finishing,* Vol 60 (No. 2), Summer 1982, p 68-73
22. G.A. Malone, New Developments in Electroformed Nickel-Based Structural Alloys, *Plating and Surface Finishing,* Vol 74 (No. 1), Jan 1987, p 50-56
23. G.A. Malone, Multi-Stage Electroforming of High Energy Chemical and Excimer Laser Components, *Plating and Surface Finishing,* Vol 75 (No. 7), July 1988, p 58-62

Nickel-Chromium

There are many references in the published literature to the deposition of nickel-chromium and iron-nickel-chromium alloys from simple salt solutions, but these solutions have not achieved commercial application except for a proprietary process used for depositing thin decorative coatings (Ref 24).

Alloys of nickel with 22% Cr can be prepared by codepositing chromium carbide particles with nickel followed by heat treatment for 24 h at 1000 °C (1800 °F) in hydrogen. Hardness of the alloy after the heat treatment is 223 HV, compared with 55 HV for similarly treated plain nickel (Ref 21, 25).

Alloys containing 19% Co or 20% Fe in addition to chromium are produced by codepositing chromium carbide from nickel-cobalt or nickel-iron base solutions and heat treating (Ref 21).

Heat treatment in hydrogen gives almost complete decarburization with the nickel-cobalt-chromium alloy, and hardness after heat treatment is 215 HV. Approximately 0.8% C remains in the nickel-iron-chromium alloy, however, which might account for its higher hardness, 332 HV.

References cited in this section

21. W.R. Wearmouth, Nickel Alloy Electrodeposits for Non-Decorative Applications, *Transactions of the Institute of Metal Finishing,* Vol 60 (No. 2), Summer 1982, p 68-73
24. M. Law, Electrodeposition of a Ternary Alloy of Chromium, *Finishing,* Vol 8 (No. 7), July 1984, p 30-31
25. A.C. Hart and W.R. Wearmouth, U.K. Patent 1,476,099, 10 June 1977

Environmental, Health, and Safety Considerations

For practical purposes, the environmental, health, and safety considerations for these nickel-base alloys and their production are the same as those for nickel and nickel plating.

Environmental Considerations. Nickel is a naturally occurring constituent of our day-to-day environment. The soil worldwide contains 5 to 500 ppm Ni, with an average of 100 ppm. Food is grown and consumed in areas with higher levels still, without leading to any health problems for the inhabitants (e.g., 661 ppm in Hawaii) (Ref 26). Nickel has been determined to be an essential trace element for plant life, and some plants that accumulate nickel are regularly eaten by people with no harmful effects. Nickel is also present naturally in the atmosphere, rivers, seas, and oceans. Nonetheless, the desire to maintain the natural environment as it is has led to the establishment of maximum permitted levels for the discharge of nickel and other metals by industry. In nickel plating, the levels are attained by measures to reduce spray emission, process solution dragout, and effluent treatment. Details of all necessary techniques are available from suppliers to the metal finishing industry.

Health and Safety Considerations. Some 1.2% of men and 10 to 15% of women are sensitized to nickel and, when exposed to prolonged skin contact with nickel metal, certain nickel alloys, or nickel-containing solutions, may develop dermatitis at the point of contact. The occurrence of nickel contact dermatitis was first observed as a result of exposure to nickel-containing solutions in electrorefining of nickel. Today most electroplaters are aware of "nickel itch" but have never seen a case of it. The reason is that, despite increasing use of nickel-containing products, industry has adopted work practices that prevent occurrence of contact dermatitis. Today, nickel contact dermatitis occurs most frequently as a result of domestic exposures from close and persistent contact of the skin with nickel-plated articles or with certain nickel alloys. Accordingly, legislation in Europe will control the use of nickel metal, nickel alloys, and nickel-containing materials that come in contact with the skin. The main problem is with those articles that come into direct and prolonged contact, such as earrings, necklaces, bracelets, watch cases and straps, buttons, and rivets. It is important to note that nickel alloys that do not react with sweat do not cause dermatitis. Transient contact with nickel or nickel alloys is not damaging because there is insufficient time for reaction with sweat to form the soluble products that can penetrate the skin (Ref 27).

In nickel plating, plant design, exhaust ventilation, and methods of operation should be such as to avoid any risk of skin contact with the solutions. Protective clothing should be inspected regularly for leaks and tears. Where protective gloves are necessary it is recommended that cotton inner gloves be worn to reduce perspiration. The outer gloves should be rinsed off before removal to prevent process solution transfer to the hands or the inside of the gloves on removal (Ref 28).

A few cases of asthma, claimed to be nickel-induced, have reportedly arisen from aerosols of soluble nickel salts. The content of nickel in the atmosphere should be kept below the occupational exposure limit.

There is evidence that inhalation of some nickel compounds (nickel oxide, nickel subsulfide) occurring in the atmosphere associated with certain nickel refining operations may cause respiratory cancers in humans. There is no good evidence

that occupational exposure to metallic nickel or nickel oxide, sulfate, or chloride during plating or polishing is associated with increased mortality due to cancer (Ref 29).

References cited in this section

26. B.K. Davison, BKD Consulting, personal communication, 1994
27. "Nickel and Nickel Alloy Articles That Come into Contact with the Skin," Nickel Development Institute Status Report, Toronto, Sept 1992
28. "Nickel: Meeting the Control Limits for Nickel and Its Inorganic Compounds," Health and Safety Bulletin 1, The Metal Finishing Association, Birmingham, England, June 1991
29. The Toxicity of Nickel and Its Inorganic Compounds, Toxicity Review 19, Her Majesty's Stationery Office, London, 1987

Chromium Alloy Plating

Eric W. Brooman, Concurrent Technologies Corporation

Introduction

CHROMIUM ALLOYS, which are relatively difficult to deposit, yield alloy coatings with properties that range from completely satisfactory to marginally acceptable, depending on the end use. The idea of depositing a thin, stainless steel type of coating has been receiving renewed interest since the 1970s. Stainless steel coatings would conserve strategic metals, facilitate the manufacturing process, and lower cost if they could be applied to strip or sheet, or to a component that has been fabricated to the required size and shape. This would also mean that a component could be made from a material that is more easily worked than stainless steel.

For both chromium and stainless steel types of alloys, the most important properties to develop in a coating are corrosion resistance, abrasion and wear resistance, hardness, surface texture, and luster. Thickness requirements can range from a few microns up to a few hundred microns. Thicker coatings are rarely specified, primarily because the relatively poor throwing power of the plating solution gives an uneven surface coverage. Further, the low plating efficiencies can lead to high internal stresses from hydrogen uptake. The resulting microcracking has a detrimental effect on coating properties.

It is difficult to deposit chromium from aqueous solutions because of its low hydrogen overvoltage. As a result, cathodic coulombic efficiency typically ranges from 10 to 20% for commercial processes. In order to deposit chromium-containing alloys, it is usually necessary to implement the approaches summarized below and described more fully in Ref 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11:

- Complexing agents are needed to bring the deposition potentials of the alloying metals (e.g., nickel and iron) closer together.
- The plating solution should contain a greater proportion of chromium salts, relative to the alloy addition, in order to obtain significant amounts of chromium in the deposits.
- Care must be taken to deposit metallic coatings rather than hydrated, chromium-containing salts, especially if chloride-base solutions are used.
- Close control of temperature, agitation, current density, and pH is necessary with most of the reported solution chemistries, in order to obtain reproducible alloy compositions and properties, as well as reasonable plating rates.
- Trivalent chromium-base solution chemistries provide better prospects for depositing satisfactory alloy coatings from aqueous solutions. An additional benefit is that waste-treatment requirements are less stringent than they are for hexavalent chromium-base solutions.
- The chromium concentration in the alloy should be limited in order to avoid microcracking.
- Aqueous solutions with a low pH value (between 1 and 3) seem to produce better deposits than solutions with pH values outside this range.
- Nonaqueous solutions, especially those based on molten salts, can provide useful alloy deposits.

However, these tend to be relatively thick.

- Thin deposits offer the best prospect for providing lustrous finishes.
- Post-plating heat treatments can sometimes improve the mechanical properties and corrosion resistance of the deposits.

References to chromium alloy plating date back to the mid-1950s, when corrosion- and wear-resistant coatings were first developed for the inside of gun barrels used in military applications, and patents date back to circa 1970. This article will emphasize just the work performed since the 1980s. Those chromium alloys that contain nickel or iron or both are discussed first, because of their importance. Other alloying elements that have been deposited with chromium are discussed as a group, in less detail.

The variables and techniques available to apply coatings based on chromium and other alloys are extensive (Table 1). Because of space limitations, many of these variables or options are mentioned only briefly, where appropriate, and the discussion of deposit properties is similarly limited.

Table 1 Technology options for the deposition of chromium-base alloys

Type of bath
Aqueous
Acid
Alkaline
Nonaqueous
Organic
Molten salt
Applied current
None (electroless)
Conventional direct current
Pulsed direct current
Periodic reversed direct current
High-speed direct current
High-speed pulsed direct current
Composition
Alloy
Mixture
Amorphous
Structure
Homogeneous
Multilayer
Composite

Dispersed
Post treatments Heat treatment Diffusion Laser glazing

References

1. V.M. Dokras, Codeposition of Nickel and Chromium, *Symp. Electroplat. Met. Finish.,* Vol 5, 1952, p 134-139
2. C. Levy, Electrodeposition of Chromium Alloys, *Met. Finish.,* Vol 57 (No. 8), 1962, p 59-62
3. A. Brenner, Electrodeposition of Chromium Alloys, in *Electrodeposition of Alloys,* Vol II, Academic Press, Inc., 1963
4. M. Sarojamma and T.L. Rama Char, Electrodeposition of Stainless Steel, *Electroplat. Met. Finish.,* Vol 23 (No. 10), 1970, p 13-20
5. R. Sivakumar and T.L. Rama Char, Electrodeposition of Ternary Alloys: 1964-1969 Developments, *Electroplat. Met. Finish.,* Vol 24 (No. 1), 1971, p 14-27
6. M. Bonnemay and J. Royon, "Electrolytic Deposition of Chromium Alloys: Factors of Electrolysis," Bulletin of the Information Center for Hard Chromium, June-July 1973, p 12-22
7. H. Benninghoff, Functional Electroplating: Properties of Electrodeposited Metal and Alloy Coating, II--Chromium, Chromium-Iron-Nickel Alloys, Copper Plus Nickel Plus Chromium Systems, Nickel Plus Chromium Systems, Dispersion Systems, *Metalloberfläche,* Vol 33 (No. 9), 1979, p 361-371
8. S.C. Srivastava, Electrodeposition of Ternary Alloys: Developments in 1972-1978, *Surf. Technol.,* Vol 10, 1980, p 237-257
9. M.A. Shulgar and L.D. Tok, New Electrolytes for Chromium and Chromium Alloy Plating, *Zh. Vses. Khim, Ova. im D.I. Mendeleeva,* Vol 33 (No. 3), 1988, p 297-305
10. V.V. Bondar et al., Electrodeposition of Amorphous Chromium and Alloys Based on It, *Itogi Nauki Tekh., Ser.-Electrokhhim.,* Vol 33, 1990, p 37-49
11. "Electroplating of Chromium (Latest Citations from the Compendex Database)," NTIS Accession No. PB93-873412/XAB, NERAC, Inc., June 1993

Chromium-Iron, Chromium-Nickel, and Chromium-Iron-Nickel Alloys

Chromium-Iron Alloys. In contrast to nickel-iron alloys, which have been investigated to replace materials based on iron-nickel alloys in magnetic applications, relatively little work has been done on the chromium-iron analog. No well-defined, large-volume manufacturing application exists for the latter.

Chromium-iron alloys have been deposited from sulfate solutions. Early work in India favored a mixed sulfate-citrate solution (Ref 12), but more recent work used sulfates (Ref 13). Deposits were obtained at low pH levels, near-ambient temperatures, and low current densities (~10 A/dm^2, or 100 A/ft^2). In Japan, the emphasis has been on using modified, commercial trivalent chromium solutions (Ref 14, 15). One patent specifically calls for the presence of divalent chromium ion (Ref 16). The divalent chromium solution also operates at a pH less than 2.0, but at higher temperatures (30 to 80 °C, or 80 to 175 °F) and higher current densities (10 to 80 A/dm^2, or 100 to 800 A/ft^2). In the United States, some work has been performed with a mixed trivalent/hexavalent solution (Ref 17, 18, 19). These efforts focused on using organic additives, such as alcohol, to improve deposit properties. However, solution chemistry and plating efficiencies

changed with time, and the deposits tended to be lamellar (banded). Different bands contained different amounts of chromium (up to 90 wt%). The addition of barium carbonate was said to give crack-free coatings.

If suitable additives are used, then chromium can be deposited as an amorphous coating with excellent properties (Ref 19). Recently, it has been shown that amorphous coatings containing chromium, iron, and other minor elements (such as phosphorus and carbon) also can be electrodeposited. Corrosion-resistant amorphous alloys have been obtained from an acid-citrate-base solution containing sodium hypophosphite (Ref 20). Unfortunately, deposits from this solution with greater than 10 wt% Cr are rough and porous. Also, a semipermeable membrane is needed to prevent oxidation of trivalent chromium at the anode.

Other investigators have reported on the use of a chromic acid/formic acid solution containing ferrous chloride and sulfuric acid (Ref 21), or a sulfate-base solution containing organic additives such as sodium citrate and several organic acids (Ref 22). Deposition conditions were similar to those described above for chromium-iron alloys plated from trivalent chromium-type solutions. The sulfate-base solution type also required the use of a semipermeable membrane.

Chromium-Nickel Alloys. The early work on the deposition of chromium-nickel alloys from aqueous and nonaqueous (organic) plating solutions is summarized in Ref 23. Most of the solutions referenced gave poor deposits, and plating efficiencis were low. Deposit quality decreased as plating time increased and as the solution aged. As a result, banded deposits were often obtained, and each band had a slightly different composition. Subsequent work in the United States and Europe gave similar results.

For example, a patented process (Ref 24) calls for using a solution comprising chromous (trivalent) chloride, nickelous chloride, formic acid, boric acid, and sodium nitrate. The solution is operated at 20 to 60 °C (70 to 140 °F), and the chromium content in the deposit is a function of current density and the duty cycle of the pulsed current used. Low duty cycles and high current densities (>70 A/dm^2, or 700 A/ft^2) yield the highest chromium contents (about 60 to 70 wt%). The layered alloy structures are more corrosion resistant in acidic and chloride environments than sulfamate nickel, hard chromium deposits, or conventional stainless steels.

Continued interest has been shown in dimethylformamide-base solutions containing between 10 and 50% water (Ref 25, 26). Water content, temperature, and current density exert a strong influence on deposit quality and composition with such solutions. At low temperatures (7 to 15 °C, or 45 to 60 °F) and high current densities, chromium-rich alloys can be obtained. At higher temperatures (20 to 35 °C, or 70 to 95 °F), nickel-rich deposits are produced. Thicker deposits were cracked and layered in those solutions that contained chromic (hexavalent) chloride, nickelous chloride, ammonium chloride and boric acid, with vanadyl sulfate in some cases. Agitation helps to minimize the banding effect (Ref 26).

Two problems to avoid when plating chromium-nickel alloys are localized pH changes at the cathode surface, which can lead to the precipitation of a hydrated chromium compound, and excessive amounts of divalent chromium in trivalent chromium solutions (Ref 27). Divalent chromium is a strong reducing agent and can precipitate nickel as metal, leading to dark, powdery deposits. In some sulfate-base solutions, commercial nickel-chromium alloy anodes are not satisfactory (Ref 28) because they passivate, or dissolve, to produce hexavalent chromium, which interferes with the alloy deposition process. A plating cell that can alleviate this problem incorporates an ion-exchange membrane (Ref 29). If chloride ions are present in the solution, the problem with passivation can be overcome (Ref 28).

A Japanese patent (Ref 30) claims that satisfactory alloy deposits can be obtained from an organic (imide base) electrolyte containing boric acid and nickel and chromium sulfates. Bright deposits are said to be obtained at a pH equal to 2.5, a temperature of 50 °C (120 °F), and a current density of about 25 A/dm^2 (250 A/ft^2). A nickel-chromium alloy anode can be used.

Amorphous chromium-nickel deposits, which are similar to chromium-iron coatings, also can be obtained, either by electroless (Ref 31, 32) or electrolytic (Ref 33, 34) techniques. These amorphous coatings contain either phosphorus or boron as a minor alloying element, and they provide excellent corrosion resistance if they do not contain any microdiscontinuities, such as pores and cracks.

Chromium-Nickel-Iron Alloys. Although electrodeposited stainless steel type alloys have been deposited, they have had limited commercial success. These coatings did not exhibit comparable corrosion resistance, unless a significant thickness of nickel was first deposited. Although lustrous coatings can be obtained, they tend to be darker in color than the "blue-white" color traditionally associated with decorative chromium or polished stainless steel.

Several patents exist for depositing chromium-nickel-iron alloys (Ref 35, 36, 37), but only one process has been made available commercially. It is known as the "Oztelloy" process, originally promoted in the United Kingdom in the early 1980s (Ref 38). The coating consists of two layers. The first layer is a thick deposit of nickel, and the second layer is an alloy of 55Cr-10Ni-35Fe (wt%). To obtain good corrosion resistance, at least 8 wt% Ni is necessary. The solution is a complexed chloride-base electrolyte operating at a pH of 2.4, a temperature of 25 °C (77 °F), and a current density ranging from 12 to 22 A/dm^2 (120 to 220 A/ft^2). Carbon rods are used as anodes. The deposition rate is slow for the alloy layer (~0.2 to 0.3 μm/min, or 8 to 12 μin./min), and chlorine gas is evolved at the anode. Therefore, proper ventilation above the plating tank is required. Other investigators (Ref 39, 40) have attempted to use complexed, mixed chloride solutions to deposit ternary alloys, but with less success.

Ternary chromium-nickel-iron alloys have been obtained by some Japanese researchers (Ref 41), who used a mixed sulfamate electrolyte with an excess of the iron salt and a high concentration of the chromium salt. The solution also contained potassium citrate and potassium fluoride. It was operated at temperatures ranging from 30 to 50 °C (85 to 120 °F) and a current density ranging from 1.0 to 2.5 A/dm^2 (10 to 25 A/ft^2). The cathode efficiency ranged from 20 to 40%, and bright, fine-grained, homogeneous deposits were said to have been obtained. Fine-grained, semibright to fully bright deposits also have been obtained from a mixed sulfate solution containing boric acid and glycine (Ref 42). However, in chloride solutions, the corrosion resistance of those deposits was not as good as that of comparable conventional stainless steels.

In an effort to obtain homogeneous, crack-free deposits, techniques based on high-speed interrupted current (Ref 43) and periodically reversed current (Ref 44) have been tried, but their success also has been limited. Both pulsed current approaches used a trivalent chromium solution as the base electrolyte, with various additives. With the periodically reversed current approach, low-carbon steel anodes and a semipermeable membrane were used. The pulse frequency was 10 to 15 Hz, and the current density was approximately 20 A/dm^2 (200 A/ft^2). In the former approach, a semipermeable membrane was not necessary because a flowing electrolyte was used. Ternary iron-chromium-nickel alloys (stainless steels) were used as anodes. Deposits with low internal stress were obtained, but only thick coatings provided good corrosion resistance. Heat treating the highly stressed coatings obtained with the periodically reversed current technique did not improve their properties.

In the United States, a novel approach to producing chromium-nickel-iron coatings has been developed specifically for applications that require thick coatings or electroforms (Ref 45). The technique consists of codepositing chromium particles from a nickel-iron sulfate-base alloy plating solution. Subsequent heat treatment of the deposit at 1100 °C (2010 °F) for 8 h in a vacuum or under an inert gas yields a homogeneous, ternary, stainless steel type alloy coating. When depositing the coating, care must be exercised to prevent oxidation of the ferrous ions in the solution. When ferric ions are present, they prevent the occlusion of the chromium particles. The deposited coatings can be polished to provide a lustrous finish.

Other Chromium-Base Alloys. Attempts to deposit chromium-cobalt alloys have been made using fluoborate and dimethylformamide/water solutions (Ref 46). Like many chromium alloys that were plated from similar solutions, it was difficult to sustain a reasonable rate of deposition. Consequently, only thin films (with controlled composition) could be obtained.

Chromium-molybdenum alloy coatings have been used on automobile wheels (Ref 47). The plating solution for this alloy consisted of sulfuric acid, chromous oxide, ammonium molybdate, and sodium hexafluosilicate. It was operated at a temperature of 48 °C (120 °F) and a current density of 25 A/dm^2 (250 A/ft^2).

The literature (Ref 48, 49) also contains a number of references to the deposition of chromium-zinc coatings, with zinc being the major alloying element. Russian workers have used an acidic glycine-base solution, both with and without the application of a pulsed current. Some Japanese steel companies have developed techniques for depositing a chromium-zinc alloy on steel sheets to improve either the subsequent bonding of a (modified) polyethylene film (Ref 50, 51) or the corrosion resistance of the alloy (Ref 52, 53). A chloride-base solution has been used to deposit a ternary zinc-nickel-chromium alloy for similar applications (Ref 54).

Other alloying elements that have been deposited with chromium include gold, molybdenum, rhenium, selenium, tellurium, titanium, vanadium, and zirconium.

The bath compositions and operating parameters for depositing binary and ternary chromium-base alloys are summarized in Table 2. A discussion of the properties of some of these and other electrodeposited alloys is provided in Ref 55.

Table 2 Summary of bath compositions and plating parameters for deposition of selected chromium-base alloys

Alloy	Bath composition	pH	Operating temperature		Current density		Anode	Comments	Ref
			°C	°F	A/dm^2	A/ft^2			
Chromium-iron	250 g/L CrO_3; 72.2 g/L $CrCl_3$; 62.6 g/l $FeCl_2$; 1 ml/L H_2SO_4; 20 ml/L CH_3OH	. . .	40	105	25	250	Lead	Current efficiency 55% (max), decreased as bath aged; shiny deposits	18
Chromium-iron	250 g/L CrO_3; 72.2-143 g/L $FeCl_2$; 1 ml/L H_2SO_4; 20 ml/L CH_3OH	. . .	40	105	11-35	110-350	Lead	Composition and current efficiency changed as bath aged; shiny deposits	18
Chromium-iron	100 g/L CrO_3; 5 g/L H_2SO_4; 60 g/L $FeCl_2$; 20 ml/L (85%) HCOOH	. . .	50	120	40	400	Lead-5% antimony	Amorphous deposits, gray, slightly bright deposits; 6% current efficiency	21
Chromium-iron	167 g/L $Cr_2(SO_4)_3$; 40 g/L $Fe(NH_4)(SO_4)_2$; 80 g/L $(NH_4)_2SO_4$; 10 g/L NaH_2PO_2; 20 g/L K_2SO_4	1-2	30	85	20-90	200-900	Platinum	Nafion membrane used lowered chromium content in deposit; current efficiency ~10% (max), deposits contained phosphorus and were amorphous	22
Chromium-nickel	100 g/L CrO_3; 250 g/L nickel fluoborate; plus CH_3COOH	. . .	20	70	50	500	. . .	Alloys contained 9-10% Cr	23
Chromium-nickel	300 g/L $CrCl_3$; 100 g/L $NiCl_2$	. . .	20	70	20	200	. . .	Alloy contained 9% Cr; cathode efficiency 25%	23
Chromium-nickel	400 g/L $CrCl_3$; 100 g/L nickel fluoborate; plus CH_3OH	. . .	20	70	50-100	500-1000	. . .	Alloys contained 15-30% Cr	23
Chromium-nickel	100 g/L $CrCl_3$; 30-40 g/L $NiCl_2$; 30-40 H_3BO_3; 80 g/L sodium citrate; 35-40 g/L HCOOH; plus other organic additives	~3.5	35	95	10-100	100-1000	. . .	Pulsed current; alloys contained 1-60% Cr; hydrogen bromide optional additive	23
Chromium-nickel	270 g/L $CrCl_3$; 100 g/L $NiCl_2$; 30 g/L NH_4Cl; 10 g/L boric acid; 1 g/L vanadium chloride	2.4	7-20	45-70	1	10	. . .	Electrolyte was dimethylformamide with 10% water; higher temperatures decreased chromium content	25
Chromium-nickel	0.8M $CrCl_3$; 0.2M $NiCl_2$; 0.5M NH_4Cl; 0.5M NaCl;	. . .	25	75	4	40	Graphite	Electrolyte was dimethylformamide with 25% water; composition changed	27

	0.15M H_3BO_3							as bath aged	
Chromium-nickel	0.5M $Cr_2(SO_4)_3$; 0.5M $NiCl_3$; 1M lactic acid; 1.4M NaCl	. . .	60	140	20-50	200-500	Nichrome	Nichrome not satisfactory if chloride not present	28
Chromium-nickel-iron	0.15-0.3M chromium sulfamate; ~0.01M nickel sulfamate; 0.4-0.8 iron sulfamate; 0.25-0.5 potassium citrate; plus potassium fluoride	2-4	30-50	85-120	1-25	10-250	. . .	Current efficiency 24-40%; excellent brightness	41
Chromium-nickel-iron	36.4 g/L $Cr_2(SO_4)_3$; 1.47 g/L $NiSO_4$; 2.7 g/L $FeSO_4$; 147 g/L sodium citrate; 50 g/L H_3BO_3; plus sodium and potassium sulfates, sodium disulfite	. . .	25	75	5-20	50-200	Steel	Semipermeable membrane and pulsed current used	44
Chromium-nickel-iron	0.8M $CrCl_3$; 0.2M $NiCl_2$; 0.03M $FeCl_2$; 0.5M NH_4Cl; 0.5M NaCl; 0.15M H_3BO_3	~2	25	75	4	40	Graphite, steel	Electrolyte was dimethylformamide with 50% water; semibright to bright deposits	39
Chromium-nickel-iron	0.2M $KCr(SO_4)_2$; 0.45M $NiSO_4$; 0.35M $FeSO_4$; 0.5M H_3BO_3; 1M glycine	2	20-30	70-85	15-20	150-200	Platinum	Glass frit separator, current efficiency 50-55%; bright deposits	42

References cited in this section

12. P. Elsie et al., Iron-Chromium Alloy Deposition, *Met. Finish.*, Vol 68 (No. 11), 1970, p 52-55, 63
13. R. Murti et al., Electrodeposition of Iron-Chromium Alloy from Sulfate Solutions, *J. Electrochem. Soc. India,* Vol 38 (No. 1), 1989, p 6-10
14. T. Yoshida et al., Electrochemical Behavior of Electrodeposited Iron-Chromium Alloys, *Asahi Garasu Kogyo Gijutsu Shoreikai Kenkyu Hokaku,* Vol 17, 1970, p 195-209
15. T. Hayashi and A. Ishihama, Electrodeposition of Chromium-Iron Alloys from Trivalent Chromium Baths, *Plat. Surf. Finish.,* Vol 66 (No. 9), 1979, p 36-40
16. H. Kagechika et al., "Chromium Alloy Bath," U.S. Patent 4,673,471, June 1987
17. A.M. Kasaaian and J. Dash, "Effects of Chromium Electroplating Solution Composition on Properties of the Deposits," paper presented at Sur/Fin '85 (Detroit, MI), AESF Society, July 15-18, 1985
18. A.M. Kasaaian and J. Dash, "Chromium-Iron Alloy Plating Using Hexavalent and Trivalent Chromium Ion Solutions," U.S. Patent Application, May 1986
19. S. Hoshino et al., The Electrodeposition and Properties of Amorphous Chromium Film Prepared from Chromium Acid Solutions, *J. Electrochem. Soc.,* Vol 133 (No. 4), 1986, p 681-685
20. P.K. Ng, "Iron-Chromium-Phosphorus Bath," U.S. Patent 4,758,314, July 1988
21. R.Y. Tsai and S.T. Wu, Amorphous Chromium Electroplating with Iron as an Alloying Agent, *J. Electrochem. Soc.,* Vol 137 (No. 9), 1990, p 2803-2806
22. J.C. Kang and S.B. Lalvani, Electrodeposition and Characterization of Amorphous Fe-Cr-P-C Alloys, *J.*

Appl. Electrochem., Vol 22, 1992, p 797-794

23. C.H. Chisholm, Electrodeposition of Nickel-Chromium Alloys from Solvent Based Electrolytes--I: Review, Abstract No. 238, *Extended Abstr.,* Vol 83 (No. 2), 1983, p 374-375
24. D.S. Lashmore, "Process and Bath for Electroplating Nickel-Chromium Alloys," U.S. Patent 4,461,680, July 1984
25. C.H. Chisholm and M.R. El-Sharif, Deposition of Chromium-Nickel Alloys from Dimethylformamide/Water Electrolytes, *Plat. Surf. Finish.,* Vol 72 (No. 8), 1985, p 58-61
26. C.H. Chisholm and M.R. El-Sharif, Chromium-Nickel Codeposits from Dimethylformamide Baths Containing 10 Percent Water, *Plat. Surf. Finish.,* Vol 72, 1985, p 82-84
27. A. Watson et al., "The Role of Chromium II and VI in the Electrodeposition of Chromium-Nickel Alloys from Trivalent Chromium-Amide Electrolytes," paper presented at Annual Tech. Conf. (Bournemouth, UK), IMF, April 15-19, 1986
28. I.A. Polunina and A.J. Falicheva, Nichrome Soluble Anode for Electrodeposition of Nickel-Chromium Alloys, *Z. Metallov.,* Vol 24 (No. 2), 1988, p 258-261
29. H. Ariga, Chromium Alloy Plating by Ion Exchange Membrane, *Jpn. Kokai Tokkyo Koho,* No. 86/00594, 1986
30. M. Kamata and A. Shigeo, Electroplating of Nickel-Chromium Alloys Using Chromic Complexes, *Jpn. Kokai Tokkyo Koho,* No. 86/113,788, 1986
31. I. Nakayama et al., A Study of Electroless Nickel-Chromium Alloy Plating Baths, *Hyomen Gijutsu,* Vol 43 (No. 9), 1992, p 835-838
32. C.E. Cedarleaf, Solution for Electroless Chromium Alloy Plating, U.S. Patent 4,028,116, June 1977
33. J. Gruberger et al., A Sulfate Solution for Deposition of Nickel-Chromium-Phosphorus Alloys, *Surface Coat. Technol.,* Vol 53 (No. 3), 1992, p 203-213
34. K.L. Lin and J.K. Ho, Electrodeposited Nickel-Chromium and Nickel-Chromium-Phosphorus Alloys, *J. Electrochem. Soc.,* Vol 39 (No. 5), 1992, p 1305-1310
35. B.A. Shenoi et al., "Electrodeposition of Iron-Chromium-Nickel Alloy," Indian Patent 114,867, 1970
36. E. Terada, Improvement of Stainless Steel Plating Method, *Jpn. Kokai Tokkyo Koho,* No. 55-148,794, 1980
37. G.R. Schaer, "High Rate Chromium Alloy Plating, " World Patent 82103095, September 1982
38. L. Free, "Electrodeposition of a Stainless Steel Finish," paper presented at Annual Tech. Conf. (Bournemouth, UK), IMF, April 15-19, 1986
39. C.H. Chisholm and M.R. El-Sharif, Sustained Electrodeposition of Chromium-Nickel-Iron Ternary Alloys by Control of Transient Trivalent Chromium Levels, *Proc. Sur./Fin. '87* (Chicago, IL), AESF Society, July 13-16, 1987
40. M. Yasuda et al., Electroplating of Iron-Chromium-Nickel Alloys from the Chloride-Glycine Baths, *Kinzuku Hyomen Gijutsu,* Vol 39, 1988, p 19
41. T. Ishiguro and H. Ochiai, Studies on the Electrodeposition of Iron-Chromium-Nickel Alloys from Sulfamate Solution - Part I, *Puretingu to Kotingu,* Vol 6 (No. 2), 1986, p 79-90
42. M. Matsuoko et al., Electrodeposition of Iron-Chromium-Nickel Alloys, *Plat. Surf. Finish.,* Vol 74 (No. 10), 1987, p 56-60
43. M.F. El-Shazly et al., "The Development of Electrodeposited Stainless Steel Type Alloys," Final Report of Multiclient Research Project, Battelle National Laboratory, December 30, 1986
44. J. Krüger and J.P. Nepper, Galvanic Deposition of Iron-Chromium-Nickel Alloy Using Modulated Current, *Metalloberfläche,* Vol 40, 1986, p 107-111
45. G.R. Smith and J.E. Allison, Jr., "Alloy Coating Method," U.S. Patent 4,601,795, July 22, 1986
46. C.U. Chisholm, Cobalt-Chromium Coatings by Electrodeposition: Review and Initial Experimental Studies, *Electrod. Surf. Treat.,* Vol 3 (No. 5-6), 1975, p 321-333
47. L. Herbansky, Czechoslovakia Patent 214,553, 1985
48. N.B. Berezin et al., Role of Complex Formation During the Cathodic Deposition of Zinc-Chromium

Electroplates from Acidic Glycine-Containing Baths, *Zashch. Met.,* Vol 28 (No. 6), 1992, p 961-966

49. N.B. Berezin et al., Electrodeposition of Zinc-Chromium Alloy with a Pulsed Current, *Zashch. Met.,* Vol 29 (No. 1), 1993, p 99-105
50. M. Matsumoto et al., Manufacturing of Corrosion-Resistant Steel Laminates, *Jpn. Kokai Tokkyo Koho,* No. 92/357439, 1992
51. M. Kimoto et al., Electroplating of Zinc-Chromium Alloy on Steel Sheet, *Jpn. Kokai Tokkyo Koho,* No. 93/09779, 1993
52. T. Komori et al., Manufacture of Steel Sheet Electroplated with Zinc-Chromium Alloy, *Jpn. Kokai Tokkyo Koho,* No. 92/36495, 1992
53. H. Sakai et al., Manufacture of Steel Sheet Electroplated with Zinc-Chromium Alloy, *Jpn. Kokai Tokkyo Koho,* No. 91/120393, 1991
54. C. Kato et al., Alloy Electroplated Steel Sheet with High Corrosion Resistance, and its Manufacture, *Jpn. Kokai Tokkyo Koho,* No. 90/031394, 1990
55. W.H. Safranek, *The Properties of Electrodeposited Metals and Alloys,* 2nd ed., The AESF Society, 1986

Multiple-Layer Alloy Plating

Daniel T. Schwartz, University of Washington

Introduction

MULTIPLE-LAYER ALLOY PLATING is an emerging technology for engineering desirable properties into thin surface layers through the use of carefully controlled deposit microstructures. As implied by the name, multiple-layer alloy electrodeposition involves the formation of an inhomogeneous alloy consisting of lamellae of different composition, as shown schematically in Fig. 1 for a binary alloy composed of species A and B. Each lamella of species A (or species B) in the film has a nearly uniform thickness λ_A (or λ_B). The modulation wavelength ($\lambda = \lambda_A + \lambda_B$) characterizes the imposed compositional microstructure and typically takes a value anywhere from angstroms to microns in thickness. Multiple-layer thin films with spatially periodic compositional microstructures of the type shown in Fig. 1 are sometimes referred to in the literature as composition-modulated alloys (CMAs) or as superlattice alloys. A wide variety of binary and ternary alloy systems have been electroplated as multiple-layer films, including Ni/Cu, Ag/Pd, Cu/Ni-Fe, Cu/Ag, Cu/Co, Cu/Pb, Cu/Zn, Ni-P/Ni-Co-P, and Ni/Ni-P, to name a few. In many cases these alloys can be electroplated from a single electrolyte bath using either current or potential pulsing schemes. A common feature to many single-bath electroplating strategies is the use of hydrodynamic modulation that is synchronized in some manner with the pulsed plating. Multiple-layer alloys are often found to exhibit unusual (and sometimes highly desirable) mechanical, magnetic, electrical, and chemical properties, especially when the modulation wavelength λ is of the order of nanometers.

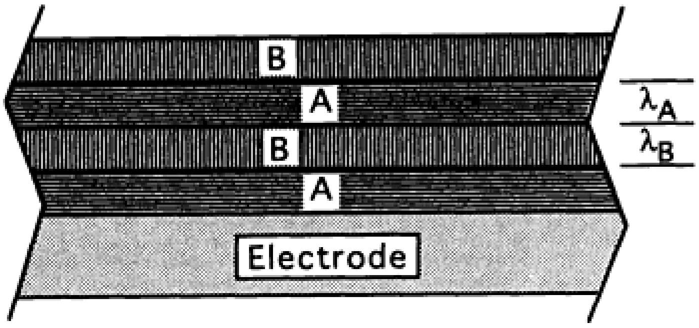

Fig. 1 Schematic representation of a multiple-layer alloy consisting of alternating lamellae of species A and species B. The thicknesses of the A and B layers are given by λ_A and λ_B, respectively. The modulation wavelength that characterizes the multiple-layer superlattice structure is $\lambda = \lambda_A + \lambda_B$. Multiple-layer alloys often exhibit a spatially periodic compositional wave throughout the film, rather than the discrete interface depicted between each lamella.

In short, multiple-layer alloy plating combines the best attributes of electroplating--high throughput, low cost, and simple equipment--with an extra degree of freedom to engineer surface film properties. The potential impact of multiple-layer plating on the performance and economics of engineered surface layers appears to be large, although most commercial applications of the technology are still being developed. This article is focused mainly on the science and engineering of multiple-layer metallic alloys with nanometer-scale modulation wavelengths, because these are the materials that have gained the most attention for surface engineering. Throughout this chapter a solidus, or virgule (/) is used to denote the two materials that are spatially modulated to form a superlattice structure, whereas a dash between elements indicates that the species is an alloy. Using this nomenclature, Fig. 1 shows an A/B alloy. If species A happens to be copper and species B is a Ni-Fe alloy, then the figure denotes a Cu/Ni-Fe multiple-layer alloy.

Applications

For the most part, applications that take advantage of the material properties of nanometer-scale multiple-layer films are still in the development stage. Within the past few years, however, a number of promising applications have emerged that seem especially well suited for multiple-layer alloy plating.

The magnetic properties of electroplated multiple-layer alloys have received a great deal of attention for applications related to magnetic recording. For example, Ref 1 shows that multiple-layer thin films of Cu/Ni-Fe ($\lambda_{Cu} \approx 10$ nm and $\lambda_{Ni\text{-}Fe} \approx 50$ nm) eliminate the classical edge-closure domains that give rise to noise in thin-film inductive heads. At the same time, the remaining magnetic properties of the multiple-layer Cu/Ni-Fe alloy are comparable to homogeneous Ni-Fe alloy properties. The combination of reduced domain noise in the multiple-layer alloy with excellent magnetic properties makes these materials extremely attractive for thin-film inductive heads with very narrow track width. It is also likely that electroplated multiple-layer alloys will soon affect the performance of magnetoresistive head technology, given the recent discovery of giant magnetoresistance in electroplated Cu/Co-Ni-Cu multiple-layer alloys with $\lambda_{Cu} < 1$ nm (Ref 2).

Electroplated multiple-layer foils of Ni/Cu alloy (with $\lambda_{Cu} \approx 2$ nm and $\lambda_{Ni} \approx 18$ nm) exhibit tensile strengths that exceed homogeneous nickel or copper foil strengths by more than a factor of three (Ref 3), and steel that is coated with an electroplated Ni/Cu multiple-layer film ($\lambda_{Cu} \approx 3.8$ nm and $\lambda_{Ni} \approx 3.8$ nm) exhibits a high resistance to sliding wear (Ref 4). Because of these enhanced mechanical properties, electroplated Ni/Cu multiple-layer surface coatings are being used to extend the lifetime of printing press components that are subject to sliding-wear damage.

Other applications of electroplated multiple-layer thin films that are being explored include the use of Cu/Ag and Cu/Co alloys for high-temperature applications in rocket thrust aligners, where protective surface films are used to minimize hydrogen embrittlement.

References cited in this section

1. L.T. Romankiw and J.D. Olsen, Electroplated Laminated Cu/Ni-Fe Films from a Single Plating Bath for Inductive Recording Heads and Magnetic Shields, *Proceedings of the Symposium on Magnetic Materials, Processes, and Devices,* L.T. Romankiw and D.A. Herman, Jr., Ed., Electrochemical Society, 1990, p 339-345
2. M. Alpers, K. Attenborough, R. Hart, S.J. Lane, D.S. Lashmore, C. Younes, and W. Schwarzacher, Giant Magnetoresistance in Electrodeposited Superlattices, *Applied Physics Letters,* Vol 63, 1993, p 2144
3. S. Menezes and D.P. Anderson, Wavelength-Property Correlation in Electrodeposited Ultrastructured Cu/Ni Multilayers, *Journal of the Electrochemical Society,* Vol 137, 1990, p 440
4. A.W. Ruff and D.S. Lashmore, Effects of Layer Spacing on Wear of Ni/Cu Multilayer Alloys, *Wear,* Vol 151, 1991, p 245

Process Description and Engineering Parameters

Nanometer-wavelength multiple-layer alloys were initially fabricated in the late 1960s using vapor-phase evaporation to test theories on the thermodynamic stability and interdiffusion of layered materials. Although vacuum evaporation techniques have been used to form reproducible multiple-layer thin films, sputtering and electroplating techniques are currently the preferred fabrication methods. Multiple-layer alloys can be electroplated from a single bath that contains ions of all of the species to be deposited, or plating can take place sequentially by moving the electrode between multiple

plating baths that contain individual species of interest. From a throughput standpoint, single bath plating techniques are preferred, although not all electrolyte chemistries and species redox properties are compatible with single-bath plating.

Multiple-layer alloy plating from a single bath typically requires that the deposition of each species in the multiple-layer pair occur at potentials that differ by more than 100 mV. The more noble component of the alloy is normally plated at the mass transfer limited rate, and the less noble component is plated under kinetics limited conditions. Figure 2 is a schematic showing deposition rate versus potential for an ideal multiple-layer alloy plating bath. The more noble species A plates readily at potentials that are negative of V_A, and the less noble species B plates at potentials negative of V_B. Within the potential window between V_A and V_B, it is possible to electroplate a film that is essentially pure in the noble component A. Conversely, the less noble component B is always codeposited with the more noble species A to form a B-A alloy. Periodically switching the potential (or current) between the region where pure A deposits and the region where B-A alloy deposits results in an A/B-A multiple-layer film. The thickness of each lamella is related to the deposition charge through Faraday's law (a knowledge of the current efficiency is also needed). Figure 2 suggests that species A is codeposited with species B at the mass transfer limited rate ($R_{A.MT}$). The mole percent of species B (in the B-A alloy) is dictated largely by the potential (or current) at which deposition occurs, the strength of agitation in the cell, and the relative concentrations of reducible species A and B that are dissolved in the electrolyte. Decreasing the agitation during species B deposition serves to reduce the rate of which species A ($R_{A.MT}$) is added to the film, and increasing the concentration ratio of B to A in the electrolyte directly affects the ratio of $R_{B.MT}$ to $R_{A.MT}$. The formulation of a multiple-layer plating bath normally begins with an electrolyte that is known to work well for plating the less noble component B at high rates. A small concentration of the more noble species A ($\approx$1% of B) is then added to the bath in an effort to minimize the amount of A that codeposits with B. Using this strategy, it is possible to make an A/B alloy in which each lamella is nearly pure (>95%).

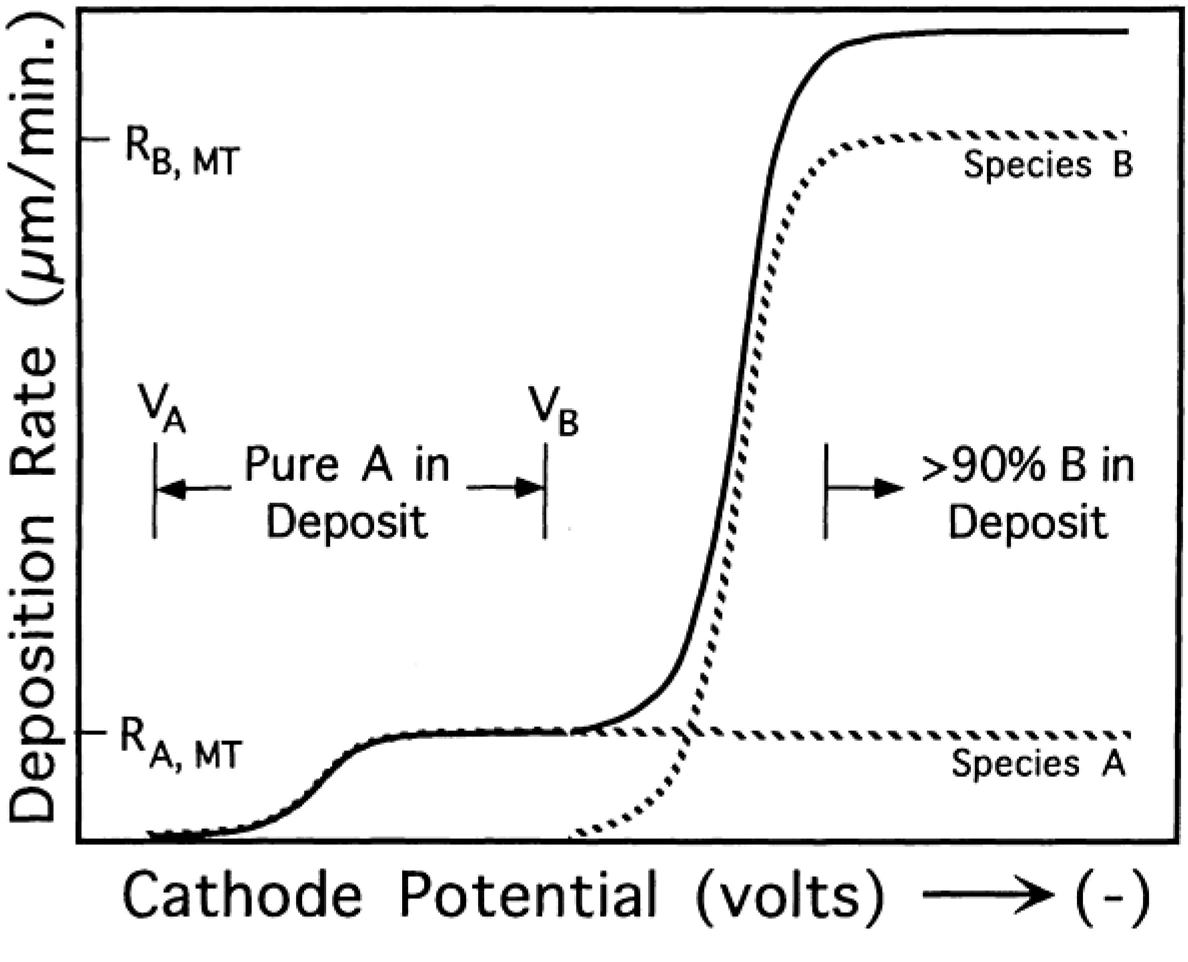

Fig. 2 Schematic of ideal deposition rate vs. applied cathodic potential characteristics for electroplating an A/B multiple-layer alloy. The dashed lines denote deposition rates for plating each individual species, and the solid line represents the total deposition rate. Note that pure A is deposited in the potential window between the reversible potential for species A (V_A) and the reversible potential for species B (V_B), whereas an impure A-B

alloy forms at potentials cathodic of V_B.

The ideal deposition conditions represented in Fig. 2 are nearly matched in reality by some alloy systems. For example, a variety of bath chemistries and deposition conditions have been found for plating Ni/Cu multiple-layer alloys, where copper is more noble than nickel by nearly 600 mV. For the case of Ni/Cu alloy plating, one often starts with a nickel-sulfate-based electrolyte (Watts nickel bath) or a nickel sulfamate bath. Small amounts of copper sulfate (50 to 1000 ppm Cu^{+2}) are then added to the bath. Table 1 shows typical sulfate and sulfamate plating baths for making Ni/Cu multiple-layer alloys. The deposition protocols for creating multiple-layer Ni/Cu alloys from these baths are nearly identical.

Table 1 Characteristic plating baths for making nanometer-scale Ni/Cu multiple-layer alloys

Plating bath	Typical bath composition	Temperature, °C
Nickel sulfate	330 g/L $NiSO_4 \cdot 6H_2O$, 45 g/L $NiCl_2 \cdot 6H_2O$, 35 g/L H_3BO_4, 0.05-0.1 g/L Cu^{+2}, 0.1 g/L coumarine, 0.1 g/L sodium dodecyl sulfate, pH ≈ 2	≈ 60
Nickel sulfamate	70-90 g/L Ni, 0.3-0.9 g/L Cu (as sulfate), 30-45 g/L boric acid, 0.15 g/L sulfamate nickel anti-pit, pH ≈ 3.5	≈ 50

Pulsed-potential plating of Ni/Cu multiple layers from either bath listed in Table 1 requires the copper lamella to be deposited at a potential near -0.4 V (referenced against a saturated calomel electrode, SCE) and each nickel lamella to be plated at a potential between -1.0 and -1.5 V versus SCE. Under these conditions, the copper deposition rate is controlled by the rate of Cu^{+2} mass transfer, and the nickel deposition rate is controlled by either electrode kinetics or by mixed mass transfer and kinetics. Copper plating proceeds with nearly 100% current efficiency, but the nickel plating has a lower current efficiency due to the simultaneous evolution of hydrogen. The electrolyte is often strongly agitated during copper plating so that higher mass transfer limited copper deposition rates are achieved. Conversely, the agitation rate is often reduced when the nickel is deposited so that the purity of the nickel layer can be increased by reducing the rate of copper codeposition. An important feature of the single-plating bath formulations described here is that the more noble species, copper, has a low deposition rate compared to nickel and therefore requires a longer duration pulse to achieve a comparable layer thickness. Reference 4 provides an example of pulsed-potential plating of Ni/Cu multiple-layer alloys from a sulfamate bath.

Pulsed-current plating is somewhat more common for making high-quality multiple-layer alloys than is pulsed-potential plating. Moreover, the best results are achieved using a triple-current-pulsing scheme that employs a brief high-current nickel deposition pulse, followed by a brief zero-current pulse and then a long-duration, low-current copper deposition pulse. The size and duration of each pulse depend on details of the electrolyte agitation, the bath formulation, and the modulation wavelength desired. The two triple-pulse-plating protocols given in Table 2 are representative of conditions that lead to coherent nanometer-wavelength Ni/Cu multiple-layer alloys (both studies used plating baths that fall in the range of the sulfamate formulations given in Table 1). The triple-pulse protocol given in Ref 3 results in a high plating rate and a high nickel alloy. The high plating rate is achieved, in part, by agitating the cell using a rotating cylinder cathode. Also contributing to the high plating rate is the formation of a high-nickel-content alloy (recall that the less noble component normally plates at high rates compared to the more noble component). The triple-pulse protocol given in Ref 5 results in lower plating rates and higher-copper-content alloys than the protocol used in Ref 3. The low overall deposition rate reported in Ref 5 is a direct result of forming a high-copper alloy using a quiescent plating bath. In the protocol given in Ref 3, the strength of agitation is modulated during each stage of current pulsing. The use and synchronization of a time-periodic agitation scheme should be carefully considered when developing a multiple-layer alloy plating protocol (Ref 6). Additional information is available in the article "Pulsed-Current Plating" in this Volume.

Table 2 Two representative triple-current-pulsing schemes for plating coherent, nanometer-scale Ni/Cu multiple-layer alloys from sulfamate electrolytes

Characteristic triple-pulse condition	Bath agitation	Growth rate (μm/h)	$\lambda Ni/\lambda Cu$	Reference

Nickel pulse: 90 mA/cm^2 for ≈ 0.7 s	60 rpm			3
"Rest" pulse: 0 mA/cm^2 for 0.25 to 1 s		≈ 7	≈ 10	
Copper pulse: 1.5 mA/cm^2 for ≈ 4 s	600 rpm			
Nickel pulse: 12-20 mA/cm^2 for ≈ 0.5 s	None			5
"Rest" pulse: 0 mA/cm^2 for ≈ 0.5 s		≈ 1	≈ 2	
Copper pulse: 0.3 mA/cm^2 for ≈ 11 s	None			

Multiple-layer alloys that are plated using two baths are not limited to species with widely separated deposition potentials, nor is it necessary to modify well-established bath chemistries. However, plating a multiple layers using two baths requires the substrate cathode to be periodically moved between the baths. If transferring the cathode between baths takes substantial time, then forming nanometer-wavelength multiple-layer alloys with appreciable total film thickness becomes prohibitively slow. Reference 7 describes the use of a novel dual-bath plating cell that provides nanometer-wavelength Ni/Ni-P multiple-layer alloys at a high deposition rate (2 to 4 μm/h). The cell employs a disk-shape cathode substrate that rotates with an angular velocity of 12 to 20 rpm. The rotating substrate is exposed to each plating bath once per revolution. After each exposure to a plating bath, the cathode is mechanically wiped free of electrolyte to avoid cross-contamination of the electrolytes. A voltage divider is used with a single power supply to control the current flowing through each bath (each bath contains a separate nickel anode). Conventional nickel and nickel phosphorous bath formulations are used in the dual-bath cell to deposit each lamella of the multiple layer. Compared to single-bath strategies, the dual-bath approach substitutes a mechanically complex plating apparatus for a much simpler electrolyte formulation.

A new two-bath electroplating strategy for making multiple-layered materials with molecular-level compositional control is described in Ref 8. The technique, called electrochemical atomic layer epitaxy (ECALE), takes advantage of the underpotential deposition (UPD) phenomenon that occurs when the first monolayer (or partial monolayer) of a surface film is formed. The energetics of the first atomic layer of a deposit is often favorable compared to bulk material deposition, thus resulting in deposition at potentials that are noble of bulk deposition. The ECALE concept has been tested for Cd/Te electrodeposition. The chemistry of each bath was manipulated to provide cathodic UPD of cadmium and anodic UPD of tellurium (at potentials that did not strip the cadmium monolayer from the surface). Low-energy electron diffraction verified the formation of ordered cadmium deposits on tellurium and ordered tellurium deposits on cadmium (Ref 8). Despite the initial verification of the ECALE concept, practical applications of the technique await further development.

References cited in this section

3. S. Menezes and D.P. Anderson, Wavelength-Property Correlation in Electrodeposited Ultrastructured Cu/Ni Multilayers, *Journal of the Electrochemical Society,* Vol 137, 1990, p 440
4. A.W. Ruff and D.S. Lashmore, Effects of Layer Spacing on Wear of Ni/Cu Multilayer Alloys, *Wear,* Vol 151, 1991, p 245
5. D.S. Lashmore and M.P. Dariel, Electrodeposited Cu/Ni Textured Superlattices, *Journal of the Electrochemical Society,* Vol 135, 1988, p 1218
6. D.T. Schwartz, P. Stroeve, and B.G. Higgings, Electrodeposition of Composition-Modulated Alloys in a Fluctuating Flow Field, *AIChE Journal,* Vol 35, 1989, p 1315
7. L.M. Goldman, B. Blanpain, and F. Spaepen, Short Wavelength Compositionally Modulated Ni/Ni-P Films Prepared by Electrodeposition, *Journal of Applied Physics,* Vol 60, 1986,p 1374

8. B.W. Gregory, D.W. Suggs, and J.L. Stickney, Conditions for the Deposition of CdTe by Electrochemical Atomic Layer Epitaxy, *Journal of the Electrochemical Society,* Vol 138, 1991, p 1279

Characterization of Multiple-Layer Alloys

One of the most common methods for characterizing nanometer-wavelength multiple-layer alloys is x-ray diffraction (XRD), which provides information about the crystalline texture and superlattice structure of a multiple-layer material. The superlattice structure of the alloy is revealed as satellite peaks located at low and high angles around the crystallographic Bragg peaks in the diffraction pattern. The dispersion angle of the satellite peaks provides the modulation wavelength of the multiple layer, and the number and amplitude of the satellite peaks provide a measure of the interfacial "sharpness" between each lamella. The wavelength of a multiple-layer alloy (λ) is quantitatively related to the first-order satellite peak locations through the relationship

$$\lambda = \frac{\lambda_x}{\sin(\theta^+) - \sin(\theta^-)}$$

where λ_x is the x-ray source wavelength, θ^+ is the high-angle satellite peak location, and θ^- is the low-angle satellite peak location. Transmission electron microscopy and Auger electron spectroscopy (used with sputtering) have both been employed to study nanometer-scale structure in multiple-layer alloys, but these techniques require significantly more sample preparation and handling than XRD. Moreover, the sample preparation for these techniques requires destructive treatment of the multiple-layer material.

Once the structural characteristics of a multiple-layer alloy are known, then the material properties are normally analyzed using conventional techniques. Relationships have been observed between the superlattice structure of multiple-layer alloys and their mechanical properties (e.g., tensile strength, moduli), their electrical properties (e.g., conductivity), their magnetic properties (e.g., magnetoresistance, magnetostriction, saturation magnetization), and their chemical properties (e.g., corrosion resistance).

The growing technological need for inexpensive, high-performance thin-film materials is propelling academic and industrial research efforts to understand the processing-structure-property relationships in a wider range of plated multiple-layer alloys. The degree to which plated multiple-layer films will ultimately meet the technological challenges that face surface engineers remains to be answered.

Selective (Brush) Plating

Introduction

SELECTIVE PLATING, also known as brush plating, differs from traditional tank or bath plating in that the workpiece is not immersed in a plating solution (electrolyte). Instead, the electrolyte is brought to the part and applied by a hand-held anode or stylus, which incorporates an absorbent wrapping for applying the solution to the workpiece (cathode). A direct current power pack drives the electrochemical reaction, depositing the desired metal on the substrate. In practice, movement between the anode and cathode is required for optimum results when plating, stripping, activating, and so on. A schematic of the selective plating process appears in Fig. 1.

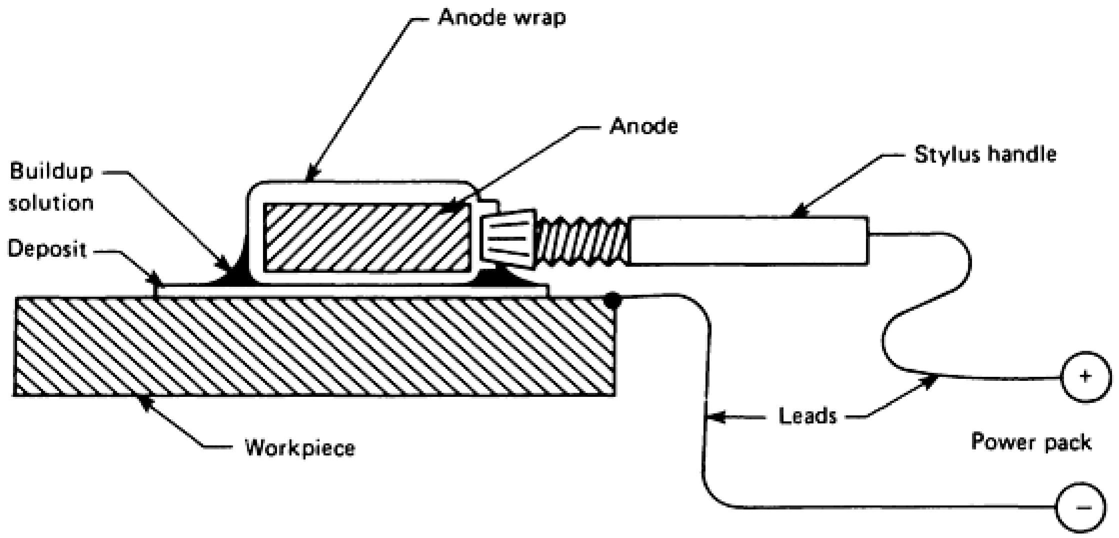

Fig. 1 Manual operation of selective plating process. Source: Ref 1

Currently, a broad range of elements and alloys can be brush plated; the majority are listed in Table 1. Even though selective plating can be done in a tank, labor-intensive masking and subsequent removal often make this option impractical.

Table 1 Energy factors for selective plating

Element or alloy	Energy factor
Cadmium	0.006
Chromium	0.200
Cobalt	0.014
Copper	0.013
Gallium	0.014
Gold	0.006
Indium	0.009
Iridium	0.069
Iron	0.025

Lead	0.006
Mercury	0.008
Nickel acid	0.047
Nickel alkaline	0.017
Nickel, black	0.025
Nickel, natural	0.025
Palladium	0.019
Platinum	0.015
Rhodium	0.030
Silver, noncyanide	0.750
Silver, pure	0.004
Babbitt	0.006
Brass	0.017
Bronze	0.017
Cobalt-nickel	0.019
Cobalt-tungsten	0.015
Nickel-cobalt	0.020
Nickel-tungsten	0.020
Tin-cadmium	0.007
Tin-indium	0.008
Tin-lead (90/10)	0.006

Tin-lead (60-40)	0.007
Tin-nickel	0.010

Note: The energy factor is the ampere-hours required to produce a deposit thickness of 0.003 mm (0.0001 in.) on a square inch of area.

Acknowledgements

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Reference

1. M. Rubinstein, *Electrochemical Metallizing,* Vinmar Press, 1987

Advantages and Limitations

The key advantage of selective plating is portability. Many systems can be moved to various locations in a production facility or be transported to the job site. Selective plating is also versatile; it permits most electroplate types to be deposited onto any conductive substrate that can be touched with an electrode. Cast iron, copper, steel, stainless steel, high-temperature nickel-base alloys, aluminum, and zinc are commonly plated by this method and exhibit good adhesion. Limited adhesion can be obtained with other materials, such as titanium, tungsten, and tantalum.

Selective plating allows higher current densities than tank plating, which translate into higher deposition rates, up to 0.010 mm/min (0.0004 in./min). In addition, inherently precise thickness control permits plate buildup or repair without the need for subsequent machining. In regard to deposit hardness, a 70 HRC trivalent chrome is available for selective plating of thick deposits, which places selective plating on a par with hexavalent tank chrome. The exceptions are the harder deposits of cobalt and gold (Table 2). Table 3 provides a point-by-point comparison of selective plating with competitive processes, including tank plating.

Table 2 Deposit hardness attainable with selective plating versus bath plating

Metal type	Microhardness, DPH	
	Bath plating	Selective plating
Cadmium	30-50	20-27
Chromium	750-1100[(a)]	850-1100
Cobalt	180-440	510
Copper	53-350	140-210
Gold	40-100	140-150

Lead	4-20	7
Nickel	150-760	280-580
Palladium	85-450	375
Rhodium	550-1000	800
Silver	42-190	70-140
Tin	4-15	7
Zinc	35-125	40-54

Source: Ref 2

(a) Usual range, but hardnesses of 280-1200 DPH are possible.

Table 3 Selective plating versus other processes

Characteristic	**Selective plating**	**Welding**	**Flame spray or plasma metallizing**	**Electroplating**
Precision buildup capability	Excellent	Poor	Poor	Fair to good
Quality of bond	Excellent	Excellent	Fair to good	Good
Heat distortion or stresses	None	Frequently	Sometimes	None
Heat cracking	None	Frequently	Sometimes	None
Speed of deposit	Fast	Very fast	Very fast	Slow
Density of deposit (porosity)	Very dense[(a)]	Very dense, but with blowholes	70-90% of theoretical density	Moderately dense
Portability	Yes	Yes	Sometimes, but over-spray precludes its use	No
Requirement for post-machining	Not required on thicknesses up to 0.254 mm (0.010 in.) on smooth surface	Always required	Almost always required	Usually required

Hydrogen embrittlement	No[b]	No	No	Yes

Source: Ref 1

(a) Generally 25% less porous than electroplating and 70% less porous than flame spray or plasma metallizing.

(b) Specific cadmium, nickel, and nickel-tungsten deposits have been tested on high-strength steel and were found to be nonembrittling. Other deposits may not cause embrittlement.

Besides electroplating, selective plating systems can perform several other ancillary operations:

- *Electrostripping* for deplating of many metals and alloys
- *Anodizing* for protecting aluminum and alloys
- *Electromilling* for removing base metal, as in chemical milling
- *Electroetching* for permanently identifying parts
- *Electropolishing* for refining a surface chemically

Depending on part size, dimensional considerations, and required surface characteristics, all of these operations can be done with the same equipment and similar electrodes. Only the solutions are different.

Selective plating of small parts is more the exception than the rule, and large volumes of small parts are more economically plated by high-production-rate processes, such as barrel plating. Plating of entire components with complex geometries is better left to processes such as tank plating, which is more economical because solutions are less costly and throughput is higher. Another limitation is deposit rate; both flame spraying and welding deposit metal at a considerably faster rate.

References cited in this section

1. M. Rubinstein, *Electrochemical Metallizing,* Vinmar Press, 1987

2. J.C. Norris, Brush Plating: Part I, *Metal Finishing,* July 1988, p 44-48

Applications

In many cases, an operator brush plates only one part at a time. Nevertheless, selective plating is an effective and economical electroplating process when used in application for which it is designed. These include plating of parts that are too large to immerse in solution, plating a small area of a larger component, and touchup and repair of components, large or small, that would cost too much to strip and remanufacture. The largest parts ever plated are building domes and church steeples, up to about 1390 m^2 (15,000 ft^2), in copper, nickel, and gold. The smallest are cells on rotogravure rolls, 0.076 by 0.038 mm (0.003 by 0.0015 in.). The process can also perform at high production volumes, such as 4,000,000 parts/day for nickel-plated brass electrical contacts on alkaline batteries.

Cosmetic or decorative applications involve parts that range in size from jewelry to large exterior structural domes and lobby interiors.

Corrosion protection applications allow touchup of small rusted or corroded areas without disassembly. Examples include aircraft landing gears, virtually all kinds of machinery, mixing vats, and tanks. Parts too large to fit into plating tanks are almost always good candidates.

Repair of electronic parts is usually done with precious metals, such as gold, silver, and rhodium. Typical applications are repair of broken circuits and small circuit board contacts, and application of conductive coatings on high-

voltage sources. Selective plating minimizes scrap, allows immediate repair on site, and does not require immersion of the entire part in solution.

Restoration of large parts is a natural application for selective plating if the parts are permanent fixtures that cannot be removed or disassembled. The process makes it possible to repair and restore dimensions or apply a wear-resistant or corrosion-resistant surface to just about any part. Portable systems allow access to parts at great elevations and in remote areas, such as protecting the inside surface of a large mixing vessel and repairing critical equipment on ships at sea.

Specialized applications of selective plating involve unusual environments or the need for certain properties, such as conductivity or impact resistance. Examples include blocking radio frequency interference with a soft, radiowave-resistant material such as tin; plating aluminum to facilitate soldering; plating machinery components to ensure initial lubrication; and even plating test probes to resist extreme environmental conditions.

Following are examples of specific applications of selective plating and anodizing:

- *Adhesive-bonded aircraft parts:* anodizing (phosphoric acid) used to prepare aluminum skins and frames for adhesive repair of damaged skins
- *Aircraft engine components:* sulfamate nickel on high-temperature nickel alloys used as a prebrazing operation for second-stage turbine vanes, blades, and stator segments; also used for restoration of bearing area on turbine exhaust case, bearing housing and support, and cooling air duct
- *Aircraft landing gears:* cadmium touchup; on 2014 aluminum, hard coat on inner diameter of oil air strut used to accommodate press fit of bronze bearing
- *Aircraft skins:* anodizing (chromic acid or sulfuric acid) used to repair damaged chromic-acid and sulfuric-acid coatings, respectively
- *Aircraft wheel:* anodizing (sulfuric acid) used to correct a mismachined bearing bore
- *Bus bars:* silver on copper or aluminum used for electrical contacts
- *Electric motors:* nickel and copper used for dimensional restoration of motor shafts and bearing end caps; tin used for low-power motors to reduce vibration; and platinum, gold, or rhodium used to increase wear life and reduce arcing of commutators and slip rings
- *Hydraulics:* copper, nickel, cobalt, or chrome used to repair steel- or chrome-plated hydraulic components, often without disassembly
- *Metal recovery systems:* platinum coating used on titanium permanent anodes
- *Missile launch rail:* hard coat used on a 6061-T6 surface to bring dimensions into tolerance and provide wear resistance and corrosion resistance
- *Mold repair:* gold plating used on plastic molds where corrosive gases attack existing chrome; final plating of chrome used to repair rubber molds; copper, nickel, and cobalt used to repair other types of molds
- *Printed circuit boards:* gold over copper used on contact tabs, fingers, etc.
- *Printing presses:* copper, silver, nickel, cobalt, or chrome plating used to repair cylinders; in-press overhaul plating of side frame used for bearing retention and to correct out-of-concentricity condition
- *Railroad axles:* nickel used for dimensional restoration on bearing journals and sealing wear ring grooves
- *Space shuttle manifolds:* up to 0.5 mm (0.20 in.) of copper used to increase wall strength of a nickel-electroformed hydrogen-oxygen manifold for the prototype "Columbia" engine
- *Steel mill coating line:* cadmium, zinc, or nickel-zinc used to increase the thickness of the protective coating on steel sheet moving at 137 m/min (450 ft/min)
- *Submarines:* rhodium and gold used on copper slip rings
- *Turbines:* cobalt, nickel, nickel/cobalt, or chrome used to restore dimensions on bearing and seal surfaces; silver used to repair steam cuts on horizontal seal surfaces

Equipment

Typical selective plating systems include a power pack, plating tools (called *styli* or *anodes*), anode covers, specially formulated plating solutions, and any auxiliary equipment required for the particular application. To achieve optimum deposits, equipment should be designed expressly for selective plating. Although tank plating solutions and rectifiers are

occasionally used, they are not usually recommended because the resultant deposits are thin and quality is typically below par.

Power packs (rectifiers) supply the direct current and are specially designed with the features and/or controls required by the process. Output voltage can typically be varied from 0 to between 25 and 30 V, compared to the usual 6 to 12 V for tank-plating power packs. Power packs are available in a variety of ratings to suit specific applications (Table 4).

Table 4 Commercially available power packs

Alternating current input, V	Phase	Maximum output current, A[(a)]
115 or 230	1	30
115 or 230	1 or 3	60
230 or 460	1 or 3	100
230 or 460	1 or 3	150
230 or 460	1 or 3	200
230 or 460	3	500

Source: Ref 2

(a) At 25 V dc.

Voltage control is extremely important because it regulates the current supplied to the process. In turn, the amount of current consumed over time, measured in ampere-hours (A · h), determines the deposit thickness. Ampere-hour requirements vary widely for different types of electroplates, as indicated by the energy factors in Table 1.

Stepless voltage control is a typical feature of selective plating power packs; most can be adjusted from 0 to 100%. The magnitude of power required depends on the part size, the deposit thickness required, and the plating type. For example, for delicate electronics parts, an output of 5 A and 12 V should be ample, whereas plating of large areas with thick buildups requires a much larger source.

A voltmeter and an ammeter should be available and should show 0 to 100% ranges. The voltmeter permits monitoring of the voltage required to plate a given part. The ammeter displays the amount of current flowing between the anode and the cathode, allowing calculation of the current density.

A polarity-reversing switch allows the operator to automatically change current flow direction, which is necessary in preparatory operations (e.g., etching and desmutting) and in stripping, when the current must run opposite to the direction used in electroplating. Otherwise, the connections to the anode and cathode must be changed manually, slowing down the entire process. Indicator lights to show polarity direction may also be incorporated.

Safety circuit breakers instantly shut off the current should a short circuit occur between the anode and the workpiece. Typically, shutdown is within one-half cycle (1/120 s), preventing workpiece damage and injury to the operator.

Energy counters (ampere-hour meters) are required by many industrial and government specifications. Besides keeping track of the energy being used, these meters make it possible to control the thickness of the deposit. Counters may incorporate set points with visual and/or audio warnings to indicate when the desired thickness has been reached.

Optional microprocessor-controlled systems reduce the chance of miscalculation and allow continuous monitoring of the process via an alphanumeric readout. The amount of energy required for an area to be plated to the desired thickness and the applicable parameters are determined by a microprocessor, not the operator. Such equipment is also of merit for plating multiple parts to the same specifications. In some systems, the software prompts the operator for data entry for a particular operation, then displays the correct process parameters.

The plating tool (stylus) must have an insulating handle and an anode material that is inert, insoluble in plating solutions, and able to carry high current. Graphite is by far the most practical choice for anode material. High purity is preferred; any additive used to harden the graphite or give it a different physical characteristic interferes with its beneficial qualities. Graphite can be machined or shaped to fit the contour of the part being processed. Stainless steel is much more durable, but it dissolves in some plating solutions, and after a short time it changes the characteristics of the electrolyte being used. Platinum-iridium, platinum-clad niobium, and platinum-clad titanium are inert to all of the electrolytes used in selective plating operations, and they are used for smaller-diameter anodes. Their disadvantages are increased cost and high hardness, which makes shaping difficult.

The anode covers (wrapping materials) serve as an insulator between the anode and cathode and help ensure smooth deposits at high current densities. Because they hold the electrolyte, they must be absolutely free of oil and foreign materials. Any substance that contaminates the electrolyte has a detrimental effect on the plating. For example, any oil contamination whatsoever results in poor adhesion. Consequently, in a machine shop or other environment where oil is widely used, the work area should be carefully selected. When necessary, applicable part surfaces can be solvent or vapor degreased or go through a separate cleaning cycle.

Various fiberlike materials make suitable covers. Cotton works very well if it is sterile, long fiber. Synthetic fibers, such as polyester and nylon, do not wet or hold electrolytes as well as cotton, but this does not preclude their use. Polyester felt is typically selected when the same anode will be used for numerous parts or for heavy deposits. Most of these materials work well in the form of tube gauze ("bandage covers") as covers over cotton. Scotch-Brite has been used when heavy/hard deposits are required, and it can also function as a burnishing tool, improving the surface as plating continues. If a surface is soft and easily scratched, a different wrap should be chosen.

Reference cited in this section

2. J.C. Norris, Brush Plating: Part I, *Metal Finishing,* July 1988, p 44-48

Key Process Elements

Anode-Cathode Motion. Controlling continuous movement between the anode and the workpiece, or cathode, is a key element in obtaining high-quality brush-plated deposits. However, quality also depends on plating within a specific current density range, so both variables affect ultimate deposit quality. This relationship is illustrated in Fig. 2. Solution suppliers routinely recommend ranges of anode-cathode speeds and current density values for each solution; a representative list is given in Table 5.

Table 5 Anode-cathode motion and current density for selective plating solutions

Selective plating solution	Anode-cathode motion		Current density	
	m/s	ft/min	A/dm^2	A/ft^2
Cadmium (acid)	0.26-0.561	50-110	86.4	864
Cadmium LHE (low hydrogen embrittlement formula)	0.20-0.41	40-80	86.4	864

Chromium	0.02-0.03	4-6	86.4	864
Cobalt (machinable)	0.13-0.26	25-50	115.2	1152
Copper (high speed, acid)	0.20-0.51	40-100	144.0	1440
Gold	0.15-0.31	30-60	28.8	288
Lead	0.15-0.26	30-50	86.4	864
Nickel (acid)	0.10-0.26	20-50	86.4	864
Nickel (high speed)	0.20-0.41	40-80	144.0	1440
Nickel-tungsten alloy	0.10-0.15	20-30	72.0	720
Rhodium	0.03-0.05	5-10	43.2	432
Silver (heavy build)	0.10-0.31	20-60	72.0	720
Tin (alkaline)	0.10-0.41	20-80	86.4	864
Zinc (alkaline)	0.15-0.612	30-120	115.2	1152

Data courtesy of SIFCO Selective Plating

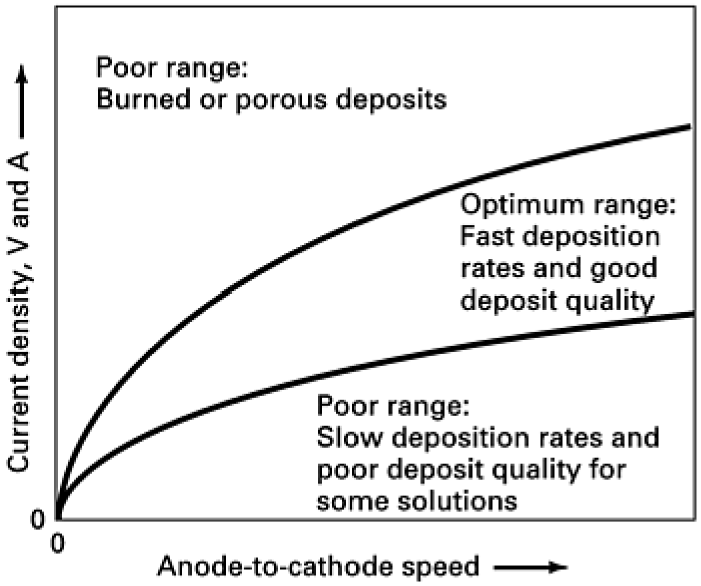

Fig. 2 Relationship between current density and anode-to-cathode speed. Source: Ref 3

The visual appearance of the electroplate is also an indicator of quality. A dark gray or black color usually corresponds to a burnt deposit, which results from too high a current density or insufficient movement. In contrast, inadequate current density or too much movement produces a generally shiny surface.

Anode-to-cathode movement may be achieved manually or mechanically, such as by using turning equipment to provide a constant rotational speed for cylindrical parts (Fig. 3) or by using specially designed tilting turntables to rotate large parts at controlled speeds. Another option is the rotostylus (Fig. 4), which rotates the anode instead of the workpiece.

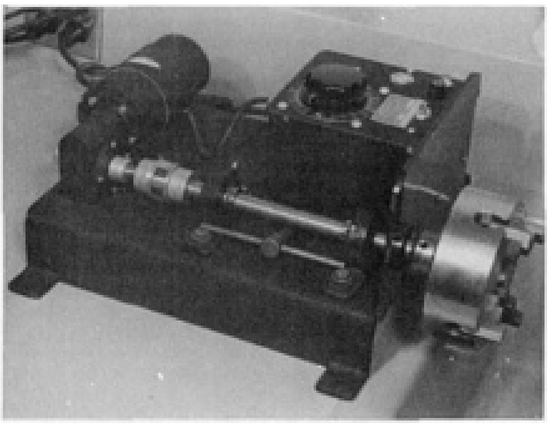

Fig. 3 Turning head. Courtesy of SIFCO Selective Plating

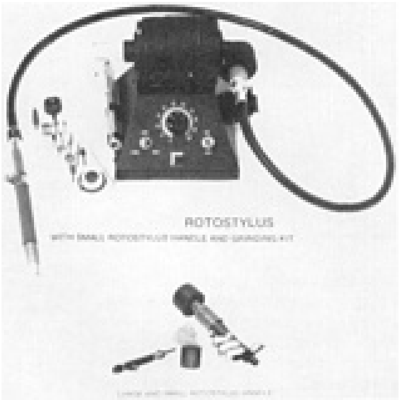

Fig. 4 Rotostylus. Courtesy of SIFCO Selective Plating

Anodes and Flowthrough. For the plating process to be efficient, the plating solution must flow between the anode and the area being plated. Solution can be supplied by periodically dipping the plating tool into the electrolyte. However, the most efficient method is to pump the solution through the block anode and into the interface between the anode and the workpiece (Fig. 5). Plating of large areas at high currents *requires* the use of a pump to recirculate the solution. This keeps the solution from overheating, results in thicker buildups on large areas, and allows the use of higher current densities. In addition, the entire process is faster. Various types of pumps can be used, depending on the amperage and on whether preheating and/or filtering is necessary for the solution used.

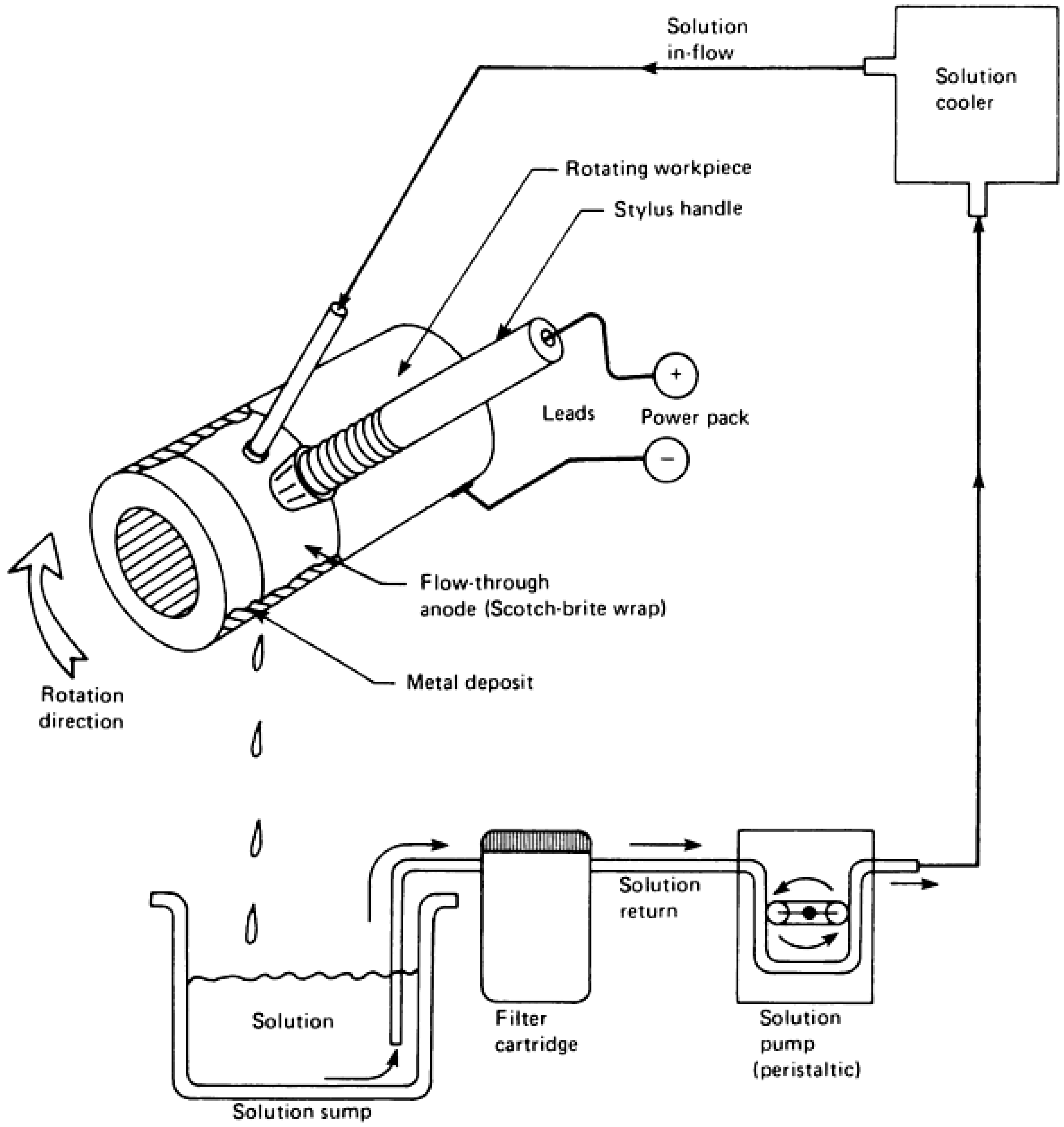

Fig. 5 Flow-through deposition. Courtesy of Vanguard Pacific, Inc.

Solutions. Three basic types of solutions are used in selective plating: preparatory, plating, and special-purpose. Table 6 shows the most common solutions and their uses. The base metal and the type of plating generally dictate which solutions are appropriate.

Table 6 Typical selective plating solutions

Preparatory solutions
Activating (for industrial hard chromium)
Cadmium activator
Chromium activator (for decorative applications)
Cleaning (for most materials)

Desmutting (for cast iron, carbon and alloy steels, copper alloys)
Etching (for aluminum alloys, steels, cast iron)
Etching and activating (for high-temperature nickel-base alloys and stainless)

Plating solutions for ferrous and nonferrous metals

Nickel (acid strike)
Nickel (alkaline)
Nickel (dense)
Nickel (ductile, for corrosion protection)
Nickel (neutral, for heavy buildup)
Nickel (sulfamate, hard, low stress)
Nickel (sulfamate, moderate hardness)
Nickel (sulfamate, soft, low stress)
Antimony
Bismuth
Cadmium (acid)
Cadmium (alkaline)
Cadmium (no-bake)
Chromium (hexavalent)
Chromium (trivalent)
Cobalt (for heavy buildup)
Copper (acid)
Copper (alkaline)
Copper (high-speed acid)
Copper (high-speed alkaline for heavy buildup)
Copper (neutral)
Iron
Lead (alkaline)
Lead (for alloying)
Tin (alkaline)
Zinc (acid)
Zinc (alkaline)
Zinc (bright)
Zinc (neutral)

Plating solutions for precious metals

Gallium
Gold (acid)
Gold (alkaline)
Gold (neutral)
Indium
Palladium
Platinum
Rhenium
Rhodium
Silver (hard)
Silver (noncyanide)
Silver (soft)

Plating solutions for alloys

Babbitt Navy Grade 2
Babbitt SAE 11
Brass
Cadmium-tin
Cobalt-tungsten
Nickel-cobalt
Nickel-tungsten

Tin-indium Tin-lead-nickel
Special-purpose solutions
Anodizing (chromic) Anodizing (hard coat) Anodizing (sulfuric) Chromate treatment Electropolishing solution

Source: Ref 2

Preparatory solutions clean the substrate surface so that it can effect a better bond with the electroplate. Preparation typically involves precleaning, electrocleaning, and electroetching; some base materials also require desmutting, activation, and preplate operations. Parts with heavy corrosion, lubricants, oil, and so on ordinarily require more aggressive cleaning, such as vapor/solvent degreasing or grit blasting, prior to precleaning.

Plating solutions used for selective plating have a much higher concentration of metal, usually as organometallic salts, than do solutions used for tank plating. This higher metal content permits the use of higher current densities, which results in faster deposition, better bond strength, and less porosity than in tank plating.

Two basic kinds of plating solutions are used. One deposits a thin preplate ("strike") that boosts adhesion on certain metals and alloys, and the other builds up the coating to its functional thickness. Suppliers usually offer a choice of solution for each type of electroplate, because different properties are required for different applications (e.g., high hardness and wear resistance for one, ductility for another).

Special-purpose solutions include those used for post-treatment, anodizing, and electropolishing.

Thickness Control. The thickness of a deposit can be controlled by monitoring the ampere-hour meter. Each solution has a prescribed energy factor, which indicates how many ampere-hours are required to deposit a given metal thickness on a given area:

$$\mathrm{A} \cdot \mathrm{h} = F \times A \times T$$

where $\mathrm{A} \cdot \mathrm{h}$ is the ampere-hours required, F is the energy factor, A is the area to be plated (in square centimeters), and T is the thickness of the deposit (in microns). The calculation yields a fixed value that can be monitored on the meter (or set on the ampere-hour counter, if the power pack is so equipped). If needed, simple additional calculations can also be performed to determine the optimum current, plating time, volume of plating solution, and even rotational speed (Ref 4).

References cited in this section

2. J.C. Norris, Brush Plating: Part I, *Metal Finishing,* July 1988, p 44-48

3. DALIC Process Instruction Manual, 5th ed., SIFCO Selective Plating, 1990

4. J.C. Norris, Brush Plating: Part II, *Metal Finishing,* Aug 1988, p 45-47

Specifications

Since the mid 1950s, when the first commercial selective plating specification was introduced, the number of specifications has surpassed 100. The following list includes some of the more important industrial, government, and military specifications:

- MIL-STD-865C (U.S. Air Force)
- MIL-STD-2197SH (U.S. Navy)

- BAC 5849, 5854 (Boeing)
- DPS 9.89 (Douglas Aircraft)
- MPS 1118A (Lockheed Aircraft)
- SS 8413, 8494 (Sikorksy Aircraft)
- BPSFW 4312 (Bell Helicopter)
- FPS 1046 (General Dynamics)
- HA 0109-018 (North American Rockwell)
- GSS PO60B (Grumman)
- Standard Practice Manual 70-45-03 and T.M. No. 72-191 (General Electric)
- PS 137, Issue 1 (Dowty Rotol Ltd., England)
- ITF 40-839-01 (Messier-Hispano, France)
- TCMK-5 (Saab-Scania, Sweden)
- Report NAEC-AML 1617 (Naval Air Engineering Center, Philadelphia)
- M-967-80 (Association of American Railroads)
- AC 43.13-1A, Chg. 1 (Federal Aviation Administration)
- AMS 2439, 2441, 2424C
- SPOP 321 (Pratt & Whitney)

In addition to the above specifications, many U.S. Navy and U.S. Air Force activities have generated instructions for selective plating of specific hardware or components at specific military facilities.

In the electronics field, the repair of printed circuit boards for military applications is authorized by MIL-STD-865C. For commercial applications, the Institute for Interconnecting and Packaging Electronic Circuits approves the use of selective plating for repair of both bare and assembled printed circuit boards (Ref 5). In addition, many electronics companies have issued their own specifications for in-house repair of circuit boards and other electronic components.

Reference cited in this section

5. *Modification and Repair for Printed Boards and Assemblies,* Manual IPC-R700B, Institute for Interconnecting and Packaging Electronic Circuits

Health and Safety Considerations

There are two safety issues in selective plating: the chemicals and the equipment used to apply the chemicals. Overall, the process meets the safety requirements set by the Occupational Safety and Health Administration (OSHA) for in-plant use. Electrical protection of the power pack, workpiece, and operator are provided by a direct current circuit breaker within the power pack. This circuit breaker trips when an overload occurs. If the anode shorts out by contacting the part, or if the power pack exceeds its amperage rating, the breaker almost instantly stops power flow.

Today, manufacturers provide material safety data sheets (MSDS) with solutions, in conformance with OSHA requirements. The solutions are industrial chemicals and should be handled as such. Ventilation to remove fumes is recommended, and conventional safety guidelines, including the use of safety glasses and rubber gloves, should be routinely followed. Reviewing the MSDS will alert personnel to any special handling or other safety precautions required.

Pulsed-Current Plating

Chuck VanHorn, Enthone-OMI, Inc.

Introduction

CONVENTIONAL PULSED-CURRENT PLATING (commonly referred to as *pulse plating*) can be defined simply as metal deposition by pulsed electrolysis. In its simplest form, it involves using interrupted direct current to electroplate parts. This is accomplished with a series of pulses of direct current, of equal amplitude and duration in the same direction,

separated by periods of zero current. The pulse rate (frequency) and "on" and "off" times (duty cycle) can be controlled to meet the needs of a given application. The ideal shape of the pulsed current is shown in Fig. 1(a). An oscilloscope should be used to reveal how well the equipment controls the output (Fig. 1b).

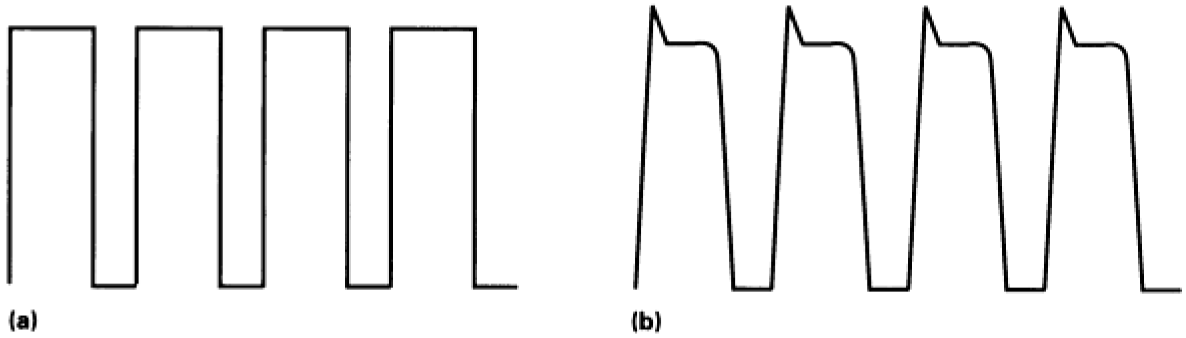

Fig. 1 Current patterns in conventional pulsed-current plating. (a) Ideal pattern. (b) Typical pattern as seen using an oscilloscope

Pulse plating has gained acceptance in a number of metal finishing industries, especially the electronics industry. With the advent of solid state pulse plating power supplies, the imprecision has been taken out of the process. The amount of time the current is on and off is set directly on digital thumb-wheel switches or via programmable software. Two different modes of operation are used: constant current and constant voltage. Figure 2 illustrates the constant-current mode of operation. The tops of the current pulses are kept flat by allowing the voltage to vary during the pulse on-time. In the constant-voltage mode (Fig. 3), the tops of the voltage pulses are kept flat by varying the current. Because of the shape of the current pulse in the constant-voltage mode, the peak current is not useful for controlling the plating rate. An amp-minute controller is needed to accurately control the plating thickness.

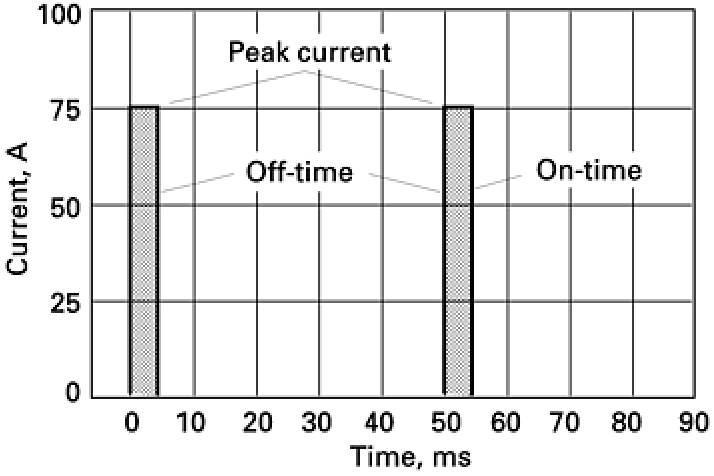

Fig. 2 Constant-current pulse plating with an on-time of 5 ms, an off-time of 45 ms, and a peak current of 75 A. Because the current is on one-tenth of the time, the average current is 7.5 A.

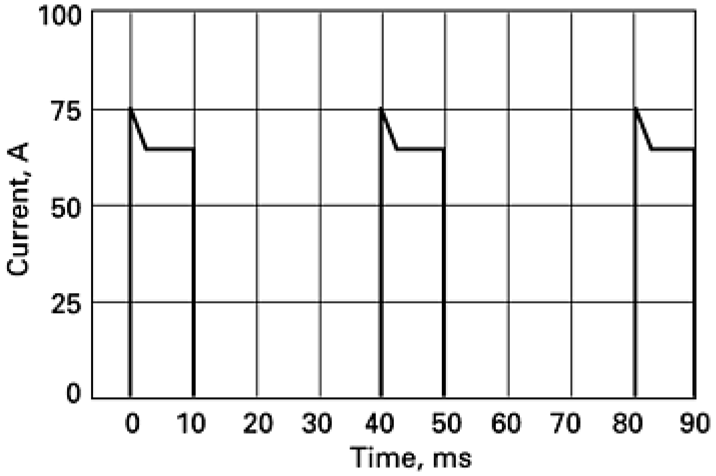

Fig. 3 Typical current pattern for constant-voltage pulse plating. The current falls during the on-time because of the increasing resistance of the cathode. On-time, 10 ms; off-time, 30 ms

Metals that are commonly deposited using pulsed current include gold and gold alloys, nickel, silver, chromium, tin-lead alloys, and palladium. Pulsed current is also used for anodizing and, in select cases, for etching, electrocleaning, and electroforming.

The advantages of pulse plating vary from one application to the next. The most common (relative to plating with conventional continuous current) include the following:

- Deposits are smooth, dense, fine-grained, and almost completely free of pinholes.
- Variation in plate thickness from one part to the next is considerably reduced.
- Plating speeds can normally be increased.
- Current efficiency generally is improved.
- Use of organic additives, in most cases, can be reduced by 50 to 60%. Deposits are free from dendritic growth even if additives are not used.
- For some electrodeposits, such as gold, less metal is required in the plating solution to meet end-use specifications.

The limitations of pulse plating include the fact that the cost of a pulsed-current rectifier is greater than that of a conventional dc unit. Also, optimization of results requires planning and experimentation, and plating equipment may need to be redesigned or upgraded.

Process Principles

The theory behind pulse plating is simple (Ref 1, 2). The cathode film is kept as rich in metal ions as possible and as low in impurities as possible. During the period when the current is on, the metal ions next to the cathode are depleted and a layer rich in water molecules is left. During the portion of the cycle when the current is off, the metal ions from the bulk of the plating solution diffuse into the layer next to the cathode. Then the process is repeated again. Also during the time the current is off, gas bubbles and impurities that have been adsorbed on the cathode have a chance to desorb.

Typical on-time range from 0.1 to 9.9 ms, and typical off-times range from 1 to 99 ms. If an ammeter is inserted into a pulsed-current plating circuit, it responds to the average current. In order to have the same plating rate using pulsed current as with conventional continuous current, the average current must be the same. This can be achieved by adjusting the peak current, the on-time, or the off-time. The physical and chemical properties of deposits can be very precisely controlled through the careful selection of pulse-plating parameters.

Concepts and Terminology. Selected terms that have special meaning when applied to pulse plating are defined as follows:

- *Cathodic (forward) and anodic (reverse)* are used to describe current direction; *cathodic* indicates flow is in the normal (plating) direction, *anodic* indicates flow is in the reverse (deplating) direction. In normal operation of a reversing pulse unit, current direction alternates in a controllable forward and reverse pattern.
- *Envelope* is the time span during which current may flow in only one direction. The time spans of the forward envelope and the reverse envelope are set individually.
- *Pulse train* is a regularly interrupted current flow in either the cathodic or anodic direction. A pulse train exists within the envelope.
- *Pulse* is the individual interval in a pulse train, consisting of one "on and off" period.
- *Pulse rate* is the number of times the current is switched on in a given period of time (usually 1 *s*).
- *Duty cycle* is the ratio of time an individual pulse is on compared to the total (on and off) pulse time. For example, 5 ms on and 5 ms off is a 50% duty cycle, 4 ms on and 1 ms off is an 80% duty cycle, and so on. (*Note:* if the duty cycle is 100%, there is no off time; the current is on for the duration of the envelope and there is no pulse or frequency.)
- *Frequency* is the pulse rate expressed as hertz units (e.g., 100 Hz = 100 pulses/s).
- *Pulse width* is the time span of the on portion of a pulse. Pulse width is a function of both frequency and duty cycle. For example, a 1000 Hz pulse with a duty cycle of 50% has a pulse width of 0.5 ms.

References cited in this section

1. H.Y. Chen, *J. Electrochem. Soc.,* Vol 118, 1971, p 551

2. R.J. Tedeschi, *Met. Finish.,* Nov 1971, p 49

Process Control

Microprocessor-controlled modulation of applied direct current to improve the electrodeposition process has found use in reel-to-reel selective plating, automatic tab plating, barrel line plating, still plating, electroforming, anodizing, electrocleaning, electropolishing, and electromachining. It recently has been adapted for use with semiconductor bump and wafer plating technologies.

The use of this sophisticated power control can result in greatly increased plating speeds, improved deposit distribution, lower deposit stress, finer grain structure, increased ductility, improved adhesion, increased micro-throwing power, reduced susceptibility to hydrogen embrittlement, and a markedly decreased need for additives.

The use of modulated dc power supplies with advanced electronic circuitry enables the user to control output patterns with extreme precision. A high-quality unit will superimpose periodic reverse on a high-frequency pulse. The power pattern that results is quite complex, with a wide range of profiles. The output--a series of pulses with controllable amplitude, frequency, duration, and polarity--influences the deposition characteristics of any solution. The characteristics obtained with modulated power supplies are quite different from those obtained with conventional pulse or periodic-reverse equipment. By "tuning" or shaping the output power pattern to a given plating application, the operator can dramatically enhance the rate of deposition and the character of the deposit.

In periodic-reverse plating, the polarity of a constant dc output is switched back and forth in a regular pattern. Figure 4(a) depicts the ideal output; Figure 4(b) shows the actual output from a slow-response control unit.

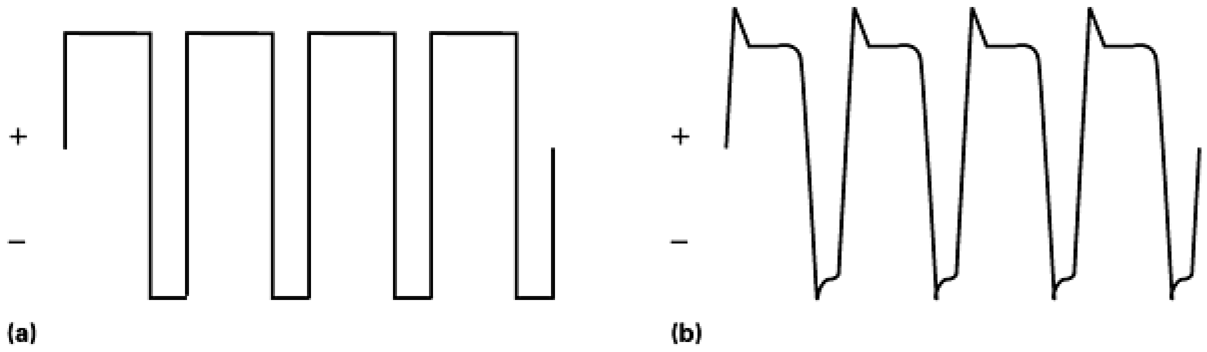

Fig. 4 Current patterns in periodic-reverse pulsed-current plating. (a) Ideal pattern. (b) Pattern of a slow-response control unit as seen using an oscilloscope

The sharpness of the output current pattern as revealed by an oscilloscope depends on the degree of ripple in the rectifier output and the quickness of response in the internal switching circuitry of the controller. High-quality units produce extremely sharp square-wave patterns (Fig. 3 and 4). Figure 5 illustrates the wave form of the forward (cathodic) and reverse (anodic) output of a high-quality unit.

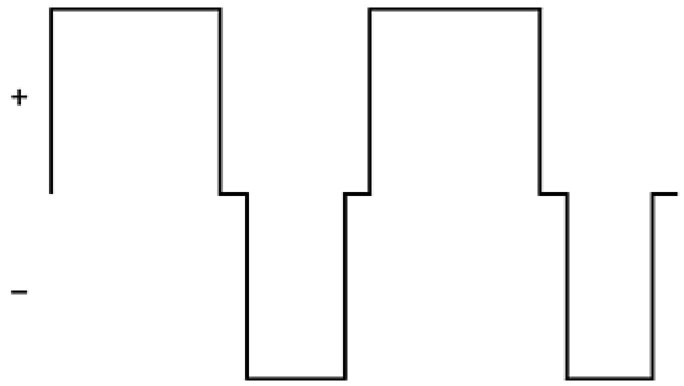

Fig. 5 Square-wave current pattern of the forward and reverse envelopes in periodic-reverse pulse plating

The duration of the current in each direction (the forward and reverse envelopes) can be individually controlled from 0.1 ms to 99.99 s. (A zero current delay of less than 0.1 ms between forward and reverse is a design feature of high-quality units that serves to prevent transistor failure due to "shoot through.") The simple, square-wave pattern shown in Fig. 5 is the result of a precisely controlled periodic-reverse output; pulse frequencies can then be superimposed upon this output pattern. Within each envelope, a square-wave pulse is generated (Fig. 6). The frequency and the duration of the pulses are set independently for the forward and reverse envelopes; frequencies range from 10 to 9999 Hz. Duty cycle settings in percentages determine the on and off times for each pulse.

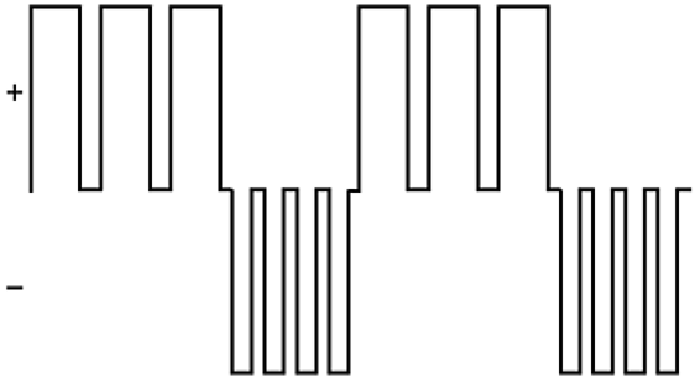

Fig. 6 Current pattern for periodic-reverse pulse plating in which pulse frequencies have been superimposed on the forward and reverse envelopes

On some models, forward and reverse amplitude can be controlled individually (Fig. 7). This permits, for example, a higher current density in the reverse (deplating) stage than in the forward (plating) stage, which is highly desirable for some applications. (More complete explanation of output control with specific units is available in the operation manuals supplied by their manufacturers.)

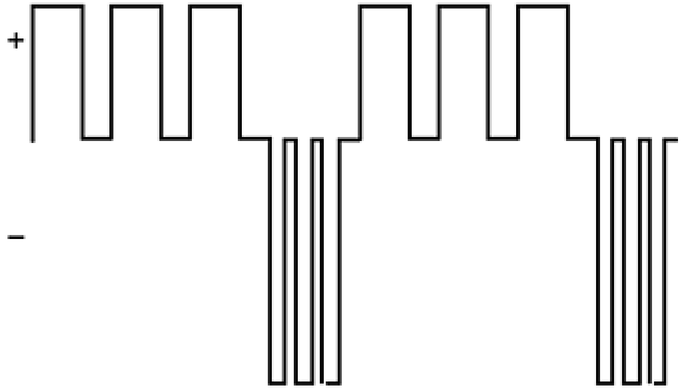

Fig. 7 Current pattern for periodic-reverse pulse plating in which pulse frequencies of different current densities have been superimposed on the forward and reverse envelopes

Solution Composition and Operating Conditions

With the changes that take place in the plating tank when a modulated periodic reverse pulse is impressed on the electrolyte, changes in the other operating conditions or even in the formulation may be required. Generally speaking, better results are obtained with simple, rather than sophisticated, formulations (Ref 3). Typical solutions used in pulse plating are given in Table 1.

Table 1 Typical solutions used in pulsed-current plating

Constituent or condition	**Amount or value**
Watts nickel solution for reel-to-reel plating	
Nickel sulfate, g/L (oz/gal)	650 (87)

Boric acid, g/L (oz/gal)	50 (7)
Temperature, °C (°F)	60 (140)
pH	3-4
Anodes[(a)]	Platinized niobium (insoluble)
Organic additives	None
Pure gold	
Potassium citrate, g/L (oz/gal)	150 (20)
Citric acid, g/L (oz/gal)	15 (2)
Potassium phosphate, g/L (oz/gal)	26 (3)
Boric acid, g/L (oz/gal)	72 (10)
Gold metal, g/L (oz/gal)	8.2 (1)
Temperature, °C (°F)	60 (140)
pH	3.5-4.0
Anodes	Platinized titanium
Hard gold	
Citric acid, g/L (oz/gal)	65 (9)
Potassium citrate, g/L (oz/gal)	50 (7)
Cobalt, g/L (oz/gal)[(b)]	0.5-0.6(0.07-0.08)
Gold, g/L (oz/gal)	8.2 (1)
pH	3.8-4.0
Temperature, °C (°F)	32-38 (90-100)

(a) When using soluble nickel anodes with reversing pulse modes, the use of an anode activator such as chloride is not required because the reversing current keeps the anode active and soluble.

(b) The higher voltage of pulse plating relative to continuous dc plating favors the deposition of the alloying agent. The operator should analyze the deposits to determine if the amount of cobalt in the solution should be adjusted. In most cases, the amount of available cobalt (or other alloying agent) should be reduced (from the amount used with continuous current) to obtain the desired properties.

Additives. The polarization imposed by the power pattern on the bath reduces, or even eliminates, the need for some addition agents. In many cases, additives can actually inhibit the effectiveness of the pulsed-current pattern. For example, large-molecule additives do not respond as they do under conventional power; in a high-frequency pulse field, their molecular size is a disadvantage. Small-molecule organics or inorganics will generally function well as additives. In many cases, the use of brighteners can be reduced as much as 90% without diminishing the brightness of the deposit because of the improved grain structures. If brightener levels are not reduced, longer pulses--i.e., lower frequencies and/or higher duty cycles--may be required (Ref 3).

Electrolyte conductivity must be maintained at a high level to allow the peak pulse current to be completely effective. If the conductivity is not high enough, an excess in voltage will be required to attain the desired peak current. Such peaks are power-inefficient and less effective.

Anode-to-cathode ratios for pulse plating are rarely the same as those for conventional power applications. Generally speaking, in acid or alkaline nonchelating formulations, the anode area should be reduced. In cyanide or other chelating formulations, the reverse is generally the case, and a greater anode area is required.

Temperature and agitation conditions for conventional processes may also have to be altered for modulated power pattern plating. Unfortunately, no general rule applies; each application has its own requirements, and optimum conditions must be established on a case-by-case basis.

Reference cited in this section

3. J. Padden, J. Lochet, and C. VanHorn, "Improvement of Electrodeposition through Modulated dc Power Patterns," 1981

Equipment Modification

One factor that should always be checked when planning a change from conventional to pulsed-current power is the tank electrical contact system. Some anode and/or cathode contacts that may be perfectly suitable for conventional plating may present unwanted resistance to high-frequency peak currents. Overlooking this factor may prevent the realization of the full benefits of a modulated power supply.

The major consideration, of course, is the power system itself. Existing rectifiers may or may not be suitable for use with modulated periodic reverse or direct pulse units. For pulse plating, a high-voltage, quick-response rectifier is required, and the lower the ripple, the more precise and predictable the output. Although pulse units are available for use with existing power supplies, models with self-contained rectifiers give greater assurance that full benefit of the control system will be realized.

Pulse units with self-contained power can be operated in either a constant-average-current or constant-voltage mode. The significance of this option is illustrated in Fig. 8. Figure 8(a) depicts a pulse train with a 50% duty cycle. The *average* current delivered is 50% of the *peak* value. Figure 8(b) shows the effect of reducing the duty cycle to 25% when in a constant-voltage mode. The peak current remains the same, but the average current changes directly with the duty cycle, in this case dropping to half its former value. The current density of the pulsed current remains the same, but twice as much real time is required to deliver the same amp-minutes of current. Figure 8(c) shows the effect of reducing the duty cycle from 50 to 25% when operating in constant-average-current mode. In this case, the peak current changes inversely to the duty cycle, increasing in value to maintain the same average current delivered as before but in shorter pulses.

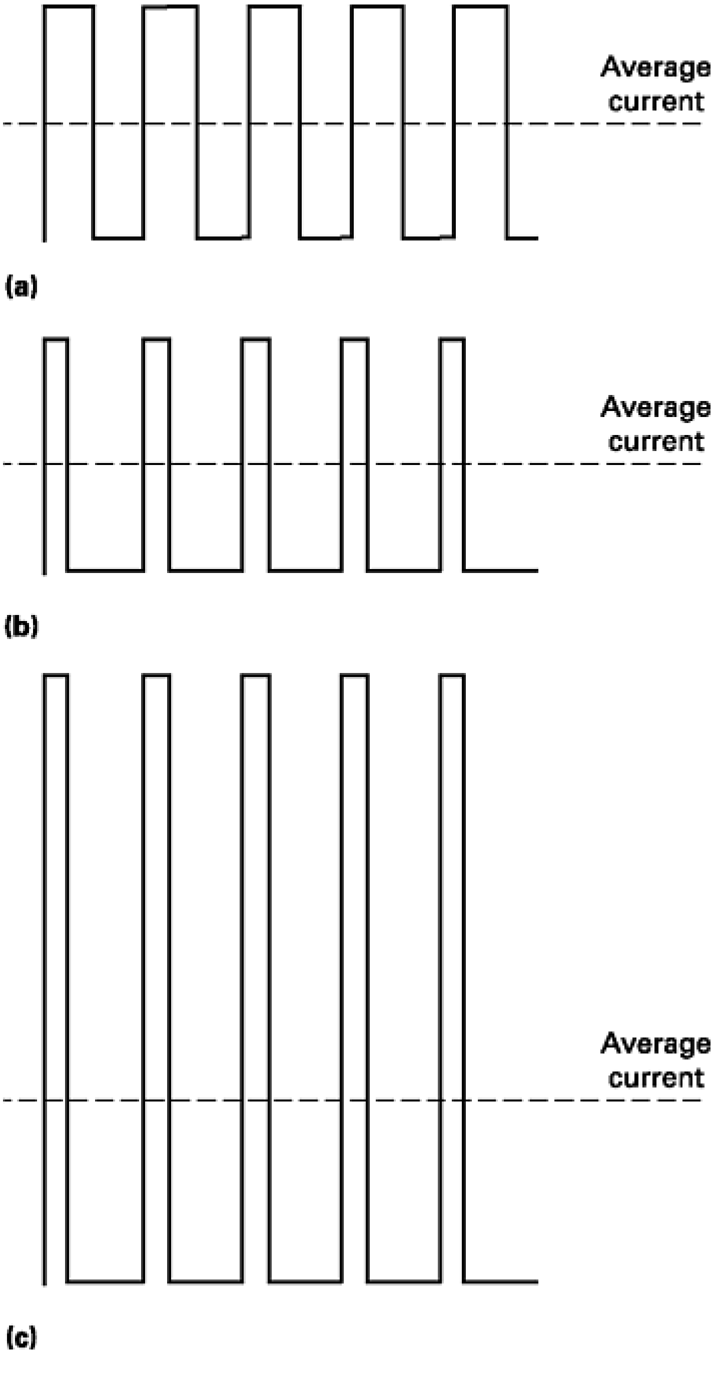

Fig. 8 Effect of changes in the duty cycle on constant-average-current and constant-voltage pulsed-current plating. (a) 50% duty cycle, with average current 50% of the peak value. (b) Duty cycle reduced to 25% in constant-voltage mode; average current drops with duty cycle. (c) Duty cycle reduced to 25% in constant-current mode; the peak current changes inversely to the duty cycle.

Although a change in frequency also changes the pulse width, it does not effect either peak or average current, regardless of output mode (Fig. 9). Unlike conventional plating rectifiers, which are rated by average current capacity (ignoring the ripple), modulated periodic reverse pulse units are normally rated by their peak current capacity. Because both peak and average current values are intrinsic to modulated power pattern plating, both output capacities must be considered. Depending on the internal circuitry of the unit, the average current output capacity of some models can be as low as 25 or 30% of the peak capacity. With such a low value for average current, the rated peak current output would be attained even at average current capacity only if a duty cycle as low as 25 or 30% was used. Attempting to push average current up would drastically shorten the life of the unit. Experience has shown that effective duty cycles are usually not less than 50% (although they can be as low as 10% for pure precious metals), and most units are designed to deliver an average

current capacity of 50 to 60% of the peak current capacity rating. However, any desired duty cycle can be used or specified, but the operator must keep in mind that the average current is the percentage (duty cycle) of the peak rating.

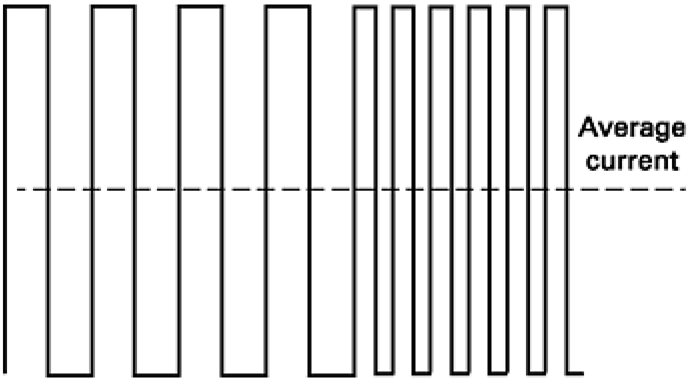

Fig. 9 Effect of change of frequency on current pattern in pulsed-current plating. Only pulse width is altered; peak current, average current, and duty cycle remain constant.

Electroforming

Glenn Malone, Electroformed Nickel, Inc.; Myron E. Browning, Matrix Technologies

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Introduction

ELECTROFORMING is the process by which articles or shapes can be exactly reproduced by electrodeposition on a mandrel or form that is later removed, leaving a precise duplicate of the original. In certain applications, the mandrel is designed to remain as an integral part of the final electroformed object. Electroforms themselves may be used as parents or masters, usually with special passivating treatments so the secondary electroform can be easily removed. The same or similar electrodeposition additives as those used for electroplating are required for electroforming to control deposit stress, grain size, and other resultant mechanical properties in order to produce high-quality electroforms.

Early Applications

Electroforming was developed by a Prof. Jacobi of the Academy of Sciences in St. Petersburg, Russia in 1838 while working with an engraved copper printing plate. While Prof. Jacobi had much difficulty in trying to separate the replicated layer, he did note that once it was released the copper piece gave a perfect match of the original.

Prof. Boettger of Germany used nickel plating in the 1840s to produce exacting replicates of art objects by the electroforming process. Electroformed articles, including sculpture, bas-reliefs, and statues from nickel, iron, or copper were produced prior to 1870. Of special interest were the huge electroformed street lamps found in downtown Paris, the production of which might be considered an enormous world-record accomplishment for electrodeposition. Iron electroforming had early applications in the duplication of printing plates for coinage and currency because of its facility to produce the highest accuracy in copying engraved masters.

Modern Applications

Today, the electroforming industry sees a number of high-tech uses for nickel, copper, iron, and alloy deposits to electrofabricate exceedingly important components such as the main combustion chamber for the Space Shuttle, heart pump components, body joint implants (prosthetic devices), high-precision optical scanners and holographic masters (for credit cards, etc.), and recording masters. Fabrication of duplicating plates such as electrotypes, video disc stampers, and currency embossing plates is manufacturing technology of today that employs electroforming. High-precision parts such as molds and dies, where tolerances of internal surfaces are critical, are pieces for which electroforming can be used advantageously. Optical memory disc mold cavities, including those for compact discs (CD and video discs) rely on the virtually perfect surface reproduction found with the electroforming process. The average optical disc requires

impressions having a mean diameter of about 0.2 µm, which is well within the range of the electroforming processes practiced today. One of the most widely used applications today is nickel disc mold electroforming.

Examples of electroforming applications are almost limitless, but a few of the more exacting examples are:

- Delicate, thin-wall components such as lightweight heat or cold shields for aerospace applications, hypodermic needles, foil, fine-mesh screen, and seamless tubing
- Parts that would be difficult to make by any other means, such as electronic waveguides, regeneratively cooled thrust chambers for rocket engines, musical instruments, Pitot tubes, surface roughness gages, and complex metal bellows
- Electroform joining (cold welding) of dissimilar metals that are difficult, if not impossible, to join by thermal means

Electroforming provides unique production advantages for precision operation in the textile, medical, aerospace, communication, electronics, photocopying, automotive, and computer industries, and a number of other industries and is used in the manufacturing of items such as textile printing screens, molds and dies, mesh products, bellows, compact disc stampers, radar wave guides, and optical components.

Electroforming Determinants

Once the conceptual design for a part or component is developed, it is necessary to determine the fabrication process that best meets the functional requirements of the hardware with least cost impact. The following advantages of electroforming might be weighed:

- Parts can be mass produced with identical tolerances from one part to the next, provided that mandrels can be made with adequate replication.
- Fine detail reproduction is unmatched by any other method of mass fabrication. Examples are the electroforming of microgroove masters and stampers for the record and compact disc industries, surface roughness standards, and masters and stampers for holographic image reproduction.
- Mechanical properties of electroformed articles can be varied over a wide range by selecting a suitable plating electrolyte and adjusting operating conditions. In some instances properties can be created in electroformed metals that are difficult, if not impossible, to duplicate in wrought counterparts.
- Some shapes, particularly those with complex internal surfaces or passages, cannot be made by any other method without excessive machining costs and scrap losses. These shapes are often easily electroformed. Examples of such hardware are regeneratively cooled thrust chambers and waveguides with compound curves.
- Gearing up to high-volume production is relatively easy in many electroforming applications. For example, a number of first-generation positive replicas can be made from which a large number of second-generation negatives can be electroformed. Such technology lends itself to many molds, stamping devices, and optical surfaces requiring volume production.
- The size and thickness of parts electroformed is not limited. Larger size can be accommodated by increasing the tank volume in which the electrolyte is contained. Thickness may vary from micrometers, as in foils, to one or more centimeters, as is common in rocket thrust chamber shells.
- Without the use of thermal joining techniques, metal layers can be applied by electroforming to provide sandwich composites having a variety of functional properties. Waveguides having an inner silver electroformed layer for high electrical conductivity and an outer electroformed structural layer of copper, nickel, nickel-cobalt, or other electrodepositable alloys are examples.

There are also some disadvantages of electroforming that must be considered, such as:

- Electroforming is generally an expensive manufacturing method and is chosen when other methods are more expensive or impractical to produce the desired hardware.

- Thick electroforming is very time-consuming. Some deposits require days, or even weeks, to produce the desired thickness. However, unlike precision machining, which is also very time-consuming, electroforming is not labor-intensive once the deposition process is started.
- Design limitations exist in that deep or narrow recesses and sharp angles cause problems. Sudden and severe change in cross section or wall thickness must be avoided unless subsequent machining can be permitted.
- Most electrodeposits have some degree of stress in the as-deposited condition that may cause distortion after the mandrel is separated. Stress relieving and special attention to electrolyte chemistries and operating parameters can lessen this problem.
- Any degradation in the mandrel surface quality will be reproduced in the electroform made from it.

The Electroforming Process

Electroforming is very similar to conventional electroplating as far as facilities and electrolytes are concerned. However, the controls are more stringent, because the process consumes much more time and the product must be mechanically sound and have low internal stress for dimensional acceptance. With long deposition times, high current densities at edges and surfaces closer to the anodes result in significant buildup, leading to nodules and uncontrolled growth. This results in further current density variations that can seriously affect the mechanical properties of the deposit.

In electroforming nickel, cobalt, or iron there is significant hydrogen codeposition that, if not removed, causes pits in the deposit surface. Pumping filtered electrolyte through sprays over the surfaces being electroformed will minimize the problem and aid in maintaining a smooth deposit. Areas of high current density showing excessive and rough buildup can be corrected by using nonconducting shields as baffles to improve the current distribution. Where recessed areas exist, low current density will be experienced. Undesired trace metal impurities will codeposit in such locales, leading to inferior mechanical properties and surface appearance. Auxiliary or bipolar anodes may be necessary to overcome the low-current problem.

Electroforming solutions may be used with one or more additives to control stress, brightness, leveling (smoothness), and microstructure. When mechanical properties (including high ductility) or good electrical or thermal conductivity are important in the deposit, it is advisable to use nonadditive electrolytes. Because most additives are organic compounds, they are subject to decomposition if the deposit is subjected to elevated temperatures.

Stress-reducing agents are often used in nickel, iron, and cobalt plating baths to produce neutral or compressive residual stresses. Such agents are usually grain-refining compounds also. These deposits are generally harder, have higher yield strength, and exhibit less ductility than conventional deposits of the same metal. Advantages in neutral or compressively stressed deposits are ease of removal of electroforms from mandrels and inhibition of growth of cracks in deposits should they occur from impact. A problem with stress reducers in nickel is that sulfur codeposits form when the agent reacts at the cathode, because most stress reducers contain sulfur. Brazing or welding such deposits causes sulfur to react with nickel to form a nickel sulfide liquidus in the range of 483 °C (901 °F) to about 650 °C (1200 °F). This leads to the effect known as "hot shortness" experienced in wrought nickels. Such deposits can be alloyed with as little as 1500 ppm Mg to counter the problem.

Copper Electroforming. Acid sulfate electrolytes are the industry standard for copper electroforming. Additives are usually employed for grain refining, leveling, and brightening. The mechanical property improvements achieved are mostly a result of grain refining. Organic compounds capable of reducing copper oxides at the cathode may also be used to produce an oxygen-free, high-conductivity copper equivalent (<10 ppm oxygen). Decomposition products from copper bath additives will codeposit to degrade ductility. Without additives, acid sulfate baths produce copper with grain size increasing proportionally to deposit thickness. Intergranular voids are created that seriously degrade mechanical properties. A plating technique known as periodic current reversal will promote deposition of a copper deposit having uniform grain size and excellent mechanical properties for thicknesses of 0.5 cm (0.2 in.) or greater. This procedure requires plating in a conventional direction for a given period of time, followed by a reversal of current direction for a lesser period of time. Although the process results in a slow rate of deposition, the benefits of good mechanical properties, relatively smooth deposit surfaces, and ability to plate dense, thick deposits make this technique most useful.

Mandrel Types and Selection

Mandrels are either permanent or expendable. Permanent mandrels are usually metallic, but they can also be made of a conductive plastic. They can be used repeatedly until surface wear or scratching renders them useless. The most widely used permanent mandrels are made of metals that are resistant to adherent bonding by the metal being electroformed. The 300-series stainless steels are the preferred materials for permanent mandrels because of the naturally passive surfaces. Substrates such as copper, brass, or steel may also be used, but these must be plated with chromium to provide a passive surface for ease of separation. It is also possible to use copper or brass for engravure mandrels if they are chemically passivated to prevent electroform bonding. Nickel is frequently employed for producing multiple first-generation replicas for mass production of second-generation electroforms. Adherence on nickel is unpredictable, so it is advisable to passivate the surfaces chemically.

Plastics are suitable for permanent mandrels where flat electroforms are involved and separation is relatively simple. Such mandrels are made conductive by the silver reduction method (Ref 1) or by use of silver-filled paint. Plastic mandrels are often used for the electroforming of Fresnel lenses. Glass plates can also be used as permanent mandrels containing holographic imagery.

Expendable mandrels may consist of cast fusible metals, plaster, plastics, waxes, soluble metals, or wood. Fusible metals are commonly alloys of tin, lead, bismuth, antimony, and cadmium. Aluminum is a popular expendable mandrel material because it is easily machined and polished to close surface and dimensional tolerances. It is also easy to dissolve in caustic solutions.

Reference cited in this section

1. H. Narcus, *Metallizing of Plastics,* Reinhold Publishing Company, 1960

Mandrel Design and Preparation

Mandrels may be made to reproduce accurately external or internal surfaces. The reproduced surface will be precisely the same as the surface upon which plating is initiated. The final plated surface will be rougher as the plated thickness increases. Design features of importance are avoidance of deep grooves or recesses, avoidance of sharp internal angles, and maintenance of liberal radii on corners. Figure 1 illustrates mandrel design considerations that should be followed.

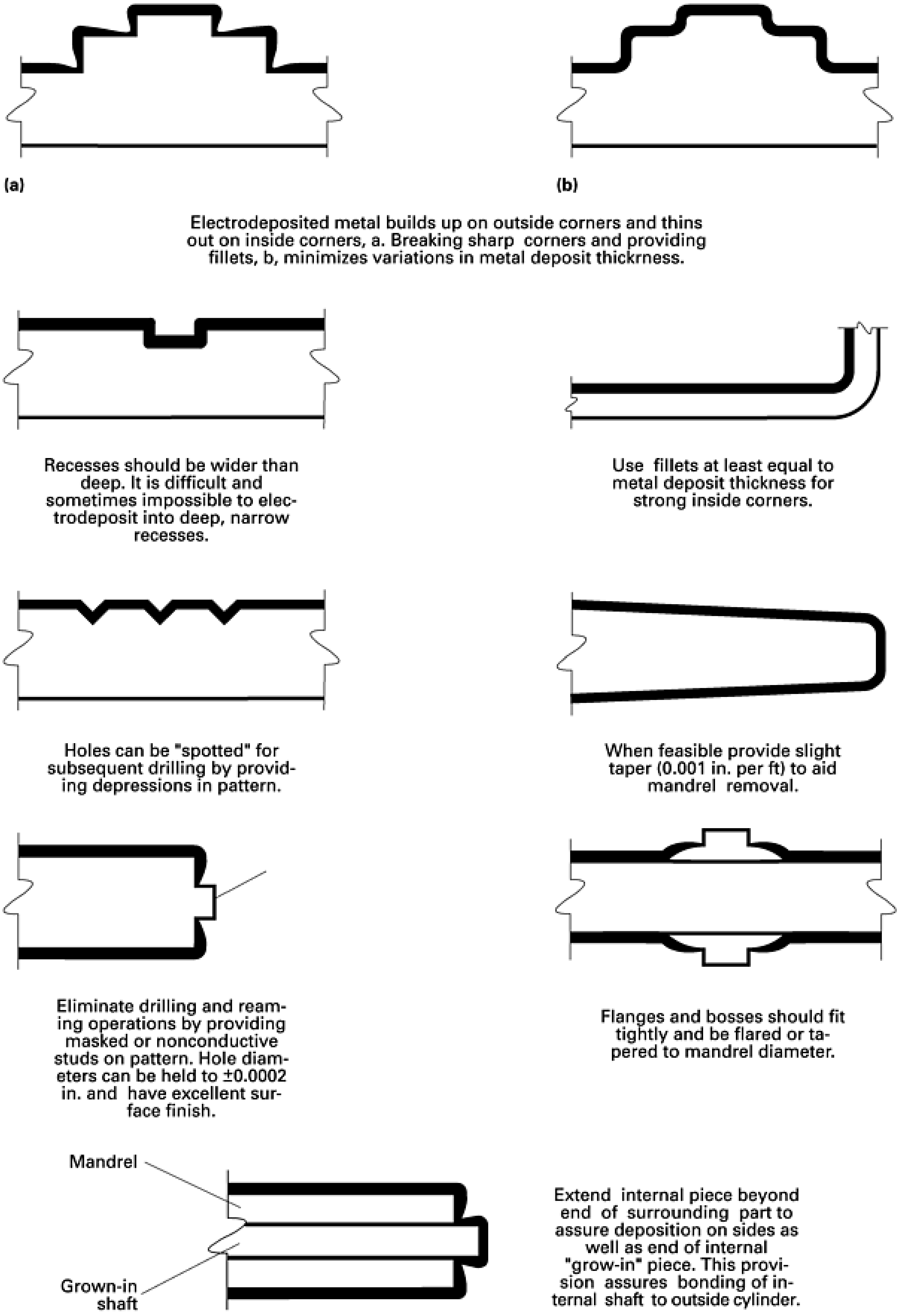

Fig. 1 Factors to consider in electroforming mandrel design. Source: Ref 2

Permanent mandrels for electroforming concentric shapes must be designed with a draft or taper to permit removal of the mandrel without damaging the electrodeposit or the mandrel. If this is not possible, expendable mandrels must be considered. ASTM B 450 provides more guidelines in the design of electroformed articles (Ref 3). Preparation of mandrels for electroforming is detailed in ASTM B 431 (Ref 4). Special design considerations are often given to permanent mandrels being developed for complex parts that are to be produced in mass quantities or are of a complex nature, requiring speedy release from the mandrel. In these cases, knockout blocks or key release sections are designed into the mold, mandrel, or matrix to ensure quick and positive release and multiple uses of the master form.

References cited in this section

2. A. Squitero, Designing Electroformed Parts, *Machine Design,* 9 May 1963

3. ASTM B 450, "Standard Practice for Engineering Design of Electroformed Articles," ASTM

4. ASTM B 431, "Standard Practice for Processing of Mandrels for Electroforming," ASTM

Electroforming Solutions and Operating Variables

Nickel Electroforming Solutions. Nickel, the most commonly electroformed metal, is plated from Watts, fluoborate, and sulfamate solutions. The last is the most widely used due to lower stresses in the deposits and ease of operation. Nickel is deposited from most baths with moderate to high tensile stress. If uncontrolled, this stress can make removal of the mandrel difficult, can result in distorted parts after mandrel separation, and can even result in deposit cracking. In general, the chloride-free sulfamate bath produces the lowest internal stresses of all the nickel baths. Typical nickel sulfamate electrolyte compositions, operating conditions, and deposit mechanical properties are shown in Table 1. Effects of changes in operating variables on mechanical properties of nickel sulfamate deposits are described in Table 2. Similar information for all commonly used nickel electroforming baths is given in ASTM B 503 (Ref 5).

Table 1 Nickel electroforming solutions and selected properties of the deposits

Parameter	**Watts nickel**	**Nickel sulfamate**
Electrolyte composition, g/L (oz/gal)	$NiSO_4 \cdot 6H_2O$--225-300 (30-40)	$Ni(SO_3NH_2)_2$--315-450 (42-60)
	$NiCl_2 \cdot 6H_2O$--37.5-52.5 (5-7)	H_3BO_3--30-45 (4-6)
	H_3BO_3--30-45 (4-6)	$NiCl_2 \cdot 6H_2O$--0-22.5 (0-3)
Operating conditions		
Temperature, °C (°F)	44-66 (115-150)	32-60 (90-140)
Agitation	Air or mechanical	Air or mechanical
Cathode current density, A/dm^2 (A/ft^2)	270-1075 (25-100)	50-3225 (5-300)
Anodes	Soluble nickel	Soluble nickel
pH	3.0-4.2	3.5-4.5
Mechanical properties		

Tensile strength, MPa (ksi)	345-482 (50-70)	410-620 (60-90)
Elongation, %	15-25	10-25
Hardness, HV_{100}	130-200	170-230
Internal tensile stress, MPa (ksi)	125-186 (18-27)	0-55 (0-8)

Table 2 Variables affecting mechanical properties of deposits from nickel sulfamate electrolytes

Property	Operational effects	Solution composition effects
Tensile strength	Decreases with increasing temperature to 49 °C, then increases slowly with further temperature increase. Increases with increasing pH. Decreases with increasing current density.	Decreases slightly with increasing nickel content.
Elongation	Decreases as the temperature varies in either direction from 43 °C. Decreases with increasing pH. Increases moderately with increasing current density.	Increases slightly with increasing nickel content. Increases slightly with increasing chloride content.
Hardness	Increases with increasing temperature within operating range suggested. Increases with increasing solution pH.Reaches a minimum at about 13 A/dm^2.	Decreases slightly with increasing concentration of nickel ion. Decreases slightly with increasing chloride content.
Internal stress	Decreases with increasing solution temperature. Reaches a minimum at pH 4.0-4.2. Increases with increasing current density.	Relatively independent of variation in nickel ion content within range. Increases significantly with increasing chloride content.

Copper electroforming solutions of significance are the acid sulfate and fluoborate baths. Table 3 lists typical compositions, operating conditions, and mechanical properties for these baths. Changes in operating variables will affect mechanical properties of copper sulfate deposits, as noted in Table 4. Similar information for effects of variable changes on copper fluoborate deposits are found in ASTM B 503 (Ref 5).

Table 3 Copper electroforming solutions and selected properties of deposits

Parameter	Copper sulfate	Copper fluoborate
Electrolyte composition, g/L (oz/gal)	$CuSO_4 \cdot 5H_2O$--210-240 (28-32)	$Cu(BF_4)_2$--225-450 (30-60)
	H_2SO_4--52-75 (7-10)	HBF_4--To maintain pH at 0.15-1.5
Operating conditions		
Temperature, °C (°F)	21-32 (70-90)	21-54 (70-129)

Agitation	Air or mechanical	Air or mechanical
Cathode current density, A/dm^2 (A/ft^2)	1-10 (9.3-93)	8-44 (75-410)
Anodes	Oxygen-free, high-conductivity copper or phosphorized copper	Soluble copper
Mechanical properties		
Tensile strength, MPa (ksi)	205-380 (30-55)	140-345 (20-50)
Elongation, %	15-25	5-25
Hardness, HV_{100}	45-70	40-80
Internal tensile stress, MPa (ksi)	0-10 (0-1.45)	0-105 (0-15)

Table 4 Variables affecting mechanical properties of deposits from acid copper sulfate electrolytes

Property	Operational effects	Solution composition effects
Tensile strength	Decreases slightly with increasing solution temperature. Increases significantly with increase in cathode current density.	Relatively independent of changes in copper sulfate concentration within the range suggested. Relatively independent of changes in sulfuric acid concentration within the range suggested.
Elongation	Decreases with increasing solution temperature. Increases slightly with increasing cathode current density.	High acid concentrations, particularly with low copper sulfate concentration, tend to reduce elongation slightly.
Hardness	Decreases slightly with increasing solution temperature. Relatively independent of change in cathode current density.	Relatively independent of copper sulfate concentration. Increases slightly with increasing acid concentration.
Internal stress	Increases with increasing solution temperature. Increases with increasing cathode current density.	Relatively independent of copper sulfate concentration. Decreases very slightly with increasing acid concentration.

Iron Electroforming Solutions. Iron electroforming, while not in major industrial production today, is technically usable if precautions are followed. Three types of electroforming baths exist as slightly acidic systems: sulfate, fluoborate, and sulfamate systems. A fourth system is the highly acidic chloride system, which uses ferrous chloride/calcium chloride operating between 88 and 99 °C (190 and 210 °F). Table 5 presents condensed details of the four baths and primary operating conditions. Except for deposits from the chloride bath, all other baths produce iron deposits brittle in nature and not usable without special thermal treatment, stress-reducing additives, or backup deposits to protect the brittle nature of the iron films. The chloride deposits can be best used with a postplating heat treatment of 260 °C (500 °F) or above to ensure ductility.

Table 5 Iron electroforming solutions and operating conditions

Parameter	**Value**
Chloride bath	
Ferrous chloride (dihydrate), g/L (oz/gal)	300-450 (40-60)
Calcium chloride, g/L (oz/gal)	150-185 (20-25)
Temperature, °C (°F)	90-99 (190-210)
pH (HCl)	0.2-1.8
Current density, A/dm^2 (A/ft^2)	
Without agitation	2-8.5 (20-80)
With agitation	2-21 (20-200)
Sulfate bath	
Ferrous sulfate, g/L (oz/gal)	240 (32)
pH	2.8-3.5
Temperature, °C (°F)	32-65 (90-150)
Current density, max, A/dm^2 (A/ft^2)	
at 32 °C (90 °F)	4.3 (40)
at 65 °C (150 °F)	10 (100)
Surface tension, dynes/cm	40
Cathode agitation	Desirable
Fluoborate bath	
Iron fluoborate, g/L (oz/gal)	227 (30.3)

Metallic iron, g/L (oz/gal)	55.2 (7.37)
Sodium chloride, g/L (oz/gal)	10.0 (1.34)
Baumé, degrees, at 27 °C (80 °F)	19-21
pH (colorimetric)	3.0-3.4
Temperature, °C (°F)	57-63 (135-145)
Current density (cathode-average), A/dm^2 (A/ft^2)	2-10 (20-90)
Tank voltage, avg	2-6
Sulfamate bath	
Ferrous iron, g/L (oz/gal)	75 (10)
Ammonium sulfamate, g/L (oz/gal)	30-37 (4-5)
Sodium chloride, g/L (oz/gal)	37-45 (5-6)
Temperature, °C (°F)	50-60 (120-140)
Current density, A/dm^2 (A/ft^2)	5.4 (50)
pH	2.7-3.0

Reference cited in this section

5. ASTM B 503, "Standard Practice for Use of Copper and Nickel Electroplating Solutions for Electroforming," ASTM

Process Controls

Because of the exacting products desired during electroforming, the controls are apt to be more stringent. Controlling metal distribution, internal stress, nodular growth, and roughness are among the potential problems that are often found in electroforming. Some of these problems are handled by using various addition agents, but special attention is often required to monitor conditions during deposition. Other significant aspects of the electroforming process that demand special consideration include the following.

Metal distribution relates to nonuniform deposition due to changes in mandrel configuration, throwing power of the bath selected, placement in the plating tank, and other features of the deposits being produced. Attempting to retain the best properties of the metal being deposited and at the same time maintain excellent throwing power is most difficult. One can improve metal distribution by using proper racking designs, employing "thieves," "robbers," shields, or auxiliary or

conforming anodes, and completely mapping out the electrical requirements of the mandrel. Computer software programs exist that aid in the design of cathode distribution systems.

Internal deposit stress is most important to control during, before, and after deposition. Before deposition it may develop within the mandrel, resulting in unwarranted partial liftoff of the electroform before it is complete. During deposition, symptoms of internal deposit stress are problems trying to separate the electroform from the mold, buckling or blistering of the deposits, and cracking of the deposit during deposition or while it is separated from the master. Most of these manifestations come from either the bath itself, impurities permitted in the bath (incomplete filtration), or lack of control of the additives needed for the bath. Careful monitoring of all operating conditions is also important for deposit stress control.

Roughness and "treeing" are conditions that may appear during electroforming if care is not taken. To minimize roughness, the electroformer must watch the filtration rates, because even small dirt particles can be the nucleation sites for rough deposits. Filtration rates may need to be as high as whole-solution-volume recycling once or more per hour. Other aids in preventing roughness include using positive pressure of an inch or so with filtered air, plus keeping the electroforming room in extra-clean condition.

The phenomenon of treeing occurs near the edges or corners of the mandrel or attachment areas. These can be minimized by the use of shields, improved racking, or "thieving" to prevent excess current in unwanted areas. Leveling agents and nodule suppressants may also be useful to reduce treeing. Often it becomes necessary to stop the electroforming, remove the part, and machine off the excess deposit. One must remember to reactivate the electroform when replacing it in the plating tank.

One other factor worthy of considering in minimizing roughness, pitting, burning, and sometimes treeing is to constantly check solution agitation, whether by air, mechanical, cathode rod, or other means. Make sure that no grease, wear particles, or other outside dirt enters the electroforming system by virtue of the agitation system.

Alloy Electroforming

Alloy electroforming using high-strength materials, such as nickel-cobalt, cobalt-tungsten, and even more complex alloys involving tungsten and the iron group metals, has made some inroads for special applications. Microfabrication of sensors, maskless jet systems, miniature computer components, and a host of newer devices rely on the properties of many electrodeposited alloys and the precision of electroforming to produce such items. Bath chemistries, deposition parameters (in some cases requiring pulse plating control), and fixturing are all very critical to control for optimal production of these advanced products.

Future Applications

Such developments as composition-modulated alloys, nanophase composites, nonaqueous plating baths, and advanced pulsed current controls are expected to open the field of electroforming to more complex and innovative applications.

Electroless Nickel Plating

Revised by Donald W. Baudrand, MacDermid Inc.

Introduction

ELECTROLESS NICKEL PLATING is used to deposit nickel without the use of an electric current. The coating is deposited by an autocatalytic chemical reduction of nickel ions by hypophosphite, aminoborane, or borohydride compounds. Two other methods have been used commercially for plating nickel without electric current, including (1) immersion plating on steel from solutions of nickel chloride and boric acid at 70 °C (160 °F) and (2) decomposition of nickel carbonyl vapor at 180 °C (360 °F). Immersion deposits, however, are poorly adherent and nonprotective, while the decomposition of nickel carbonyl is expensive and hazardous. Accordingly, only electroless nickel plating has gained wide acceptance.

Since gaining commercial use in the 1950s, electroless nickel plating has grown rapidly and now is an established industrial process. Currently, hot acid hypophosphite-reduced baths are most frequently used to plate steel and other

metals, whereas warm alkaline hypophosphite baths are used for plating plastics and nonmetals. Borohydride-reduced baths are also used to plate iron and copper alloys, especially in Europe.

Electroless nickel is an engineering coating, normally used because of excellent corrosion and wear resistance. Electroless nickel coatings are also frequently applied on aluminum to provide a solderable surface and are used with molds and dies to improve lubricity and part release. Because of these properties, electroless nickel coatings have found many applications, including those in petroleum, chemicals, plastics, optics, printing, mining, aerospace, nuclear, automotive, electronics, computers, textiles, paper, and food machinery (Ref 1). Some advantages and limitations of electroless nickel coatings include:

Advantages

- Good resistance to corrosion and wear
- Excellent uniformity
- Solderability and brazeability
- Low labor costs

Limitations

- Higher chemical cost than electroplating
- Brittleness
- Poor welding characteristics due to contamination of nickel plate with nickel phosphorus deposits
- Need to copper strike plate alloys containing significant amounts of lead, tin, cadmium, and zinc before electroless nickel can be applied
- Slower plating rate, as compared to electrolytic methods

Reference

1. K. Parker, "Recent Advances in Electroless Nickel Deposits, 8th Interfinish Conference," 1972 (Basel)

Bath Composition and Characteristics

Electroless nickel coatings are produced by the controlled chemical reduction of nickel ions onto a catalytic surface. The deposit itself is catalytic to reduction, and the reaction continues as long as the surface remains in contact with the electroless nickel solution. Because the deposit is applied without an electric current, its thickness is uniform on all areas of an article in contact with fresh solution.

Electroless nickel solutions are blends of different chemicals, each performing an important function. Electroless nickel solutions contain:

- A source of nickel, usually nickel sulfate
- A reducing agent to supply electrons for the reduction of nickel
- Energy (heat)
- Complexing agents (chelators) to control the free nickel available to the reaction
- Buffering agents to resist the pH changes caused by the hydrogen generated during deposition
- Accelerators (exultants) to help increase the speed of the reaction
- Inhibitors (stabilizers) to help control reduction
- Reaction byproducts

The characteristics of an electroless nickel bath and its deposit are determined by the composition of these components.

Reducing Agents

A number of different reducing agents have been used in preparing electroless nickel baths, including sodium hypophosphite, aminoboranes, sodium borohydride, and hydrazine.

Sodium Hypophosphite Baths. The majority of electroless nickel used commercially is deposited from solutions reduced with sodium hypophosphite. The principal advantages of these solutions over those reduced with boron compounds or hydrazine include lower cost, greater ease of control, and better corrosion resistance of the deposit.

Several mechanisms have been proposed for the chemical reactions that occur in hypophosphite-reduced electroless nickel plating solutions. The most widely accepted mechanism is illustrated by the following equations:

$$(H_2PO_2)^- + H_2O \frac{Catalyst}{Heat} \rightarrow H^+ + (HPO_3)^{-2} + 2H_{abs} \qquad \textbf{(Eq 1)}$$

$$Ni_2 + 2H_{abs} \rightarrow Ni + 2H^+ \qquad \textbf{(Eq 2)}$$

$$(H_2PO_2)^- + H_{abs} \rightarrow H_2O + OH^- + P \qquad \textbf{(Eq 3)}$$

$$(H_2PO_2)^- + H_2O \rightarrow H^+ + (HPO_3)^{2-} + H_2 \qquad \textbf{(Eq 4)}$$

In the presence of a catalytic surface and sufficient energy, hypophosphite ions are oxidized to orthophosphite. A portion of the hydrogen given off is absorbed onto the catalytic surface (Eq 1). Nickel at the surface of the catalyst is then reduced by the absorbed active hydrogen (Eq 2). Simultaneously, some of the absorbed hydrogen reduces a small amount of the hypophosphite at the catalytic surface to water, hydroxyl ion, and phosphorus (Eq 3). Most of the hypophosphite present is catalytically oxidized to orthophosphite and gaseous hydrogen (Eq 4) independently of the deposition of nickel and phosphorus, causing the low efficiency of electroless nickel solutions. Usually 5 kg (10 lb) of sodium hypophosphite is required to reduce 1 kg (2 lb) of nickel, for an average efficiency of 37% (Ref 2, 3).

Early electroless nickel formulations were ammoniacal and operated at high pH. Later, acid solutions were found to have several advantages over alkaline solutions. Among these are higher plating rate, better stability, greater ease of control, and improved deposit corrosion resistance. Accordingly, most hypophosphite reduced electroless nickel solutions are operated between 4 and 5.5 pH. Compositions for alkaline and acid plating solutions are listed in Table 1 (Ref 2, 3, 4, 5).

Table 1 Hypophosphite-reduced electroless nickel plating solutions

Constituent or condition	**Alkaline**			**Acid**		
	Bath 1	**Bath 2**	**Bath 3**	**Bath 4**	**Bath 5**	**Bath 6**
Composition						
Nickel chloride, g/L (oz/gal)	45 (6)	30 (4)	30 (4)	. . .	. . .	. . .
Nickel sulfate, g/L (oz/gal)	. . .	. . .	. . .	21 (2.8)	34 (4.5)	45 (6)
Sodium hypophosphite, g/L (oz/gal)	11 (1.5)	10 (1.3)	10 (1.3)	24 (3.2)	35 (4.7)	10 (1.3)
Ammonium chloride, g/L (oz/gal)	50 (6.7)	50 (6.7)	. . .	. . .	. . .	. . .
Sodium citrate, g/L (oz/gal)	100 (13.3)	. . .	. . .	. . .	. . .	. . .

Ammonium citrate, g/L (oz/gal)	. . .	65 (8.6)	. . .	. . .	. . .	. . .
Ammonium hydroxide	To pH	To pH	. . .	. . .	. . .	. . .
Lactic acid, g/L (oz/gal)	. . .	. . .	. . .	28 (3.7)	. . .	. . .
Malic acid, g/L (oz/gal)	. . .	. . .	. . .	. . .	35 (4.7)	. . .
Amino-acetic acid, g/L (oz/gal)	. . .	. . .	. . .	. . .	. . .	40 (5.3)
Sodium hydroxyacetate, g/L (oz/gal)	. . .	. . .	10 (1.3)	. . .	. . .	. . .
Propionic acid, g/L (oz/gal)	. . .	. . .	. . .	2.2 (0.3)	. . .	. . .
Acetic acid, g/L (oz/gal)	. . .	. . .	. . .	. . .	. . .	10 (1.3)
Succinic acid, g/L (oz/gal)	. . .	. . .	. . .	. . .	10 (1.3)	. . .
Lead, ppm	. . .	. . .	. . .	1	. . .	. . .
Thiourea, ppm	. . .	. . .	. . .	. . .	1	. . .
Operating conditions						
pH	8.5-10	8-10	4-6	4.3-4.6	4.5-5.5	4.5-5.5
Temperature, °C (°F)	90-95 (195-205)	90-95 (195-205)	88-95 (190-205)	88-95 (190-205)	88-95 (190-205)	88-95 (190-205)
Plating rate, μm/h (mil/h)	10 (0.4)	8 (0.3)	10 (0.4)	25 (1)	25 (1)	25 (1)

Aminoborane Baths. The use of aminoboranes in commercial electroless nickel plating solutions has been limited to two compounds: N-dimethylamine borane (DMAB)-$(CH_3)_2$ $NHBH_3$, and H-diethylamine borane (DEAB)--$(C_2H_5)_2$ $NHBH_3$. DEAB is used primarily in European facilities, whereas DMAB is used principally in the United States. DMAB is readily soluble in aqueous systems. DEAB must be mixed with a short chain aliphatic alcohol, such as ethanol, before it can be dissolved in the plating solution.

Aminoborane-reduced electroless nickel solutions have been formulated over wide pH ranges, although they are usually operated between 6 and 9 pH. Operating temperatures for these baths range from 50 to 80 °C (120 to 180 °F), but they can be used at temperatures as low as 30 °C (90 °F). Accordingly, aminoborane baths are very useful for plating plastics and nonmetals, which is their primary application. The rate of deposition varies with pH and temperature, but is usually 7 to 12 μm/h (0.3 to 0.5 mil/h). The boron content of the deposit from these baths varies between 0.4 and 5%. Compositions and operating conditions for aminoborane baths are listed in Table 2 (Ref 2, 5, 6).

Table 2 Aminoborane- and borohydride-reduced electroless nickel plating solutions

Constituent or condition	Aminoborane		Borohydride	
	Bath 7	Bath 8	Bath 9	Bath 10
Composition				
Nickel chloride, g/L (oz/gal)	30 (4)	24-48 (3.2-6.4)	. . .	20 (2.7)
Nickel sulfate, g/L (oz/gal)	. . .	. . .	50 (6.7)	. . .
DMAB, g/L (oz/gal)	. . .	3-4.8 (0.4-0.64)	3 (0.4)	. . .
DEAB, g/L (oz/gal)	3 (0.4)	. . .	. . .	. . .
Isopropanol, mL (fluid oz)	50 (1.7)	. . .	. . .	. . .
Sodium citrate, g/L (oz/gal)	10 (1.3)	. . .	. . .	. . .
Sodium succinate, g/L (oz/gal)	20 (2.7)	. . .	. . .	. . .
Potassium acetate, g/L (oz/gal)	. . .	18-37 (2.4-4.9)	. . .	. . .
Sodium pyrophosphate, g/L (oz/gal)	. . .	. . .	100 (13.3)	. . .
Sodium borohydride, g/L (oz/gal)	. . .	. . .	. . .	0.4 (0.05)
Sodium hydroxide, g/L (oz/gal)	. . .	. . .	. . .	90 (12)
Ethylene diamine, 98%, g/L (oz/gal)	. . .	. . .	. . .	90 (12)
Thallium sulfate, g/L (oz/gal)	. . .	. . .	. . .	0.4 (0.05)
Operating conditions				
pH	5-7	5.5	10	14
Temperature, °C (°F)	65 (150)	70 (160)	25 (77)	95 (205)
Plating rate, μm/h (mil/h)	7-12 (0.5)	7-12 (0.5)	. . .	15-20 (0.6-0.8)

Sodium Borohydride Baths. The borohydride ion is the most powerful reducing agent available for electroless nickel plating. Any water-soluble borohydride may be used, although sodium borohydride is preferred.

In acid or neutral solutions, hydrolysis of borohydride ions is very rapid. In the presence of nickel ions, nickel boride may form spontaneously. If the pH of the plating solution is maintained between 12 and 14, however, nickel boride formation is suppressed, and the reaction product is principally elemental nickel. One mol of sodium borohydride can reduce approximately one mol of nickel, so that the reduction of 1 kg (2 lb) of nickel requires 0.6 kg (1 lb) of sodium borohydride. Deposits from borohydride-reduced electroless nickel solutions contain 3 to 8 wt% B.

To prevent precipitation of nickel hydroxide, complexing agents, such as ethylene diamine, that are effective between 12 to 14 pH must be used. Such strong complexing agents, however, decrease the rate of deposition. At an operating temperature of 90 to 95 °C (195 to 205 °F), the plating rate of commercial baths is 25 to 30 μm/h (1 to 1.2 mil/h). Compositions of a borohydride-reduced electroless nickel bath are also shown in Table 2 (Ref 6).

During the course of reduction, the solution pH decreases, requiring constant additions of an alkali hydroxide. Spontaneous solution decomposition may occur if the bath pH is allowed to fall below 12. Because of the high operating pH, borohydride plating baths cannot be used for aluminum substrates (Ref 2, 5, 7).

Hydrazine Baths. Hydrazine has also been used to produce electroless nickel deposits. These baths operate at 90 to 95 °C (195 to 205 °F) and 10 to 11 pH. Their plating rate is approximately 12 μm/h (0.5 mil/h). Because of the instability of hydrazine at high temperatures, however, these baths tend to be very unstable and difficult to control.

Whereas the deposit from hydrazine-reduced solutions is 97 to 99% N, it does not have a metallic appearance. The deposit is brittle and highly stressed with poor corrosion resistance. The stress and brittleness are likely due to codeposition of small amounts of basic nickel salts, $Ni(OH)_2$, and nitrogen. Unlike hypophosphite- and boron-reduced nickels, hardness from a hydrazine-reduced electroless nickel has very little commercial use (Ref 2).

Energy

The amount of energy or heat present in an electroless nickel solution is one of the most important variables affecting coating deposition. In a plating bath, temperature is a measure of its energy content.

Temperature has a strong effect on the deposition rate of acid hypophosphite-reduced solutions. The rate of deposition is usually very low at temperatures below 65 °C (150 °F), but increases rapidly with increased temperature (Ref 5). This is illustrated in Fig. 1, which gives the results of tests conducted using bath 3 in Table 1 (Ref 7). The effect of temperature on deposition in boron-reduced solutions is similar. At temperatures above 100 °C (212 °F), electroless nickel solutions may decompose. Accordingly, the preferred operating range for most solutions is 85 to 95 °C (185 to 205 °F).

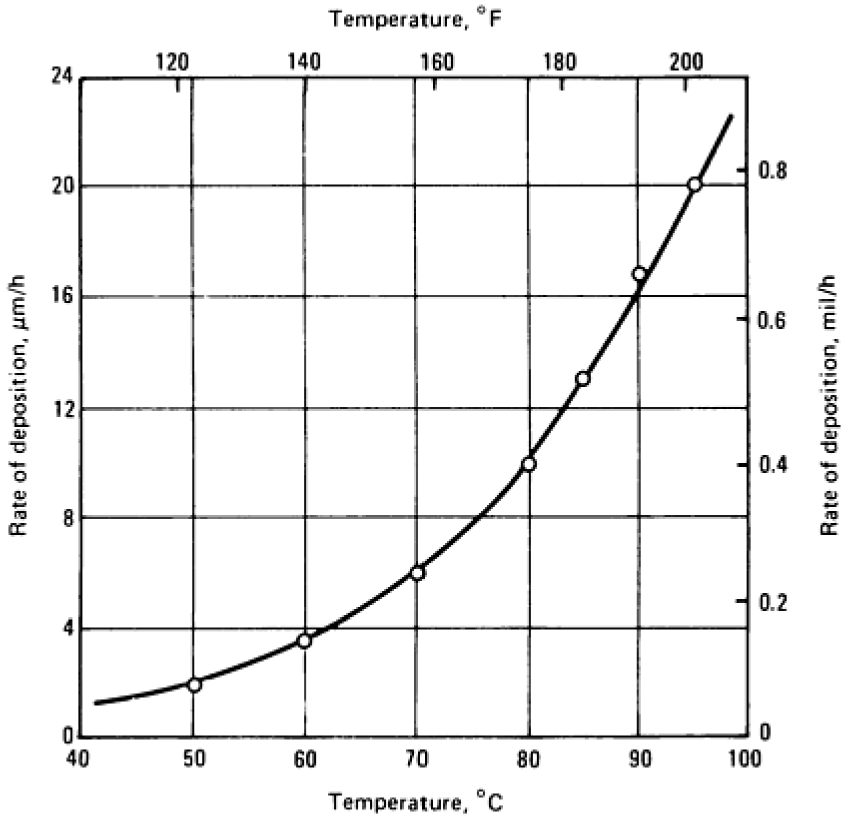

Fig. 1 Effect of solution temperature on the rate of deposition. Tests conducted on bath 3 at 5 pH

Complexing Agents

To avoid spontaneous decomposition of electroless nickel solutions and to control the reaction so that it occurs only on the catalytic surface, complexing agents are added. Complexing agents are organic acids or their salts, added to control the amount of free nickel available for reaction. They act to stabilize the solution and to retard the precipitation of nickel phosphite.

Complexing agents also buffer the plating solution and prevent its pH from decreasing too rapidly as hydrogen ions are produced by the reduction reaction. Ammonia, hydroxides, or carbonates, however, may also have to be added periodically to neutralize hydrogen.

Original electroless nickel solutions were made with the salts of glycolic, citric, or acetic acids. Later baths were prepared using other polydentate acids, including succinic, glutaric, lactic, propionic, and aminoacetic. The complexing ability of an individual acid or group of acids varies, but may be quantified by the amount of orthophosphite that can be held in solution without precipitation (Ref 2, 8). This is illustrated in Fig. 2, which shows the maximum solubility of orthophosphite in solutions complexed with citric and glycolic acids as a function of pH (Ref 9). The complexing agent used in the plating solution can also have a pronounced effect on the quality of the deposit, especially on its phosphorus content, internal stress, and porosity (Ref 8).

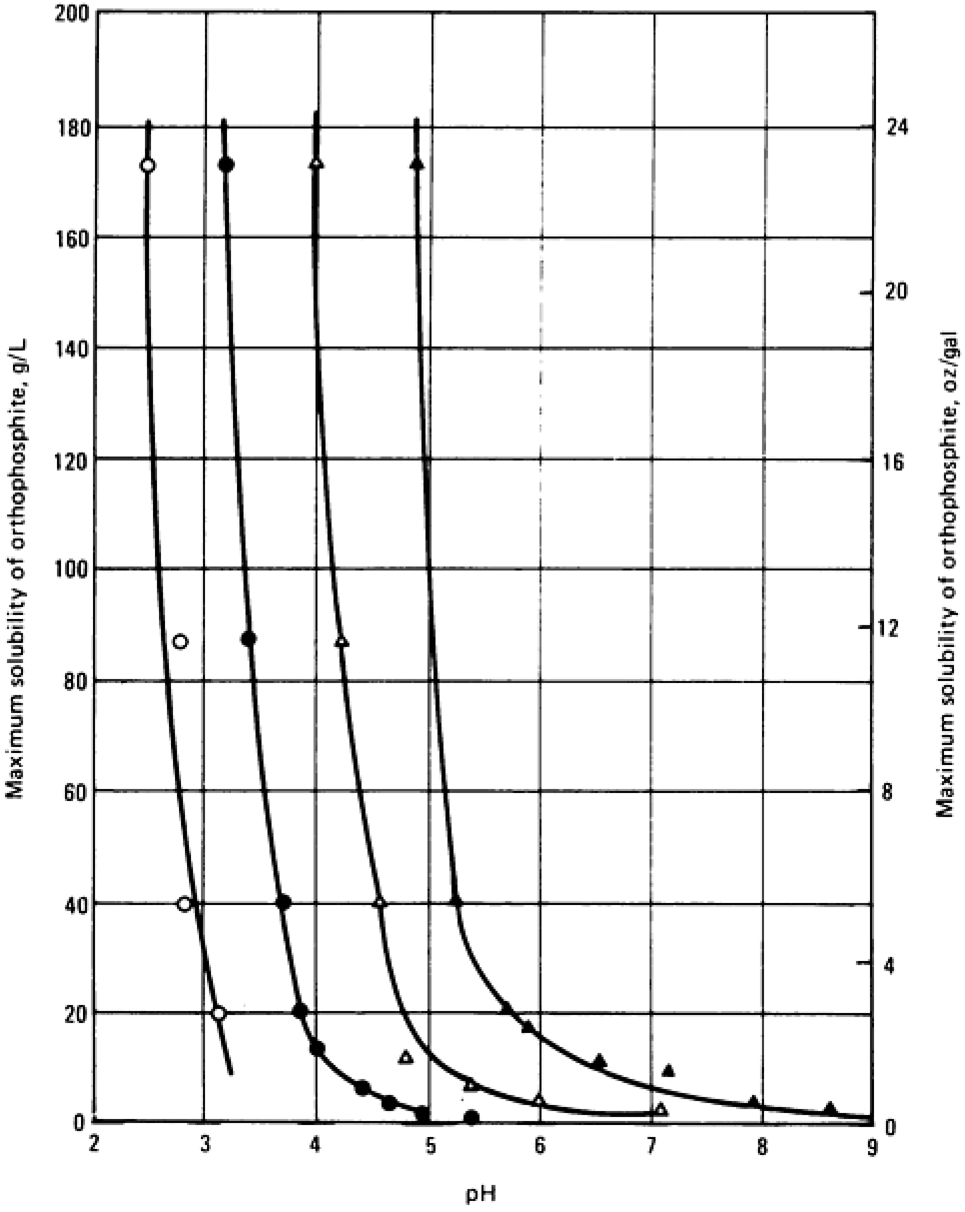

Fig. 2 Limits of solubility for orthophosphite in electroless nickel solutions. Solutions contain 30 g/L (4 oz/gal) nickel chloride ($NiCl_2$) and 10 g/L (1.3 oz/gal) sodium hypophosphite (NaH_2PO_2). d , without a complexing agent; •, with 15 g/L (2 oz/gal) citric acid; ∨ , with 39 g/L (5.2 oz/gal) glycolic acid; ▲, with 78 g/L (10 oz/gal) glycolic acid.

Accelerators

Complexing agents reduce the speed of deposition and can cause the plating rate to become uneconomically slow. To overcome this, organic additives, called accelerators or exultants, are often added to the plating solution in small amounts. Accelerators are thought to function by loosening the bond between hydrogen and phosphorous atoms in the hypophosphite molecule, allowing it to be more easily removed and absorbed onto the catalytic surface. Accelerators activate the hypophosphite ion and speed the reaction shown in Eq 1 (Ref 2, 3). In hypophosphite-reduced solutions, succinic acid is the accelerator most frequently used. Other carbonic acids, soluble fluorides, and some solvents, however, have also been used (Ref 2). The effect of succinate additions upon deposition rate is illustrated in Fig. 3 (Ref 3).

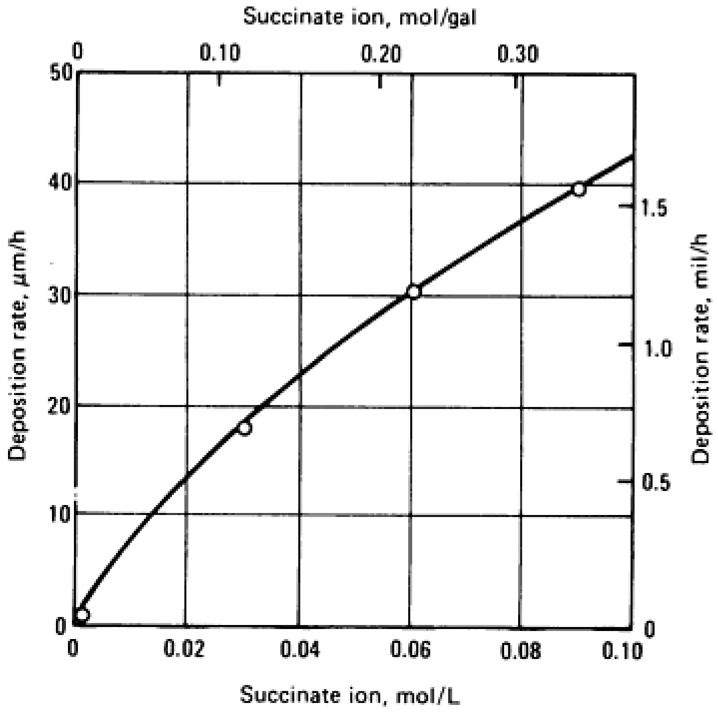

Fig. 3 Effect of succinate additions on the plating rate of an electroless nickel solution. Solutions contain 16 g/L (2.1 oz/gal) nickel chloride ($NiCl_2$) and 24 g/L (3.2 oz/gal) sodium hypophosphite (NaH_2PO_2). 5 g/L (0.7 oz/gal) ammonium hydroxide (NH_4OH) and 1 mg/L (4 mg/gal) lead at 5 pH and 95 °C (205 °F).

Inhibitors

The reduction reaction in an electroless nickel plating bath must be controlled so that deposition occurs at a predictable rate and only on the substrate to be plated. To accomplish this, inhibitors, also known as stabilizers, are added. Electroless nickel plating solutions can operate for hours or days without inhibitors, only to decompose unexpectedly. Decomposition is usually initiated by the presence of colloidal, solid particles in the solution. These particles may be the result of the presence of foreign matter (such as dust or blasting media), or may be generated in the bath as the concentration of orthophosphite exceeds its solubility limit. Whatever the source, the large surface area of the particles catalyzes reduction, leading to a self-accelerating chain reaction and decomposition. This is usually preceded by increased hydrogen evolution and the appearance of a finely divided black precipitate throughout the solution. This precipitate consists of nickel and either nickel phosphide or nickel boride.

Spontaneous decomposition can be controlled by adding trace amounts of catalytic inhibitors to the solution. These inhibitors are absorbed on any colloidal particles present in the solution and prevent the reduction of nickel on their surface. Traditionally, inhibitors used with hypophosphite-reduced electroless nickel have been of three types: sulfur compounds, such as thiourea; oxy anions, such as molybdates or iodates; and heavy metals, such as lead, bismuth, tin, or cadmium. More recently, organic compounds, including oleates and some unsaturated acids, have been used for some functional solutions. Organic sulfide, thio compounds, and metals, such as selenium and thallium, are used to inhibit aminoborane- and borohydride-reduced electroless nickel solutions.

The addition of inhibitors can have harmful as well as beneficial effects on the plating bath and its deposit. In small amounts, some inhibitors increase the rate of deposition and/or the brightness of the deposit; others, especially metals or sulfur compounds, increase internal stress and porosity and reduce ductility, thus reducing the ability of the coating to resist corrosion and wear (Ref 2, 3, 5).

The amount of inhibitor used is critical. The presence of only about 1 mg/L (4 mg/gal) of HS^- ion completely stops deposition, whereas at a concentration of 0.01 mg/L (0.04 mg/gal), this ion is an effective inhibitor. The effect of lead additions on a hypophosphite-reduced succinate bath at pH 4.6 and 95 °C (205 °F) is shown in Fig. 4 (Ref 3). The tests illustrated in Fig. 4 also showed that baths containing less than 0.1 mg/L (0.4 mg/gal) Pb^{2+} decomposed rapidly, whereas baths containing higher concentrations were stable. Excess inhibitor absorbs preferentially at sharp edges and corners, resulting in incomplete coverage (edge pull back) and porosity.

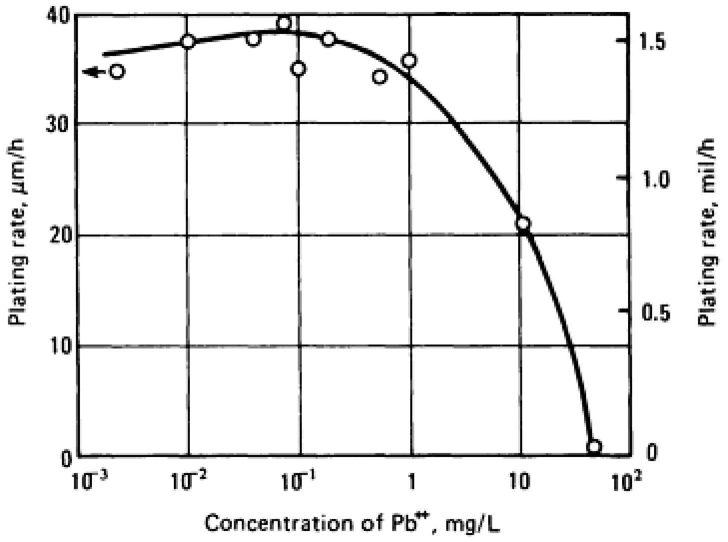

Fig. 4 Effect of lead additions on plating rate in a hypophosphite-reduced succinate-based bath. Bath at 4.6 pH and 95 °C (205 °F). Solutions containing less than 0.1 mg (0.4 mg/gal) Pb^{2+} were unstable.

Reaction Byproducts

During electroless nickel deposition, the byproducts of the reduction, orthophosphite or borate and hydrogen ions, as well as dissolved metals from the substrate accumulate in the solution. These can affect the performance of the plating bath.

Orthophosphite. As nickel is reduced, orthophosphite ion (HPO_3^{2-}) accumulates in the solution and at some point interferes with the reaction. As the concentration of orthophosphite increases, there is usually a small decrease in the deposition rate and a small increase in the phosphorus content of the deposit. Ultimately the accumulation of orthophosphite in the plating solution results in the precipitation of nickel phosphite, causing rough deposits and spontaneous decomposition. Orthophosphite ion also codeposits with nickel and phosphorus, creating a highly stressed, porous deposit.

The solubility of phosphite in the solution is increased when complexing agents, such as citric or glycolic acids, are added. This effect is shown in Fig. 2. However, the use of strong complexors, in other than limited quantities, tends to reduce the deposition rate and increase the porosity and brittleness of the deposit (Ref 8).

Borates. The accumulation of metaborate ion (BO_2^-) from the reduction of borohydride or of boric acid (H_3BO_3) from the reduction of aminoboranes has little effect on electroless nickel plating baths. Both borohydride and aminoborate baths have been operated through numerous regenerations with only a slight decrease in plating rate and without decomposing. With aminoborane-reduced solutions, the solubility of boric acid is probably increased by the presence of amine through the formation of a complex aminoborate (Ref 10).

Hydrogen ions (H^+), produced by the reduction reaction, cause the pH of the bath to decrease. The amount of hydrogen produced, however, depends on the reducing agent being used. Because they are less efficient, hypophosphite-reduced solutions tend to generate more hydrogen ions than those reduced with boron compounds.

The pH of the bath has a strong effect on both solution operation and the composition of the deposit. This is illustrated in Fig. 5, which shows the plating rate and deposit phosphorus content resulting from varying solution pH values in a bath containing 33 g/L (4.4 oz/gal) of nickel sulfate and 20 g/L (2.7 oz/gal) of sodium hypophosphite at 82 °C (180 °F) (Ref 11).

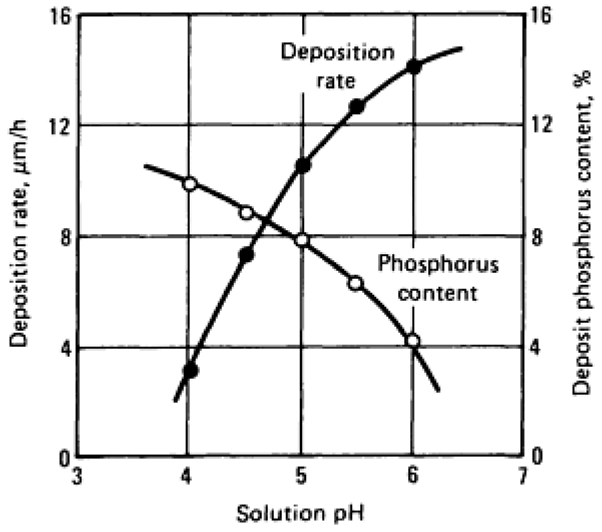

Fig. 5 Effect of solution pH on deposition rate and deposit phosphorus content

To retard pH changes and to help keep operating conditions and deposit properties constant, buffers are included in electroless nickel solutions. Some of the most frequently used buffers include acetate, propionate, and succinate salts. Additions of alkaline materials, such as hydroxide, carbonate solutions, or ammonia, are also required periodically to neutralize the acid formed during plating.

References cited in this section

2. G.G. Gawrilov, *Chemical (Electroless) Nickel Plating,* Portcullis Press, Redhill, England, 1979
3. G. Gutzeit, An Outline of the Chemistry Involved in the Process of Catalytic Nickel Deposition from Aqueous Solution, *Plat. Surf. Finish.,* Vol 46 (No. 10), 1959, p 1158
4. A. Brenner and G. Riddell, Deposition of Nickel and Cobalt by Chemical Reduction, *J. Res. Natl. Bur. Stand.,* Vol 39 (No. 11), 1947, p 385
5. G.O. Mallory, The Electroless Nickel Plating Bath, Electroless Nickel Conference, Cincinnati, Nov 1979
6. K. Stallman and H. Speckhardt, Deposition and Properties of Nickel-Boron Coatings, *Metalloberfl.; Angew. Elektrochem.,* Vol 35 (No. 10), 1981, p 979
7. K.M. Gorbunova and A.A. Nikiforova, *Physicochemical Principles of Nickel Plating,* Izdatel'stvo Akademii Nauk SSSR, Moscow, 1960
8. G.O. Mallory, Influence of the Electroless Plating Bath on the Corrosion Resistance of the Deposits, *Plating,* Vol 61 (No. 11), 1974, p 1005
9. C.E. deMinjer and A. Brenner, Studies on Electroless Nickel Plating, *Plating,* Vol 44 (No. 12), 1957, p 1297
10. G.O. Mallory, The Electroless Nickel-Boron Plating Bath; Effects of Variables on Deposit Properties, *Plating,* Vol 58 (No. 4), 1971, p 319
11. C. Baldwin and T.E. Such, The Plating Rates and Physical Properties of Electroless Nickel/Phosphorus Alloy Deposits, *Trans. Inst. Met. Finish.,* Vol 46 (No. 2), 1968, p 73

Properties of Electroless Nickel-Phosphorus Coatings

Hypophosphite-reduced electroless nickel is an unusual engineering material, because of both its method of application and its unique properties. As applied, nickel-phosphorus coatings are uniform, hard, relatively brittle, lubricious, easily solderable, and highly corrosion resistant. They can be precipitation hardened to very high levels through the use of low-temperature treatments, producing wear resistance equal to that of commercial hard chromium coatings. This combination of properties makes the coating well suited for many severe applications and often allows it to be used in place of more expensive or less readily available alloys.

Structure. Hypophosphite-reduced electroless nickel is one of the very few metallic glasses used as an engineering material. Depending on the formulation of the plating solution, commercial coatings may contain 6 to 12% P dissolved in nickel, and as much as 0.25% of other elements. As applied, most of these coatings are amorphous; they have no crystal or phase structure. Their continuity, however, depends on their composition. Coatings containing more than 10% P and less than 0.05% impurities are typically continuous. A cross section of one of these coatings is shown in Fig. 6.

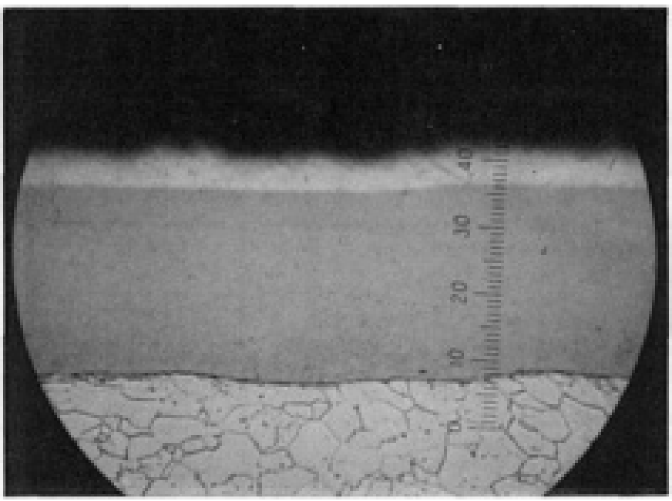

Fig. 6 Cross section of a 75 μm (3 mils) thick electroless nickel deposit. Contains approximately 10% phosphorus and less than 0.05% other elements. 400×

Coatings with lower phosphorus content, especially those applied from baths stabilized with heavy metals or sulfur compounds, are often porous. These deposits consist of columns of amorphous material separated by cracks and holes. The presence of such discontinuities has a severe effect on the properties of the deposit, especially on ductility and corrosion resistance.

As electroless nickel-phosphorus is heated to temperatures above 220 to 260 °C (430 to 500 °F), structural changes begin to occur. First, coherent and then distinct particles of nickel phosphite (Ni_3P) form within the alloy. Then, at temperatures above 320 °C (610 °F), the deposit begins to crystallize and lose its amorphous character. With continued heating, nickel phosphite particles conglomerate and a two-phase alloy forms. With coatings containing more than 8% P, a matrix of nickel phosphite forms, whereas almost pure nickel is the predominant phase in deposits with lower phosphorus content. These changes cause a rapid increase in the hardness and wear resistance of the coating, but cause its corrosion resistance and ductility to be reduced (Ref 2, 12, 13, 14).

Internal stress in electroless nickel coatings is primarily a function of coating composition. As illustrated in Fig. 7, stress in coatings used on steel containing more than 10% P is neutral or compressive (Ref 15). With lower phosphorus deposits, however, tensile stresses of 15 to 45 MPa (2.2 to 6.5 ksi) develop because of the difference in thermal expansion between the deposits and the substrate. The high level of stress in these coatings promotes cracking and porosity (Ref 12).

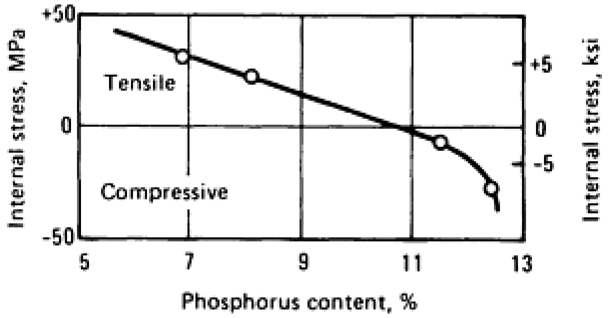

Fig. 7 Effect of phosphorus content on the internal stress of electroless nickel deposits on steel

The structural changes during heat treatment at temperatures above 220 °C (430 °F) cause a volumetric shrinkage of electroless nickel deposits of up to 4 to 6% (Ref 16). This increases tensile stress and reduces compressive stress in the coating.

Deposit stress can also be increased by the codeposition of orthophosphites or heavy metals, as well as by the presence of excess complexing agents in the plating solution. Even small quantities of some metals can produce a severe increase in stress. The addition of only 5 mg/L (20 mg/gal) of bismuth and antimony to most baths can cause the deposit tensile stress to increase to as much as 350 MPa (50 ksi). High levels of internal stress also reduce the ductility of the coating and increase cracking (Ref 2, 16).

When using reported values for stress, it is important to know how the stress was measured. There are several methods that may yield different results. It is important to know whether intrinsic stress (internal stress of the deposit independent of basis material) or total stress of the plated system is reported. Total stress includes the effect of differences in coefficient of thermal expansion of the basis metal and the plated deposit (Ref 17).

Intrinsic stress (Fig. 8) is measured using a spiral contractometer covered by ASTM B 636. Intrinsic stress is found by taking the initial and final readings at the operating temperature of the plating solution. Reading at room temperature provides the total stress, but only for the specific basis metal used for the test. It is best to specify intrinsic stress so that comparison between deposit characteristics can be made (Ref 17).

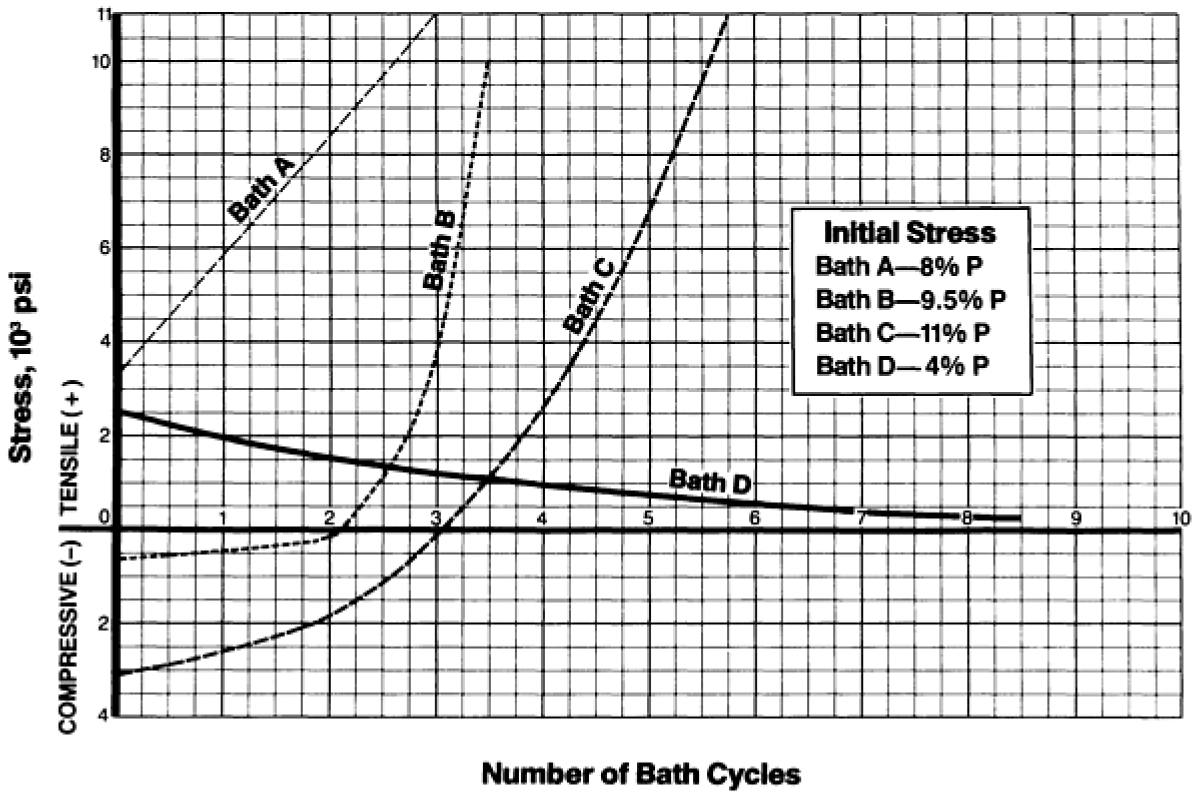

Fig. 8 intrinsic stresses as related to bath cycles for four amounts of phosphorus in deposits from acid nickel-phosphorus solutions. A *bath cycle* is defined as one complete replacement of nickel in the solution (sometimes called *bath turnover*). Nickel content, 6 g/L (0.8 oz/gal); pH, 4.8

The thickness must be constant since stress readings vary with deposit thickness. The ASTM thickness standard is 0.0006 in. (15 μm).

Uniformity. One especially beneficial property of electroless nickel is uniform coating thickness. With electroplated coatings, thickness can vary significantly depending on the shape of the part and the proximity of the part to the anodes. These variations can affect the ultimate performance of the coating, and additional finishing may be required after plating. With electroless nickel, the plating rate and coating thickness are the same on any section of the part exposed to fresh plating solution. Grooves and blind holes have the same amount of coating as the outside of a part.

With electroless nickel, coating thickness can be controlled to suit the application. Coatings as thin as 2.5 μm (0.1 mil) are applied for electronic components, whereas those as thick as 75 to 125 μm (3 to 5 mils) are normally used in corrosive environments. Coatings thicker than 250 μm (10 mils) are used for salvage or repair of worn or mismachined parts (Ref 12).

Adhesion of electroless nickel coatings to most metals is excellent. The initial replacement reaction, which occurs with catalytic metals, together with the associated ability of the baths to remove submicroscopic soils, allows the deposit to establish metallic as well as mechanical bonds with the substrate. The bond strength of the coating to properly cleaned steel or aluminum substrates has been found to be at least 300 to 400 MPa (40 to 60 ksi).

With noncatalytic or passive metals, such as stainless steel, an initial replacement reaction does not occur, and adhesion is reduced. With proper pretreatment and activation, however, the bond strength of the coating usually exceeds 140 MPa (20 ksi) (Ref 2, 12, 13). With metals such as aluminum, parts baked after plating for $1\frac{1}{2}$ h at 190 to 210 °C (375 to 410 °F) to increase the adhesion of the coating. These treatments relieve hydrogen from the part and the deposit and provide a very minor amount of codiffusion between coating and substrate. Baking parts is most useful where pretreatment has been less than adequate and adhesion is marginal. With properly applied coatings, baking has only a minimal effect on bond strength (Ref 2, 12, 14).

The adhesion of electroless nickel deposits depends on the quality of the cleaning and preparation steps prior to plating. Procedures for cleaning and preparation for electroless nickel plating are generally the same as those for electroplating. One exception is that electrocleaners sometimes cannot be used because of fixturing restraints, making soak cleaning more critical. See the section "Pretreatments for Electroless Nickel Coatings" in this article for more information.

Physical Properties. The density of electroless nickel coatings is inversely proportional to their phosphorus content. As shown in Fig. 9, density varies from about 8.5 g/cm^3 for very low phosphorus deposit to 7.75 g/cm^3 for coatings containing 10 to 11% P (Ref 2, 13, 18, 19, 20).

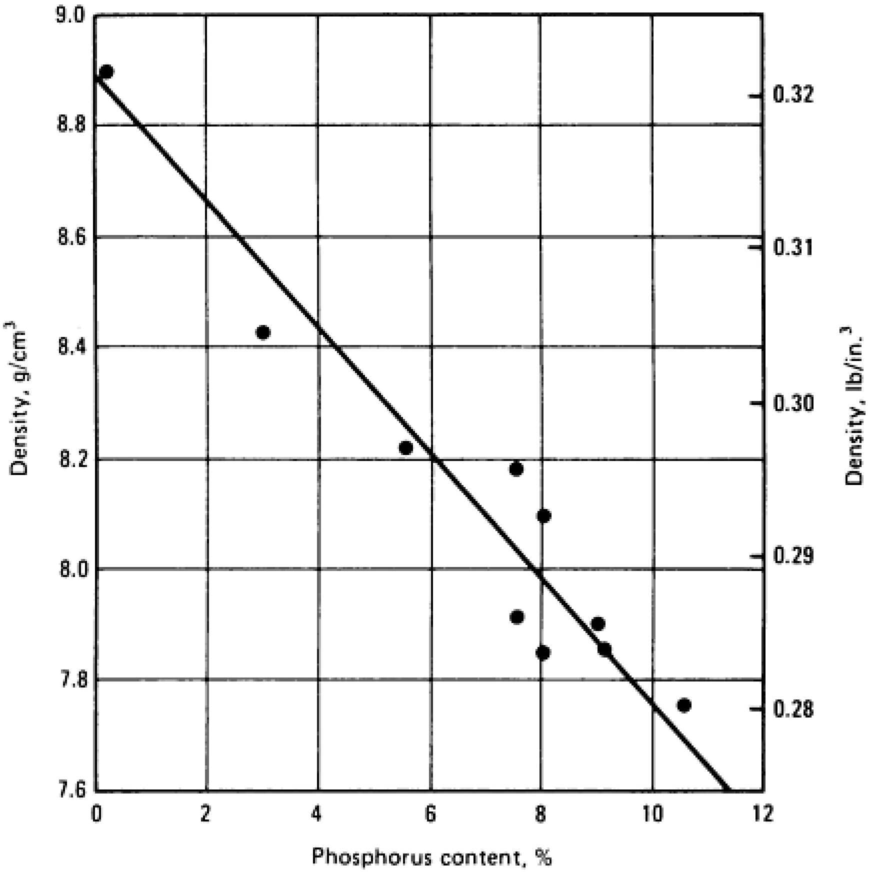

Fig. 9 Effect of phosphorus content on coating density

The thermal and electrical properties of these coatings also vary with composition. For commercial coatings, however, electrical resistivity and thermal conductivity are generally about 50 to 90 μΩ· cm and 0.010 to 0.013 cal/cm · s · °C (2.4 to 3.1 Btu/ft · h · °F), respectively. Accordingly, these coatings are significantly less conductive than conventional conductors such as copper or silver.

Heat treatments precipitate phosphorus from the alloy and can increase its conductivity by three to four times (Ref 2, 13). The formulation of the plating solution can also affect conductivity. Tests with baths containing sodium acetate and succinic acid showed electrical resistivities of 61 and 84 μΩ· cm, respectively (Ref 2).

Phosphorus content also has a strong effect on the thermal expansion of electroless nickel. This is shown in Fig. 10, which shows data for deposit stress measurements on different substrates (Ref 15). The coefficient of thermal expansion of high phosphorus coatings is approximately equal to that of steel. As deposited, coatings containing more than 10% P are completely nonmagnetic. Lower phosphorus coatings, however, have some magnetic susceptibility. The coercivity of 3 to 6% P coatings is about 20 to 80 Oe (1592 to 6366 A/m), while that of deposits containing 7 to 9% P is typically 1 to 2 Oe (80 to 160 A/m). Heat treatments at temperatures above 300 °C (570 °F) improve the magnetic response of electroless nickel and can provide coercivities of about 100 to 300 Oe (7958 to 23,873 A/m) (Ref 11, 21).

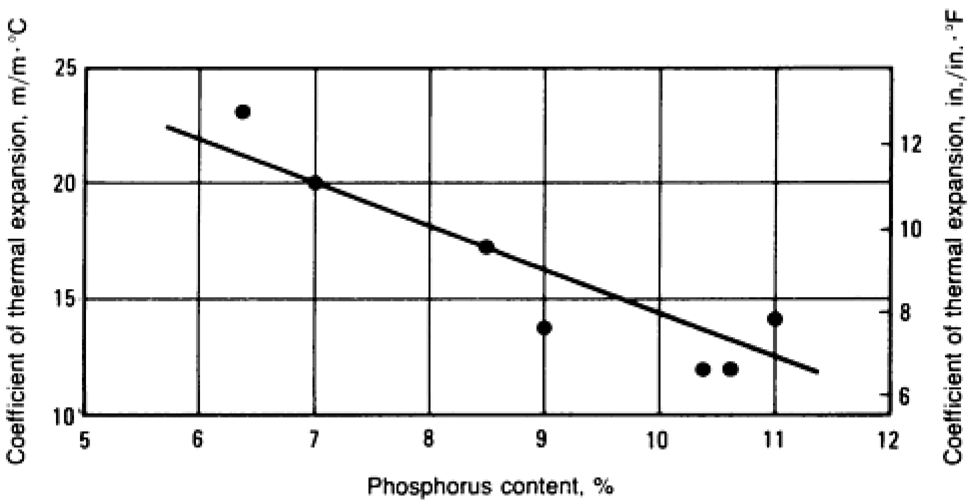

Fig. 10 Effect of deposit phosphorus content on coefficient of thermal expansion

Mechanical Properties. The mechanical properties of electroless nickel deposits are similar to those of other glasses. They have high strength, limited ductility, and a high modulus of elasticity. The ultimate tensile strength of commercial coatings exceeds 700 MPa (102 ksi) and allows the coating to withstand a considerable amount of abuse without damage. The effect of phosphorus content on the strength and strain at fracture of electroless nickel deposits is shown in Fig. 11 (Ref 22).

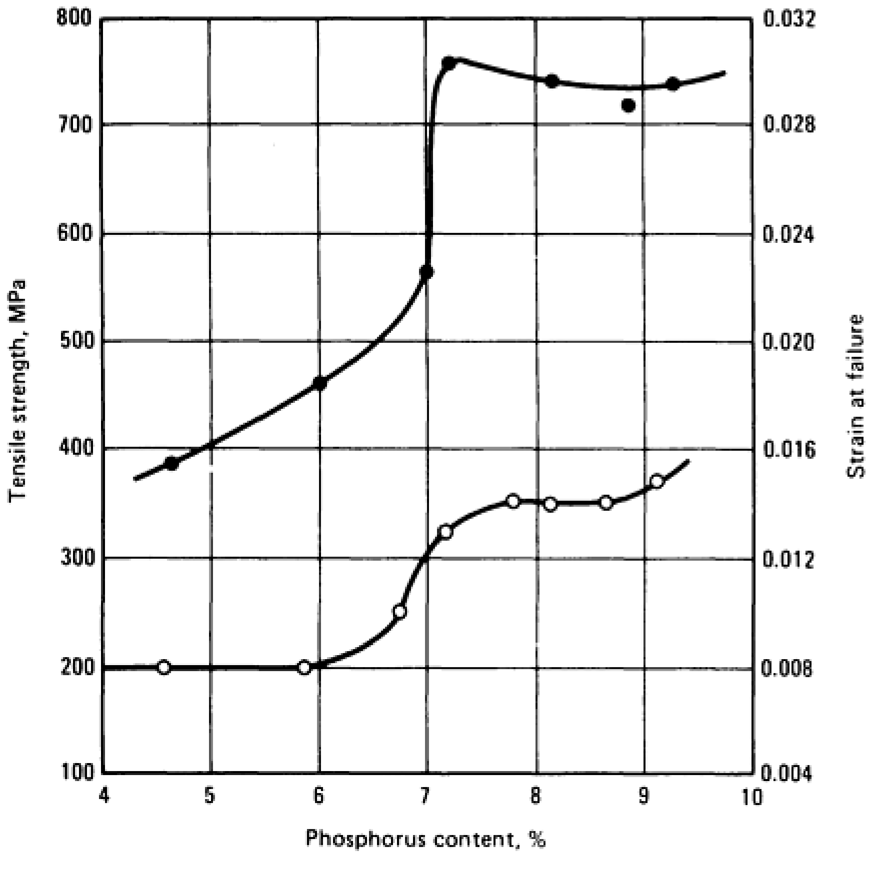

Fig. 11 Effect of deposit phosphorus content on strength and strain at fracture

The ductility of electroless nickel coatings also varies with composition. High phosphorus, high purity coatings have a ductility of about 1 to $1\frac{1}{2}$% (as elongation). Although this is less ductile than most engineering materials, it is adequate for most coating applications. Thin films of deposit can be bent completely around themselves without fracture. With lower phosphorus deposits, or with deposits containing metallic or sulfur impurities, ductility is greatly reduced and may approach zero (Ref 12, 14).

Hardening type heat treatments reduce both the strength and ductility of electroless nickel deposits. Exposure to temperatures above 220 °C (428 °F) causes an 80 to 90% reduction in strength and can destroy ductility. This is illustrated by Fig. 12, which shows the effect of different 1 h heat treatments on the elongation at fracture of brass panels coated with 6% P electroless nickel (Ref 11). The modulus of elasticity of electroless nickel coatings containing 7 to 11% P is about 200 GPa (29,000 ksi) and is very similar to that of steel.

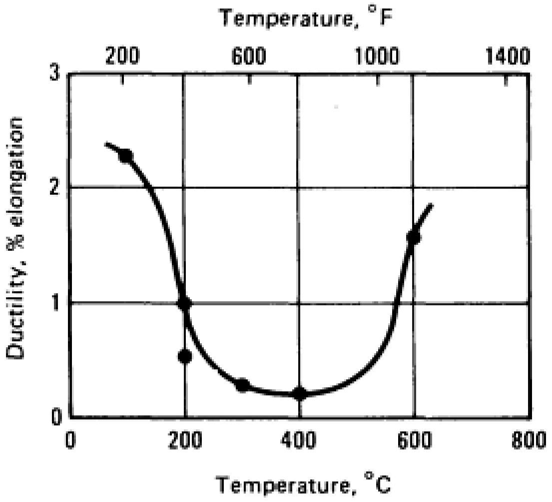

Fig. 12 Effect of heat treatment on the ductility of a 6% P electroless nickel coating

Hardness and wear resistance are extremely important properties for many applications. As deposited, the microhardness of electroless nickel coatings is about 500 to 600 HV_{100}, which is approximately equal to 48 to 52 HRC and equivalent to many hardened alloy steels. Heat treatment causes these alloys to age harden and can produce hardness values as high as 1100 HV_{100}, equal to most commercial hard chromium coatings (Ref 2, 12). Figure 13 shows the effect of different 1-h heat treatments on the hardness of electroless nickel containing $10\frac{1}{2}$% P (Ref 2).

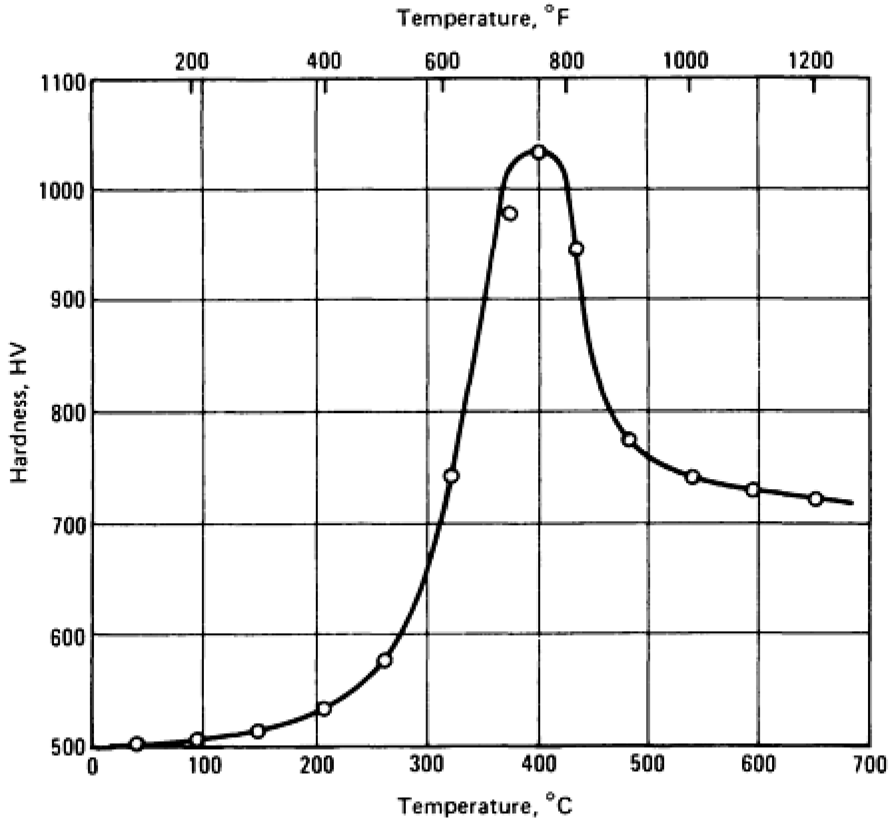

Fig. 13 Effect of heat treatment on hardness of $10\frac{1}{2}$% P electroless nickel coating

For some applications, high-temperature treatments cannot be tolerated because parts may warp, or the strength of the substrate may be reduced. For these applications, longer times and lower temperatures are sometimes used to obtain the desired hardness. This is illustrated in Fig. 14, which shows the effect of different treatment periods on the hardness of a coating containing $10\frac{1}{2}$% P (Ref 12). ASTM specification B 578 requires that the Knoop hardness method be used for plated deposits. However, Vickers hardness numbers have been widely used (Ref 23, 24, 25).

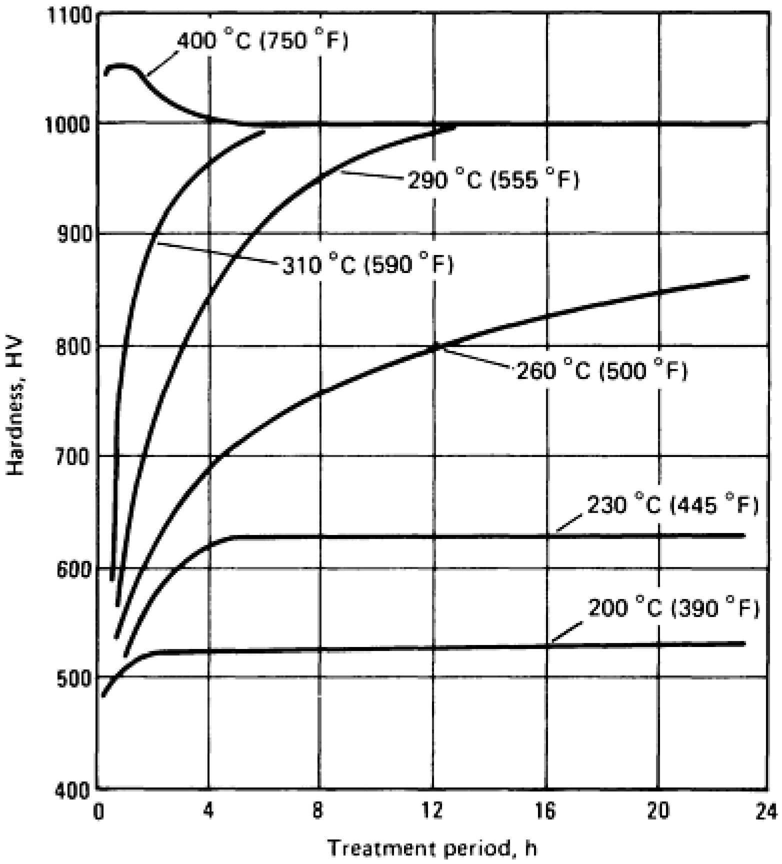

Fig. 14 Effect of different heat treatment periods on hardness of a high-phosphorus electroless nickel coating

Electroless nickel coatings also have excellent hot hardness. To about 400 °C (750 °F), the hardness of heat-treated electroless nickel is equal to or better than that of hard chromium coatings. As-deposited coatings also retain their hardness to this temperature, although at a lower level. The effect of elevated temperature on a 10% P coating is shown in Fig. 15 (Ref 26, 27).

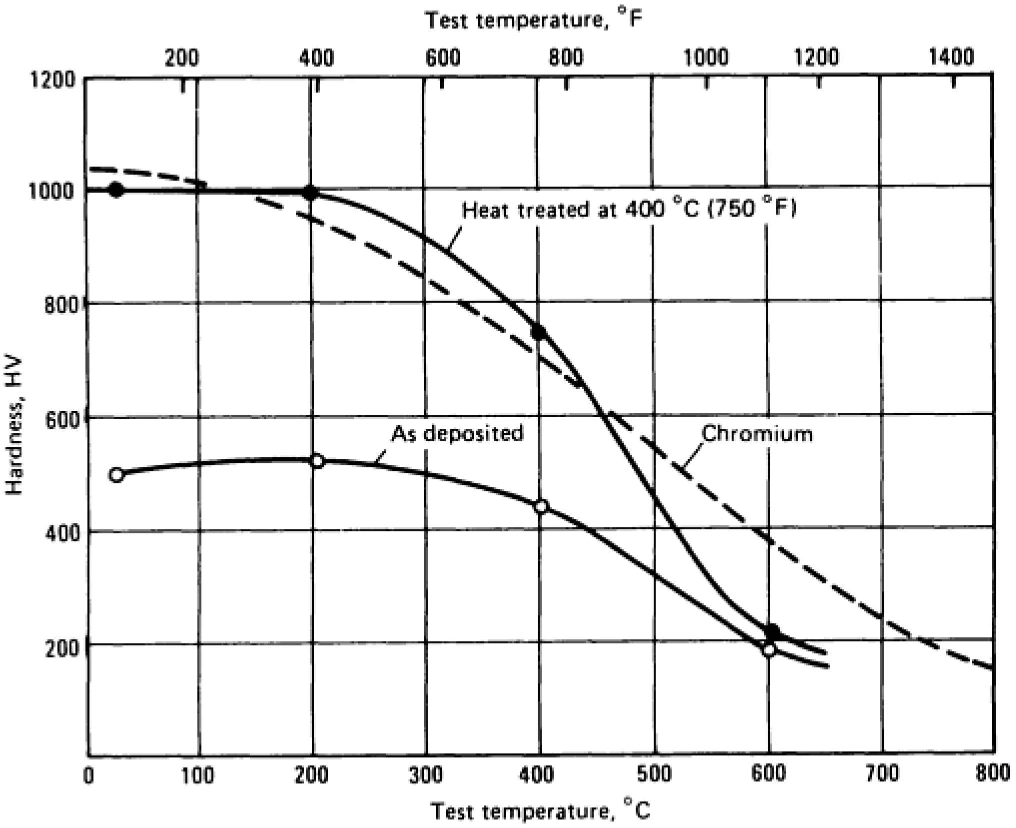

Fig. 15 Effect of temperature on the elevated-temperature hardness of a 10% P electroless nickel coating

Because of their high hardness, electroless nickel coatings have excellent resistance to wear and abrasion, both in the as-deposited and hardened conditions. Taber Abraser Index values for electroless nickel and for electrodeposited nickel and chromium are summarized in Table 3 (Ref 28, 29, 30).

Table 3 Comparison of the Taber abraser resistance of different engineering coatings

Coating	Heat treatment for 1 h		Taber wear index, mg/1000 cycles[(a)]
	°C	°F	
Watts nickel	None	None	25
Electroless Ni-P[(b)]	None	None	17
Electroless Ni-P[(b)]	300	570	10
Electroless Ni-P[(b)]	500	930	6
Electroless Ni-P[(b)]	650	1200	4

Electroless Ni-B[(c)]	None	None	9
Electroless Ni-B[(c)]	400	750	3
Hard chromium	None	None	2

(a) CS-10 abraser wheels, 1000 g load, determined as average weight loss per 1000 cycles for total test of 6000 cycles.

(b) Hypophosphite-reduced electroless nickel containing approximately 9% P.

(c) Borohydride-reduced electroless nickel containing approximately 5% B

Tests with electroless nickel-coated vee-blocks in a Falex Wear Tester have shown a similar relationship between heat treatment and wear and confirmed the coating to be equal to hard chrome under lubricated wear conditions (Ref 14, 28). The effect of phosphorus content on the wear experienced by electroless nickel coatings under lubricated conditions is summarized in Fig. 16. These rotating ball tests showed that after heat treatment, high phosphorus deposits provide the best resistance to adhesive wear (Ref 6, 31).

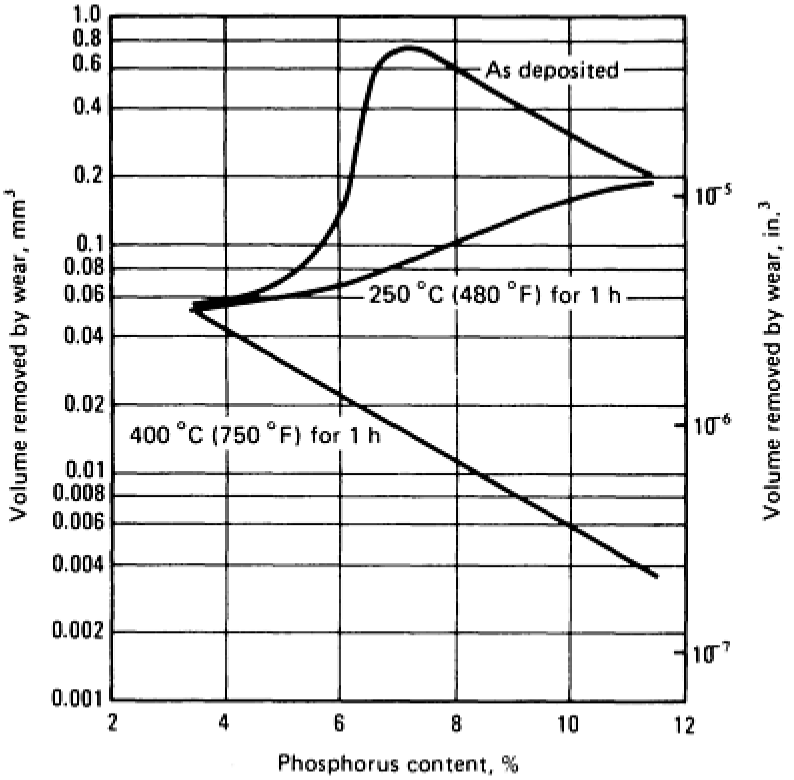

Fig. 16 Effect of phosphorus content on the wear of electroless nickel coatings in rotating ball tests

Frictional properties of electroless nickel coatings are excellent and similar to those of chromium. Their phosphorus content provides a natural lubricity, which can be very useful for applications such as plastic molding. The coefficient of friction for electroless nickel versus steel is about 0.13 for lubricated conditions and 0.4 for unlubricated conditions. The frictional properties of these coatings vary little with either phosphorus content or with heat treatment (Ref 2, 28, 31).

Solderability. Electroless nickel coatings can be easily soldered and are used in electronic applications to facilitate soldering such light metals as aluminum. For most components, rosin mildly activated (RMA) flux is specified along with conventional tin-lead solder. Preheating the component to 100 to 110 °C (212 to 230 °F) improves the ease and speed of joining. With moderately oxidized surfaces, such as those resulting from steam aging, activated rosin (RA) flux or organic acid is usually required to obtain wetting of the coating (Ref 2, 32).

Corrosion Resistance. Electroless nickel is a barrier coating, protecting the substrate by sealing it off from the environment, rather than using sacrificial action. Therefore, the deposit must be free of pores and defects. Because of its amorphous nature and passivity, the coating's corrosion resistance is excellent and, in many environments, superior to that of pure nickel or chromium alloys. Amorphous alloys have better resistance to attack than equivalent polycrystalline materials, because of their freedom from grain or phase boundaries, and because of the glassy films that form on and passivate their surfaces. Some examples of the corrosion experienced in different environments are shown in Table 4 (Ref 2, 16, 30, 33). The resistance to attack in neutral and acidic environments is increased as the phosphorus content is increased in the deposit. The reverse is true in alkaline corrosive environments.

Table 4 Corrosion of electroless nickel coatings in various environments

Environment	Temperature		Corrosion rate			
			Electroless nickel-phosphorus[(a)]		Electroless nickel-boron[(b)]	
	°C	°F	μm/yr	mil/yr	μm/yr	mil/yr
Acetic acid, glacial	20	68	0.8	0.03	84	3.3
Acetone	20	68	0.08	0.003	Nil	Nil
Aluminum sulfate, 27%	20	68	5	0.2	. . .	. . .
Ammonia, 25%	20	68	16	0.6	40	1.6
Ammonia nitrate, 20%	20	68	15	0.6	[(c)]	[(c)]
Ammonium sulfate, saturated	20	68	3	0.1	3.5	0.14
Benzene	20	68	Nil	Nil	Nil	Nil
Brine, $3\frac{1}{2}$% salt, CO_2 saturated	95	205	5	0.2	. . .	. . .
Brine, $3\frac{1}{2}$% salt, H_2S saturated	95	205	Nil	Nil	. . .	. . .
Calcium chloride, 42%	20	68	0.2	0.008	. . .	. . .
Carbon tetrachloride	20	68	Nil	Nil	Nil	Nil

Citric acid, saturated	20	68	7	0.3	42	1.7
Cupric chloride, 5%	20	68	25	1	. . .	. . .
Ethylene glycol	20	68	0.6	0.02	0.2	0.008
Ferric chloride, 1%	20	68	200	8	. . .	. . .
Formic acid, 88%	20	68	13	0.5	90	3.5
Hydrochloric acid, 5%	20	68	24	0.9	. . .	. . .
Hydrochloric acid, 2%	20	68	27	1.1	. . .	. . .
Lactic acid, 85%	20	68	1	0.04	. . .	. . .
Lead acetate, 36%	20	68	0.2	0.008	. . .	. . .
Nitric acid, 1%	20	68	25	2	. . .	. . .
Oxalic acid, 10%	20	68	3	0.1	. . .	. . .
Phenol, 90%	20	68	0.2	0.008	Nil	Nil
Phosphoric acid, 85%	20	68	3	0.1	[c]	[c]
Potassium hydroxide, 50%	20	68	Nil	Nil	Nil	Nil
Sodium carbonate, saturated	20	68	1	0.04	Nil	Nil
Sodium hydroxide, 45%	20	68	Nil	Nil	Nil	Nil
Sodium hydroxide, 50%	95	205	0.2	0.008	. . .	. . .
Sodium sulfate, 10%	20	68	0.8	0.03	11	0.4
Sulfuric acid, 65%	20	68	9	0.4	. . .	. . .
Water, acid mine, 3.3 pH	20	68	7	0.3	. . .	. . .
Water, distilled, N_2 deaerated	100	212	Nil	Nil	Nil	Nil

Water, distilled, O_2 saturated	95	205	Nil	Nil	Nil	Nil
Water, sea ($3\frac{1}{2}$% salt)	95	205	Nil	Nil	. . .	. . .

(a) Hypophosphite reduced electroless nickel containing approximately $10\frac{1}{2}$% P.

(b) Borohydride reduced electroless nickel containing approximately 5% B.

(c) Very rapid. Specimen dissolved during test

Effect of Composition. The corrosion resistance of an electroless nickel coating is a function of its composition. Most deposits are naturally passive and very resistant to attack in most environments. Their degree of passivity and corrosion resistance, however, is greatly affected by their phosphorus content. Alloys containing more than 10% P are more resistant to attack than those with lower phosphorus contents (Ref 16, 18) in neutral or acidic environments. Alloys containing low phosphorus (3 to 4%) are more resistant to strong alkaline environments than high phosphorus deposits.

Often the tramp constituents present in an electroless nickel are even more important to its corrosion resistance than its phosphorus content. Most coatings are applied from baths inhibited with lead, tin, cadmium, or sulfur. Codeposition of these elements in more than trace amounts causes the corrosion resistance to be decreased by 5 to 40 times (Ref 16).

Effect of Heat Treatment. One of the most important variables affecting the corrosion of electroless nickel is its heat treatment. As nickel-phosphorus deposits are heated to temperatures above 220 °C (430 °F), nickel phosphide particles begin to form, reducing the phosphorus content of the remaining material. This reduces the corrosion resistance of the coating. The particles also create small active/passive corrosion cells, further contributing to the destruction of the deposit. The deposit also shrinks as it hardens, which can crack the coating and expose the substrate to attack. The effect of these changes is illustrated in Table 5, which shows the results of tests with a $10\frac{1}{2}$% P deposit heat treated to represent different commercial treatments and then exposed to 10% hydrochloric acid at ambient temperature (Ref 16). Baking at 190 °C (375 °F), similar to the treatment used for hydrogen embrittlement relief, caused no significant increase in corrosion. Hardening, however, caused the corrosion rate of the deposit to increase from 15 μm/yr (0.6 mil/yr) to more than 900 μm/yr (35 mils/yr). Tests in other environments showed a similar reduction in resistance after hardening. Where corrosion resistance is required, hardened coatings should not be used (Ref 16).

Table 5 The effect of heat treatment on the corrosion of a $10\frac{1}{2}$% P electroless nickel deposit in 10% hydrochloric acid

Heat treatment	Deposit hardness, HV_{100}	Corrosion rate	
		μm/yr	mil/yr
None	480	15	0.6

190 °C (375 °F) for $1\frac{1}{2}$ h	500	20	0.8
290 °C (550 °F) for 6 h	900	1900	75
290 °C (550 °F) for 10 h	970	1400	55
340 °C (650 °F) for 4 h	970	900	35
400 °C (750 °F) for 1 h	1050	1200	47

References cited in this section

2. G.G. Gawrilov, *Chemical (Electroless) Nickel Plating,* Portcullis Press, Redhill, England, 1979
6. K. Stallman and H. Speckhardt, Deposition and Properties of Nickel-Boron Coatings, *Metalloberfl.; Angew. Elektrochem.,* Vol 35 (No. 10), 1981, p 979
11. C. Baldwin and T.E. Such, The Plating Rates and Physical Properties of Electroless Nickel/Phosphorus Alloy Deposits, *Trans. Inst. Met. Finish.,* Vol 46 (No. 2), 1968, p 73
12. R.N. Duncan, Properties and Applications of Electroless Nickel Deposits, *Finish. Manage.,* Vol 26 (No. 3), 1981, p 5
13. W.H. Metzger, Characteristics of Deposits, *Symposium on Electroless Nickel Plating,* STP 265, ASTM, 1959
14. K. Parker, Effects of Heat Treatment on th Properties of Electroless Nickel Deposits, *Plat. Surf. Finish.,* Vol 68 (No. 12), 1981, p 71
15. K. Parker and H. Shah, Residual Stresses in Electroless Nickel Plating, *Plating,* Vol 58 (No. 3), 1971, p 230
16. R.N. Duncan, Performance of Electroless Nickel Coatings in Oil Field Environments, CORROSION/82 Conference, National Association of Corrosion Engineers, March 1982
17. J. Horner and B. Durkin, "Experiences with Measuring Properties of Electroless Nickel Deposits," Electroless Nickel Conf. (Sulihill, UK), British Electroless Nickel Society, 1991
18. G.D.R. Jarrett, Electroless Nickel Plating, *Ind. Finish.* (London), Vol 18 (No. 218), 1966, p 41
19. L.G. Fitzgerald, Chemical Nickel Plating Products, *Finishing* (London), Vol 13 (No. 5), 1960, p 68
20. W.H. Roberts, "Coating Beryllium with Electroless Nickel," Report RFP478, U.S. Atomic Energy Commission, 1964
21. L.F. Spencer, Electroless Nickel Plating--A Review, *Met. Finish.,* Vol 72 (No. 12), 1974, p 58
22. A.H. Graham, R.W. Lindsay, and H.J. Read, The Structure and Mechanical Properties of Electroless Nickel, *J. Electrochem. Soc.,* Vol 112 (No. 4), 1965, p 401
23. J. Horner, Microhardness Testing of Plated Coatings; Recent Round Experiences, STP947, ASTM, 1987
24. J. Horner, "Microhardness Testing of Plated Coatings; Defining Precision and Bias," Int. Tech. Conf. Proc, AESF Surf./Finish., 1992
25. L. Weisenberger and J. Greene, "Hardness versus Wear Resistance of Electroless Nickel Alloys," Electroless Nickel Conf. Proc. on Products Finishing, 1989
26. K. Nemoto et al., The Study on Hardness of Non-Electrolytically Plated Ni-P Deposits at High Temperatures and Effects Given by Heat Treatments, *J. Met. Finish. Soc. Jpn.,* Vol 16 (No. 3), p 106
27. L. Domnikov, Chromium and Electroless Nickel Deposits, Hardness at High Temperatures, *Met. Finish.,* Vol 60 (No. 1), 1962, p 67

28. K. Parker, Hardness and Wear Resistance Tests of Electroless Nickel Deposits, *Plating,* Vol 61 (No. 9), 1974, p 834
29. Industrial Nickel Plating and Coating, International Nickel Company, New York, 1976
30. H.G. Klein et al., *Metalloberfl.; Angew. Elektrochem.,* Vol 25 (No. 9), 1971; Vol 26 (No. 1), 1972
31. J.P. Randin and H.E. Hintermann, Electroless Nickel Deposited at Controlled pH; Mechanical Properties as a Function of Phosphorus Content, *Plating,* Vol 54 (No. 5), 1967 p 523
32. D.W. Baudrand, Use of Electroless Nickel to Reduce Gold Requirements, *Plat. Surf. Finish.,* Vol 68 (No. 12), 1981, p 57
33. R.N. Duncan, "Corrosion Control with Electroless Nickel Coatings," Electroless Plating Symposium, American Electroplaters' Society, March 1982 (St. Louis, MO)

Properties of Electroless Nickel-Boron Coatings

The properties of deposits from borohydride- or aminoborane-reduced baths are similar to those of electroless nickel-phosphorus alloys with a few exceptions. The hardness of nickel-boron alloys is very high, and these alloys can be heat treated to levels equal to or greater than that of hard chromium. Nickel-boron coatings have outstanding resistance to wear and abrasion. These coatings, however, are not completely amorphous and have reduced resistance to corrosive environments; furthermore, they are much more costly than nickel-phosphorus coatings. The physical and mechanical properties of borohydride-reduced electroless nickel are summarized in Table 6 (Ref 2, 6, 34). For comparison, the properties of a hypophosphite-reduced coating containing $10\frac{1}{2}$% P are also listed (Ref 12).

Table 6 Physical and mechanical properties of electroless nickel-boron and nickel-phosphorus deposits

Properties are for coatings in the as-deposited condition, unless noted.

Property	Electroless nickel-boron[a]	Electroless nickel-phosphorus[b]
Density, g/cm^3 (lb/in.^{3})	8.25 (2.98)	7.75 (2.8)
Melting point, °C (°F)	1080 (1980)	890 (1630)
Electrical resistivity, μΩ· cm	89	90
Thermal conductivity, W/m · K (cal/cm · s · °C)	. . .	4 (0.01)
Coefficient of thermal expansion (22-100 °C, or 72-212 °F), μm/m · °C (μin./in. · °F)	12.6 (7.1)	12 (6.7)
Magnetic properties	Very weakly ferromagnetic	Nonmagnetic
Internal stress, MPa (ksi)	110 (16)	Nil
Tensile strength	110 (16)	700 (100)
Ductility, % elongation	0.2	1.0
Modulus of elasticity, GPa (10^6 psi)	120 (17)	200 (29)

As-deposited hardness, HV_{100}	700	500
Heat-treated hardness, 400 °C (750 °F) for 1 h, HV_{100}	1200	1100
Coefficient of friction vs steel, lubricated	0.12	0.13
Wear resistance, as-deposited, Taber mg/1000 cycles	9	18
Wear resistance, heat treated 400 °C (750 °F) for 1 h, Taber mg/1000 cycles	3	9

(a) Borohydride-reduced electroless nickel containing approximately 5% B.

(b) Hypophosphite-reduced electroless nickel containing approximately $10\frac{1}{2}$% P.

Structure and Internal Stress. The boron content of electroless nickel reduced with DMAB or DEAB can vary from 0.2 to 4% depending on bath formulation and operation. Commercial borohydride-reduced coatings typically contain 3 to 5% B. Unlike nickel-phosphorus coatings in the as-deposited condition, electroless nickel-boron contains crystalline nickel mixed with nickel-boron (typically Ni_2B) glass. These coatings also are not totally homogeneous and consist of phases of different composition (Ref 2, 7, 35).

During heating, electroless nickel-boron age hardens in the same manner as nickel-phosphorus alloys. At temperatures over 250 °C (480 °F), particles of nickel boride (Ni_3B) form, and at 370 to 380 °C (700 to 715 °F), the coating crystallizes. The final structure of hardened nickel-boron coatings consists of nickel-boron intermetallic compounds (principally Ni_3B and Ni_2B) and about 10% Ni (Ref 2, 7, 34).

The internal stress level of nickel-boron deposits is generally high. The effect of boron content and complexing agent on the stress in DMAB-reduced electroless nickel coatings is shown in Table 7 (Ref 10). The internal stress of borohydride-reduced coatings is typically 110 to 200 MPa (16 to 29 ksi) tensile (Ref 34).

Table 7 Effect of boron content and complexing agent on internal stress in DMAB-reduced deposits

Complexing agent	Boron content, %	Internal stress[a]	
		MPa	ksi
Malonate	4.3	120	17.4
Malein-glycine	1.2	310	44.9

(a) Based on tests with $12\frac{1}{2}$ μm thick coatings on a Brenner-Senderoff Spiral Contractometer. Stresses are tensile.

Physical and mechanical properties of borohydride-reduced electroless nickel are summarized in Table 6 (Ref 2, 6, 34). For comparison, the properties of a hypophosphite-reduced coating containing $10\frac{1}{2}$% P are also listed (Ref 12). The density of electroless nickel-boron is very similar to that of nickel-phosphorus coatings of equal alloy content. The density of borohydride-reduced coatings containing 5% B is 8.25 g/cm^3 in both the as-deposited and heat-treated condition (Ref 2, 34).

The melting point of nickel-boron coatings is relatively high and can approach that of metallic nickel. Sodium borohydride reduced coatings melt at 1080 °C (1975 °F), while the melting point of DMAB-reduced coatings varies from about 1350 to 1390 °C (2460 to 2535 °F) (Ref 2, 34).

The electrical resistivity of 5% B coatings is similar to that of nickel-phosphorus alloys ranging from 89 μΩ· cm in the as-deposited condition to 43 μΩ· cm after heat treatment at 1100 °C (2010 °F). The resistivity of 0.5% B to 1% B ranges from 10 to 20 μΩ· cm. In the as-deposited condition, nickel-boron coatings are very weakly ferromagnetic, with coercivities about 10% of that of metallic nickel. Their magnetic susceptibility, however, can be increased by heat treatments at temperatures above 370 °C (700 °F) (Ref 2, 7, 34).

The strength and ductility of nickel-boron coatings containing 5% B is only about one-fifth that of high-phosphorus deposits. Guided bend tests of panels coated with 5% Ni-B showed it strain at fracture to be 2.5 mm/m (2.5 mils/in.). In the same test, the breaking strain of a hypophosphite-reduced electroless nickel containing approximately 9% P was 5.3 mm/m (5.3 mils/in.). Unlike nickel-phosphorus coatings, however, heat treatment has little effect on the ductility of nickel-boron. As illustrated by Fig. 17, even after 12 h at 400 °C (750 °F), strain at fracture declines by only 15% (Ref 7). The modulus of elasticity of borohydride-reduced coatings ranges from 120 GPa (17,000 ksi) in the as-deposited condition to 180 GPa (26,000 ksi) for coatings heat treated at 400 °C (750 °F) for 1 h (Ref 34).

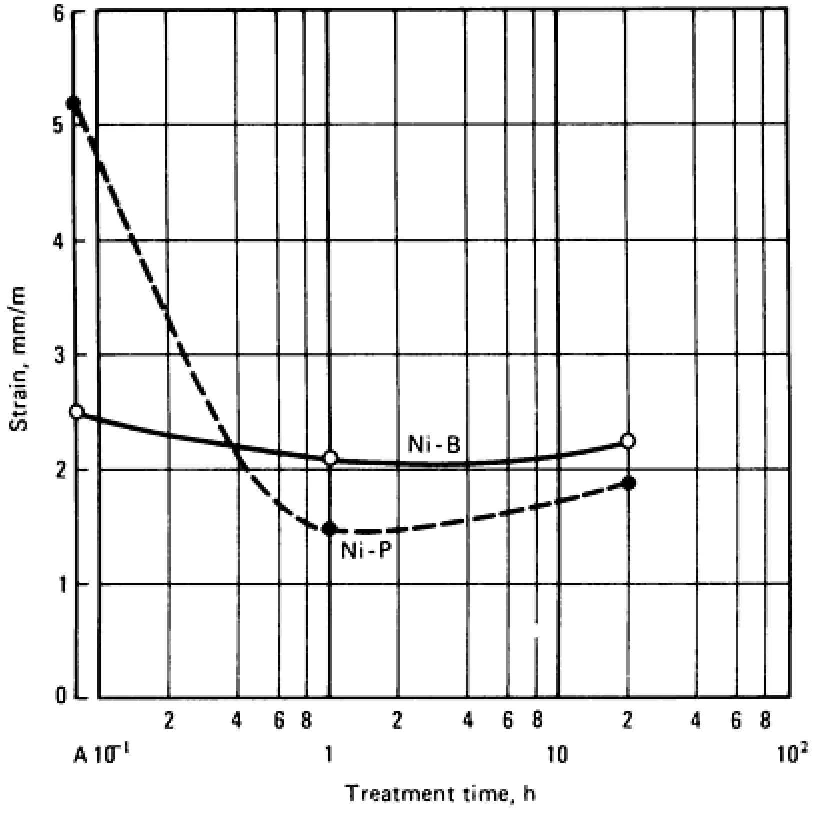

Fig. 17 Effect of heat treatments at 400 °C (752 °F) on the strain at fracture of electroless Ni-5% B and Ni-9% P coatings

Hardness and Wear Resistance. The principle advantage of electroless nickel-boron is its high hardness and superior wear resistance. In the as-deposited condition, microhardness values of 650 to 750 HV_{100} are typical for

borohydride-and aminoborane-reduced coatings. After 1-h heat treatments at 350 to 400 °C (660 to 750 °F) hardness values of 1200 HV_{100} can be produced. This is illustrated by Fig. 18, which shows the effect of heat treatment temperature on hardness (Ref 2, 7, 34).

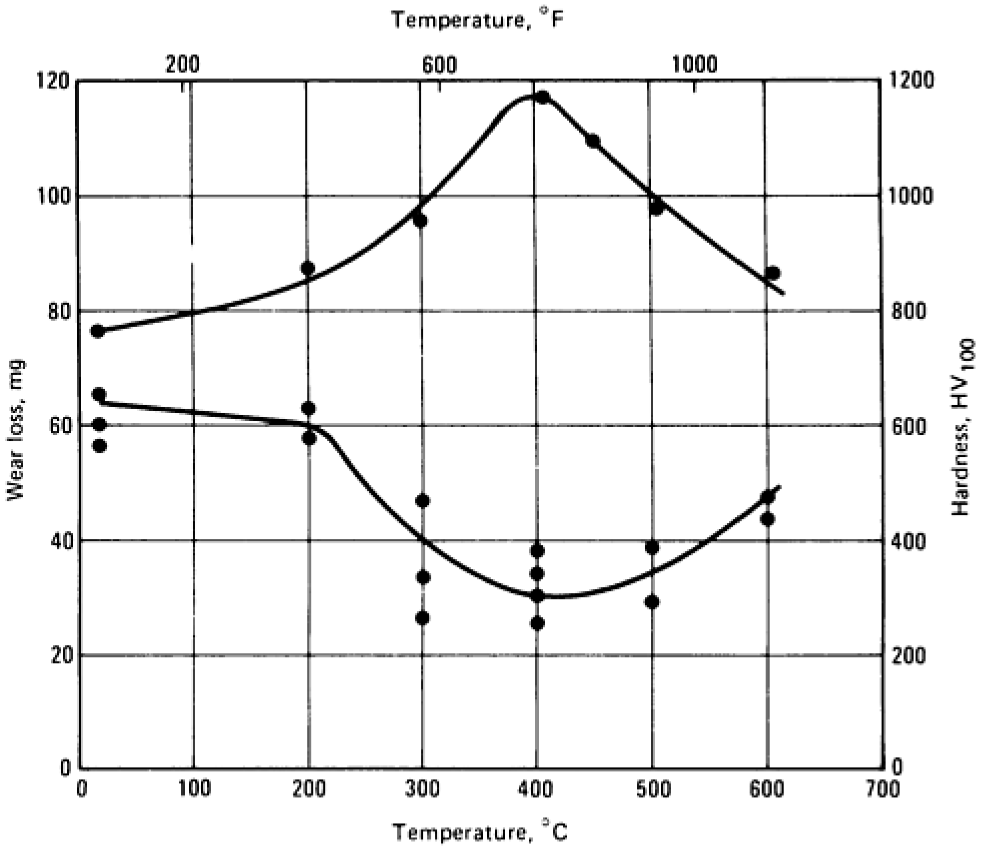

Fig. 18 Effect of different 1h heat treatments on the hardness and wear resistance of borohydride-reduced electroless nickel

Long-term treatments (30 to 40 weeks) at temperatures between 200 and 300 °C (390 and 570 °F) can produce hardness values of 1700 to 2000 HV_{100}. These low-temperature treatments result in a finer dispersion of nickel boride than do higher temperatures and in the formation of iron borides (such as Fe_2B and $Fe_3C_{0.2}B_{0.8}$) within the coating (Ref 2, 34).

The wear resistance of electroless nickel-boron is exceptional and after heat treatment equals or exceeds that of hard chromium coatings. Typical Taber wear test results for a 5% B coating is shown in Tables 3 and 6. The effect of heat treatment and hardness on the wear experienced in rotating ring and block tests (similar to the Alpha LFW-1 test described in ASTM D 2714) (Ref 35) under nonlubricated conditions is also shown in Fig. 18. Nickel-boron deposits containing 2.5 to 3% B exhibit similar wear characteristics.

Electroless nickel-boron coatings are naturally lubricious. Their coefficient of friction versus steel is typically 0.12 to 0.13 in the lubricating conditions, and 0.43 to 0.44 for dry wear (Ref 2, 34).

Corrosion Resistance. In general, the corrosion resistance of electroless nickel-boron coatings is less than that of high-phosphorus alloys. That is illustrated by Table 4, which compares the attack experience by hypophosphite- and borohydride-reduced coatings in different media. In environments that cause little corrosion of nickel-phosphorus, such as alkalis and solvents, electroless nickel-boron is also very resistant. In environments, however, that cause moderate attack of nickel-phosphorus, such as acids and ammonia solutions, nickel-boron coatings can be severely corroded. In strongly oxidizing media, of course, neither coating is satisfactory.

References cited in this section

2. G.G. Gawrilov, *Chemical (Electroless) Nickel Plating,* Portcullis Press, Redhill, England, 1979
6. K. Stallman and H. Speckhardt, Deposition and Properties of Nickel-Boron Coatings, *Metalloberfl.; Angew. Elektrochem.,* Vol 35 (No. 10), 1981, p 979
7. K.M. Gorbunova and A.A. Nikiforova, *Physicochemical Principles of Nickel Plating,* Izdatel'stvo Akademii Nauk SSSR, Moscow, 1960
10. G.O. Mallory, The Electroless Nickel-Boron Plating Bath; Effects of Variables on Deposit Properties, *Plating,* Vol 58 (No. 4), 1971, p 319
12. R.N. Duncan, Properties and Applications of Electroless Nickel Deposits, *Finish. Manage.,* Vol 26 (No. 3), 1981, p 5
34. "Technical Information about Electroless of Chemical Nickel Plating by the Nibodur Method," Paul Anke KG, Essen, West Germany
35. "Calibration and Operation of the Alpha Model LFW-1 Friction and Wear Testing Machine," Part 24, D 2714, *Annual Book of ASTM Standards,* ASTM, 1978

Effect of Electroless Nickel Coatings on the Fatigue Strength of Steel

Because of their tendency to crack under cyclic loads, electroless nickel coatings can cause a significant reduction in the fatigue strength of steel substrates. The magnitude of the reduction, however, depends on the composition, heat treatment, and thickness of the coating, as well as the original fatigue strength of the steel. Several investigations have shown that the use of electroless nickel coatings causes a 10 to 50% reduction in the fatigue strength and endurance limit of steel substrates (Ref 6, 7, 36, 37, 38). In these tests, fatigue strength of notched specimens was reduced by at least 15%, whereas unnotched samples showed relatively small reductions.

The loss of fatigue strength has principally been a problem with hypophosphite-reduced coatings containing less than 10% P, and with nickel-boron alloys. These deposits contain high levels of internal tensile stress and under cyclic stress conditions tend to crack and initiate fatigue failures. Other tests have implied that this is not a significant problem with high-phosphorus deposits (Ref 39, 40). Coatings containing $10\frac{1}{2}$% or more phosphorus are compressively stressed on steel and tend to resist cracking.

Heat treatment of electroless nickel coatings tends to exacerbate the decrease in fatigue strength. Heat-treated coatings tend to be more highly stressed than as-deposited coatings and have a greater tendency to crack. Heat treating a high phosphorus, compressively stressed coating can cause it to become tensilely stressed (Ref 14). Coatings heat treated at temperatures above 340 °C (650 °F) also tend to be cracked because of the shrinkage of the alloy. These cracks act as stress risers and further reduce fatigue resistance. Table 8 shows the effect of different 1-h heat treatments on the fatigue strength of a 0.42% C steel (C45, Werkstoff 1.0503) coated with 30 μ(1.2 mils) of borohydride-reduced electroless nickel (Ref 6). Heat treatments at very high temperatures, 650 to 800 °C (1200 to 1470 °F), produce a thick diffusion zone between the coating and the substrate, which may eliminate or at least greatly reduce the effect of the coating on fatigue strength.

Table 8 Effect of heat treatment of an electroless nickel-5% B coating on the fatigue strength of steel

Condition	Fatigue strength	
	MPa	ksi
Not coated	350	51
As-deposited	270	39
250 °C (480 °F) for 1 h	260	38

350 °C (660 °F) for 1 h	245	36
400 °C (750 °F) for 1 h	270	39

The reduction in fatigue strength produced by electroless nickel deposits is also affected by the thickness of the coating. Thicker deposits have the greatest effect on fatigue strength. This is illustrated in Fig. 19, which shows the reduction in strength of a carbon-manganese steel (St52, Werkstoff 1.0580) produced by different thicknesses of a 5% nickel coating (Ref 6).

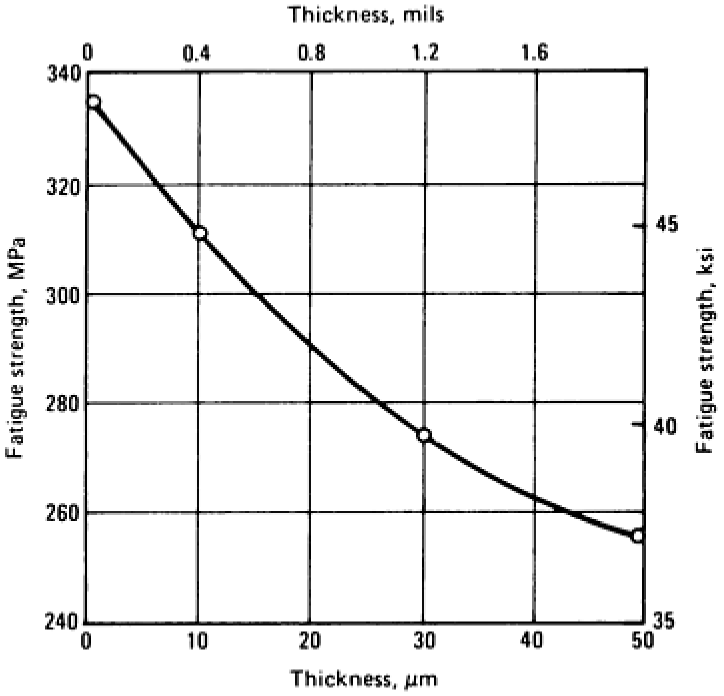

Fig. 19 Effect of coating thickness on the fatigue strength of a carbon-manganese steel

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References cited in this section

6. K. Stallman and H. Speckhardt, Deposition and Properties of Nickel-Boron Coatings, *Metalloberfl.; Angew. Elektrochem.,* Vol 35 (No. 10), 1981, p 979
7. K.M. Gorbunova and A.A. Nikiforova, *Physicochemical Principles of Nickel Plating,* Izdatel'stvo Akademii Nauk SSSR, Moscow, 1960
14. K. Parker, Effects of Heat Treatment on th Properties of Electroless Nickel Deposits, *Plat. Surf. Finish.,* Vol 68 (No. 12), 1981, p 71
36. H. Spahn, The Effect of Internal Stress on the Fatigue and Corrosion Fatigue Properties of Electroplated and Chemically Plated Nickel Deposits, Proc. 6th Int. Metal Finish. Conf., *Trans. Inst. Met. Finish.,* Vol 42, 1964, p 364
37. E.F. Jungslager, Electroless Deposition of Nickel, *Tijdschr, Oppervlakte Tech. Metalen,* Vol 9 (No. 1), 1965, p 2
38. E.W. Turns and J.W. Browning, Properties of Electroless Nickel Coatings on High Strength Steels, *Plating,* Vol 60 (No. 5), 1973
39. G. Reinhardt, "Potential Applications of Electroless Nickel in Airline Maintenance Operations," Electroless

Nickel Conference, 6-7 Nov 1979 (Cincinnati)

40. S. Izumi and Kondo, "The Fatigue Strength of Electroless Nickel Plated Steel," The 18th Japan Conf. Mater. Res., March 1975

Pretreatment for Electroless Nickel Coatings

Proper pretreatment can be as important to the successful application of an electroless nickel coating as the actual deposit. Inadequate cleaning can result in lack of adhesion, roughness, coating porosity, and early failure. The methods used to clean and prepare a metal surface for electroless nickel plating are similar to those used for conventional electroplating, although more care and control are required. One penetrant that is unique to electroless nickel plating is the application of a strike copper plate to alloys containing significant amounts of lead, tin, cadmium, or zinc. This ensures adequate coverage and prevents contamination of the electroless solution.

Pretreatment for Ferrous Alloys

To prepare ferrous alloys properly for electroless nickel plating, the combination of solvent and alkaline degreasing, acid activation, and electrocleaning are required, with intermediate water rinses. These steps are discussed in other articles in this Volume. Recommended pretreatment procedures for different ferrous alloys are summarized below:

Carbon and low-alloy steel

1. Soak clean for 10 to 30 min
2. Rinse
3. Electroclean at 5 V for 60 to 120 s
4. Rinse
5. Dip in 30% HCl for 30 to 60 s. Alternatives: 10 to 20% sulfuric acid avoids leaving chloride ions in pores and thus can improve salt spray resistance. Sulfamic acid and citric acids are also used beneficially.
6. Rinse
7. Electroclean at 5 V for 30 to 60 s
8. Rinse
9. Plate to thickness

Alloy steel (Cr or Ni > $1\frac{1}{2}$%)

1. Soak clean for 10 to 30 min
2. Rinse
3. Electroclean at 5 V for 60 to 120 s
4. Rinse
5. Dip in HCl acid for 30 to 60 s
6. Rinse
7. Electroclean at 5 V for 30 to 60 s
8. Rinse
9. Dip in 30% HCl for 30 to 60 s
10. Rinse
11. Nickel strike at 2 A/dm^2 (20 A/ft^2) for 60 s
12. Rinse
13. Plate to thickness

300 or 400 series stainless steel

1. Soak clean for 10 to 30 min
2. Rinse
3. Electroclean at 5 V for 60 to 120 s

4. Rinse
5. Dip in 30% HCl for 60 s
6. Rinse
7. Nickel strike at 2 A/dm^2 (20 A/ft^2) for 60 s
8. Rinse
9. Plate to thickness

300 series stainless steel (complex shapes)

1. Soak clean for 10 to 30 min
2. Rinse
3. Electroclean at 5 V for 60 to 120 s
4. Rinse
5. Dip in 30% HCl for 60 s
6. Rinse
7. 10% H_2SO_4 at 60 °C (140 °F) for 30 s. Alternative: nickel strike
8. Plate to thickness

400 series stainless steel (complex shapes)

1. Soak clean for 10 to 30 min
2. Rinse
3. Electroclean at 5 V for 60 to 120 s
4. Rinse
5. Dip in 30% HCl for 60 s
6. Rinse
7. Dip in 20% HCl at 50 °C (120 °F) for 30 s. Alternative: nickel strike
8. Rinse with deionized water
9. Plate to thickness

In Step 1, all alkaline soak cleaners should be operated at their supplier's maximum recommended temperature, typically 60 to 80 °C (140 to 175 °F). Unless otherwise indicated, all other processes are at ambient temperature. In Step 3, electrocleaning is with at least three reversals of current (part, cathodic/anodic, three times) at 3 to 5 A/dm^2 (30 to 50 A/ft^2). Except for 300 series stainless steel, the final current cycle should be with the part anodic; with 300 series stainless steels, the final current cycle should be with the part cathodic to minimize the formation of an oxide film on its surface.

Activation for Alloy Steels. Before electroless plating, stainless and alloy steel parts must be chemically activated to obtain satisfactory adhesion. For this, a low pH nickel strike is normally used. Two common strike baths are listed below:

Nickel sulfamate strike	
Nickel sulfamate	165-325 g/L (22-43 oz/gal)
Nickel (as metal)	35-75 g/L (5-10 oz/gal)

Sulfamic acid (~20 g/L, or 2.7 oz/gal)	to pH 1-1.5
Boric acid	30-34 g/L (4-4.5 oz/gal)
Hydrochloric acid (20° Bé)	12 mL/L (1.5 fluid oz/gal)
Temperature	Room temperature
Cathode current density	1-10 A/dm^2 (10-100 A/ft^2)
Time	30-60 s
Anodes (bagged)	Sulfur depolarized nickel
Operating pH	0.8-1.5
Woods nickel strike	
Nickel chloride	240 g/L (32 oz/gal)
Hydrochloric acid	250 mL/L (32 fluid oz/gal)
Temperature	Room temperature
Cathode current density	2-10 A/dm^2(20-100 A/ft^2)
Time	30-120 s
Anodes	Rolled depolarized nickel

Caution: Insoluble anodes cannot be used. Chlorine gas would be liberated from insoluble anodes.

(a)

Nickel strikes should not be used to cover up improper pretreatment of plain or low-alloy steel. Nickel-strike activation should be considered, however, when processing steel with chromium or nickel contents of over 1.5% carburized or nitrided steels, and stainless steels. Nickel-strike processing should follow acid activation to avoid drag-in of alkaline materials into the strike (Ref 41, 42, 43, 44, 45, 46).

Pretreatment for Aluminum Alloys

Like steel, aluminum is catalytic to electroless nickel deposition and could be plated after only a simple cleaning. Aluminum is very reactive, however, and oxides form very rapidly on its surface during rinsing or exposure to air. The oxide films that develop prevent metallic bonds from forming between the coating and the substrate and can result in adhesion failure. To avoid this problem, special processing procedures are required, including deoxidizing and zincating or acid zinc immersion. Processing procedures for aluminum alloys are discussed in the article on cleaning and finishing of aluminum alloys in this Volume.

Pretreatment for Copper Alloys

Copper-base alloys are prepared for electroless nickel plating using procedures similar to those for steel, alkaline cleaning and acid deoxidizing. Two important differences exist, however:

- Copper is not catalytic to the chemical reduction of electroless nickel, and its alloys must be activated chemically or electrolytically before they can be plated.
- Lead in amounts of $\frac{1}{2}$ to 10% is often added to copper alloys to make them easier to machine. Unless the free lead present on the surface of the part is removed, adhesion failures and coating porosity result.

Processing procedures for copper alloys are given in the article on cleaning and finishing of copper and copper alloys in this Volume.

Activation. Once a copper alloy surface is clean and oxide-free, it must be activated before electroless nickel can deposit. To prevent reoxidation, this activation should be initiated without long intermediate delays. The preferred method for initiating deposition is an electrolytic strike in the electroless nickel bath. Using a nickel anode, the parts are made cathodic at 5 V for 30 to 60 s. This applies a thin, electrolytic nickel-phosphorus coating and provides a catalytic surface. After the current is removed, the electroless deposition can continue.

Another method for initiating electroless deposition on copper alloy surfaces is to preplate surfaces with electrolytic nickel. One disadvantage of this method is that blind holes, internal surfaces, or low current density areas may not be coated by the strike, resulting in incomplete coverage or unplated areas. The use of nickel chloride strikes also may result in chloride contamination of the electroless nickel bath through drag-in.

A third method of activating copper alloys in electroless nickel solutions is to touch them with a piece of steel or with another part already coated with electroless nickel after they have been immersed in the bath. This creates a galvanic cell, producing an electric current to initiate the electroless reaction. Deposition spreads until the whole part is covered with electroless nickel. However, two problems can occur with galvanic activation:

- Galvanic currents do not travel well around sharp curves, such as those on threads or corners, and can leave bare spots or areas of reduced thickness
- Passivation of the copper can occur before the deposit spreads across the entire surface leading to poor adhesion

Other methods include immersion for 15 to 30 s in dilute solutions of palladium chloride (0.05 to 0.1 g/L), and nickel-boron nickel strike processes that use DMAB reducing agent.

Leaded Alloys. Unlike other elements added to brass or bronze, lead does not combine with copper to form an alloy. Instead, it remains in the metal as globules. The lead exposed during cutting or machining acts as a lubricant by flowing or smearing across the surface. Electroless nickel does not deposit on lead. Unless lead smears are removed, the applied coating is porous with poor adhesion. Lead remaining on the surface of parts can also contaminate electroless nickel solutions, causing a rapid decline in plating rate and deposit quality.

Surface lead is best removed by immersing parts for 30 s to 2 min in a 10 to 30% solution of fluoboric acid at room temperature. Sulfamic acid, citric acid, and dilute nitric acid have also been reported to be effective solutions for

removing lead. The removal of lead must occur before deoxidizing or bright dipping in the pretreatment cycle, and it is not a substitute for these steps (Ref 2, 41, 47).

References cited in this section

2. G.G. Gawrilov, *Chemical (Electroless) Nickel Plating,* Portcullis Press, Redhill, England, 1979
41. S. Spring, *Industrial Cleaning,* Prism Press, Melbourne, 1974
42. J. Kuczma, How to Operate Electroless Nickel More Efficiently, *Prod. Finish. (Directory),* Vol 44 (No. 12A), 1980, p 158
43. " Autocatalytic Nickel Deposition on Metals for Engineering Use," Part 9, B 656, *Annual Book of ASTM Standards,* ASTM, 1981
44. "Preparation of Low-Carbon Steel for Electroplating," Part 9, B 183, *Annual Book of ASTM Standards,* ASTM, 1981
45. "Preparation of High-Carbon Steel for Electroplating, Part 9, B 242, *Annual Book of ASTM Standards,* ASTM, 1981
46. "Preparation of and Electroplating on Stainless Steel," Part 9, B 254, *Annual Book of ASTM Standards,* ASTM, 1981
47. "Preparation of Copper and Copper-Base Alloys for Electroplating," Part 9, B 281, *Annual Book of ASTM Standards,* 1981

Equipment for Electroless Nickel Plating

Because electroless nickel is applied by a chemical reaction rather than by electrolytic deposition, special attention to design and construction of the tanks and auxiliary equipment is required to ensure trouble-free operation and quality coatings.

Plating Tanks

Cylindrical or bell-shaped tanks have been used for electroless nickel plating, although rectangular tanks have been found to be the most convenient to build and operate. Rectangular tanks have been constructed from various materials in many different sizes. A common electroless nickel plating system is shown in Fig. 20.

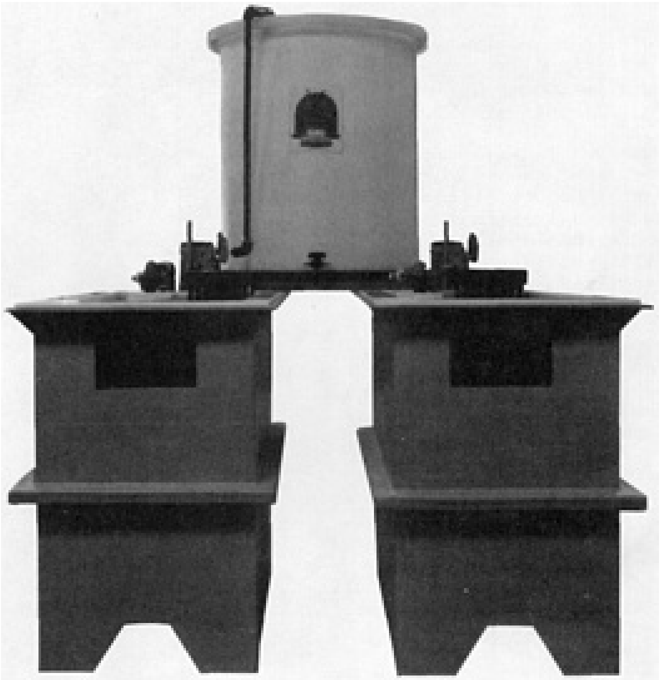

Fig. 20 Twin tank system for electroless nickel plating. Tanks are used alternately. While one tank is being used to plate, the second is being passivated. Cylindrical tank is used to store 30% nitric acid for passivation.

Physical Dimensions. The following factors should be considered when selecting the size of an electroless nickel plating tank:

- Size of the part to be plated
- Number of parts to be plated each day
- Plating thickness required
- Plating rate of the solution (most conventional electroless nickel solutions deposit between 12 and 25 μm/h, or 0.5 and 1 mil/h)
- Type of rack, barrel, or basket used to support parts
- Number of production hours available each day to process parts
- Nominal recommended work load of 1.2 dm^2/L (0.5 ft^2/gal) of working solution

The size of the part or the size of the supporting rack, barrel, or basket usually defines the minimum size tank that can be used. The minimum dimension of the tank should be at least 15 cm (6 in.) greater than the maximum dimension of the part or its support to allow proper agitation and the flow of fresh solution to all surfaces. The size of the tank may have to be increased, however, to accommodate the volume of the parts required or to provide a more suitable work area to solution volume ratio.

Construction Materials. The following factors should be considered when selecting construction materials for a plating tank:

- Operating temperature of the electroless nickel plating solution usually 85 to 95 °C (185 to 205 °F)
- Tendency of tank material to become sensitized to the deposition of electroless nickel
- Cost of tank material, including both initial construction cost and its life in a production environment

With continued exposure to heated electroless nickel solutions, almost any surface eventually becomes sensitized or receptive to deposition of the coating. The more inert or passive the material selected, the less likely that plate out can occur. All material in contact with the plating solution must be repassivated periodically with 30 vol% nitric acid to minimize deposition on its surface.

The most widely used materials for tank construction have been polypropylene, stainless steel, and steel or aluminum with a 635 μm (25 mil) thick polyvinyl chloride bag liner. Contamination from bleedout of oils or other plasticizers can have harmful effects on the plating solution. Leaching linings prior to use is recommended. However, the contaminants continue to migrate to the surface and enter the solution (Ref 48). Although all of these materials have been used successfully, a 6 to 12 mm (0.25 to 0.5 in.) thick polypropylene liner installed in a steel or fiberglass support tank, has proven to be the most troublefree material and has gained the widest acceptance. Polypropylene is relatively inexpesive and is very resistant to plate out. The smooth surface of polypropylene also reduces the possibility of deposit nucleation.

When constructing a polypropylene tank, only stress relieved, unfilled virgin material should be used. Welds should be made under an inert gas shield, such as nitrogen, to prevent oxidation of the polypropylene and incomplete fusion. All welds should be spark tested at 20,000 V before use to ensure integrity.

Heating the Solution

Steam and electricity are the two most common sources of power for heating plating solutions. Although the capital expenditures for steam or pressurized hot water are somewhat higher than that for electricity, the operating costs for steam are considerably less.

Steam. Heating with steam is accomplished using immersion coils or external heat exchangers. The most common immersion coils are those made of Teflon or stainless steel.

Teflon heat exchanger coils are made of many small diameter Teflon tubes looped into the tank between manifolds. Because of the poor conductivity of the plastic, a much larger coil surface area must be used than would be needed with a metal heater. Teflon tubes are delicate, and the tubes must be protected form mechanical damage.

Stainless steel panel coils are constructed of plates joined together with internal passages for the flow of heating medium. These coils are very efficient and economical. Their primary disadvantage is that they are easily galvanically activated and are prone to plate out. To prevent this, coils are often coated with Teflon. This, however, reduces their heat transfer and their efficiency.

Anodic passivation is also sometimes used to prevent stainless steel coils from plating. With this technique, a slight positive charge is applied to the coil preventing the deposition of electroless nickel. If the work is suspended too close to an anodically passivated coil, however, stray currents from the coil may affect the quality of the plating. Static electricity discharges from steam coils to the work can also cause nonuniform or pitted coatings. To avoid this, coils should be isolated from the steam piping with dielectric couplings.

Steam can also be used to heat the plating solution through a heat exchanger, which is mounted outside the tank. The heat exchangers are usually of shell and tube or plate coil design and are constructed of stainless steel. The solution is pumped through exchangers and returned to the tank, often through a filter. To prevent the inside of the exchanger from plating, the solution velocity must be maintained above $2\frac{1}{2}$ m/s (8 ft/s).

Electric. Heating with electricity is usually accomplished with tube immersion heaters. The resistance heating elements are sheathed in quartz, titanium, or stainless steel. Stainless steel is the most economical material and is usually preferred. Either type 304 or 316 stainless steel is acceptable. Occasionally electropolished stainless steel or Teflon-coated heaters are also used. The cost of these additions, however, cannot usually be justified for most applications. An electric immersion heater is shown in Fig. 21.

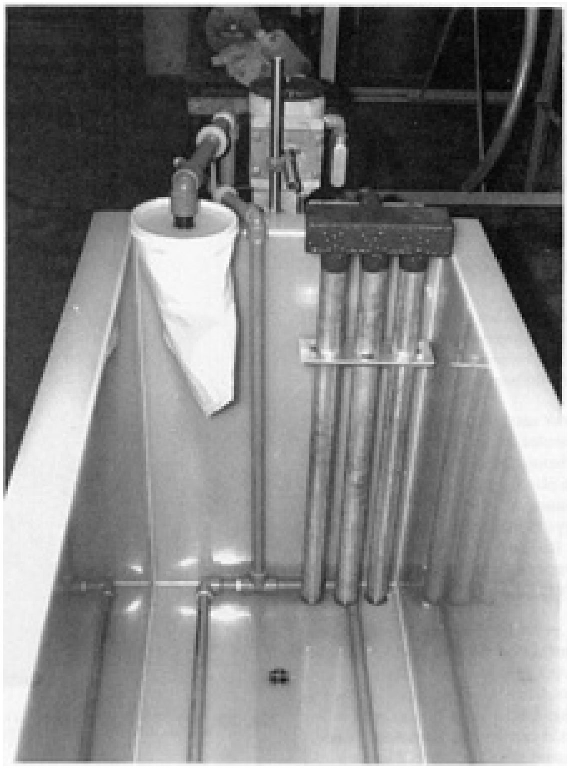

Fig. 21 Electric immersion heater. Heater mounted in a 200 L (50 gal) electroless nickel plating tank. A bag filter is mounted on the filtration pump discharge. 1000×

Pumps

Pumps are used in electroless nickel plating systems for solution transfer and filtration. The following factors should be considered when selecting pumps for electroless nickel plating systems:

- Operating temperature of the plating solution, usually 85 to 95 °C (185 to 205 °F)
- Chemicals being handled in both the electroless nickel plating solution and the 30% nitric acid solution used for passivation
- Volume flow rate (liters per minute) required to allow the total tank volume to be filtered approximately ten times each hour

Two materials, CPVC plastic and type 304 stainless steel, have been proven to be satisfactory for electroless nickel pumps. CPVC plastic is more resistant to plate out than stainless steel and is less expensive. However, large plastic pumps lack the capacity and mechanical strength needed to provide proper filtration in electroless nickel systems. Accordingly, plastic pumps are used for flow rates less than 300 L/min (80 gal/min), whereas stainless steel is used for higher flow applications.

Vertical Pumps. Vertical centrifugal pumps are now the most commonly used pumps for electroless nickel systems. These pumps can be mounted so only the impeller is below the solution level and shaft seals are not required. Consequently, maintenance of this pump is minimized. Some vertical pumps can also be mounted outside the tank, providing the maximum area for plating.

With CPVC plastic pumps, the impeller should be machined or molded; glued impellers should not be used. All gaskets and O-rings for electroless nickel systems should be fluorocarbon rubber.

The velocity of the solution through the pump should be at least $2\frac{1}{2}$ m/s (8 ft/min) to prevent the solution from plating out on the pump housing, especially when stainless steel is used. To accomplish this, a pump speed of 1750 rev/min is required.

Piping and Valves

Piping and valves available for electroless nickel systems are of four principal types: stainless steel, polyvinylidene fluoride, CPVC plastic, and polypropylene. The advantages and disadvantages of each of these materials are summarized in Table 9.

Table 9 Comparison of piping and valve materials for electroless nickel plating systems

Material	Resistance to plating temperatures	Resistance to plate out	Relative cost	Availability
Piping				
Stainless steel	High	Low	High	Good
Kynar	High	High	Moderate	Poor
CPVC	Moderate	Moderate	Low	Good
Polypropylene	Low	High	Low	Limited

Valves				
Stainless steel	High	Low	Moderate	Good
CPVC	Moderate	Moderate	Moderate	Good
Polypropylene	Moderate	High	Moderate	Good

Piping components in electroless nickel plating systems are used for air agitation spiders, tank outlet, pump inlet, and discharge pipes, solution manifolds, and deionized water fill lines. These pipes must be sized to minimize restrictions and provide proper agitation and filtration. The diameter of the tank outlet piping should be at least as large as the pump inlet connection to avoid cavitation and increased pump wear. CPVC plastic is normally used for pipe exposed to the plating solution.

Although CPVC or other plastic pipe may be joined by solvent welding, threaded joints are preferred. Threaded connections are easier to make and more trouble-free, allowing repairs or modifications to be accomplished quickly. When threading plastic pipe, a plug should be inserted inside the pipe end to support the pipe and prevent collapse or thread breakage. Threads should be wrapped with Teflon tape before joining to prevent potential leakage from the galling of the plastic.

Valves. Almost all of the valves used for electroless nickel systems are a ball and seat design. Because of prolonged exposure to stagnant plating solutions, inertness or resistance to deposit plate out is of primary importance with these valves. Accordingly, polypropylene is used most often. The reduced strength of polypropylene at plating temperatures is not a problem with valves, because of their compactness and greater thickness.

CPVC plastic valves are also used occasionally for electroless nickel systems, although their reduced resistance to deposit plate out makes them more prone to seizure and failure due to deposit buildup than polypropylene. Because of their somewhat higher cost and tendency to activation and deposition, stainless steel valves are not normally used. For valves in agitation air supply lines, plain PVC plastic valves may be used if they are mounted at least 200 mm (8 in.) away from hot plating solution. Valves and piping for steam services should be steel or stainless steel.

Agitation

Agitation of parts and solution is necessary during electroless nickel plating to provide a fresh supply of solution to the part and to remove the hydrogen produced during deposition. Without consistent renewal of plating solution, localized depleted areas can occur, resulting in nonuniform coating thickness. Hydrogen bubbles, if allowed to remain on the surface of the part, tend to mask plating and can cause pitting or fisheyes in the coating.

Agitation is accomplished by moving the part mechanically through the solution, by solution movement (preferably by discharge of solution from a suitable filter and distributed by a sparger throughout the tank), or by bubbling air through the bath to move the solution past the part. A typical air agitation spider is shown in Fig. 21. For air agitation, a clean low-pressure air source, such as is provided by centrifugal blowers, is preferred. High-pressure air from compressors can introduce oil or other contaminants into the bath and affect deposit quality.

Filtration

Two types of filtration are used for electroless nickel systems, cartridge filters and filter bags. Both require the use of an external circulation pump, and both should be capable of removing particles larger than 5 μm (0.2 mil) in size. Wound cartridge filters are supported in CPVC or polypropylene chambers located outside of the tank. The installation cost of these filters is high, however, and replacement of the cartridges is a large maintenance cost. Also the added back pressure of the filter can significantly reduce the flow of the pump and often its life.

Woven polypropylene bags are now being used to filter electroless nickel solutions. These bags are mounted above the plating tank itself, allowing the solution to flow through the bag by gravity. Filter bags are relatively inexpensive and result in only a minimum restriction on the discharge of the pump. When bags become soiled or begin to plate out, the change is obvious to the operator, and the bags can be quickly and easily replaced. Filter bags with stainless steel support rings rather than plated steel rings should be used. Plated rings can introduce cadmium or zinc into the bath and slow or stop deposition. A filter assembly is shown in Fig. 21.

Filter cartridges and bags should be washed using hot water prior to use for electroless nickel. Antistatic agents often found in these filter media can be harmful to the plating solution.

For extremely critical applications such as memory disks, filtration should be through a 1 μM filter cartridge followed by a 0.2 μM cartridge using flow rates sufficient to turn over the volume of plating solution 10 to 20 times per hour. Filter discharge is best done through a sparger to distribute the solution uniformly in the tank, and not impinge on the parts being plated.

Racking for Electroless Nickel Plating

Because electroless nickel is applied by chemical reduction, anode to cathode area relationships and current density considerations, usually of concern in electrolytical applications, are usually not important. This simplifies rack design.

Construction Materials. Racks for plating ferrous and copper alloys should be capable of carrying 3 to 6 A/dm^2 (30 to 60 A/ft^2) of part surface during electrocleaning and striking without overheating or excessive voltage loss. Suitable materials for racks include steel, stainless steel, copper, and titanium. Of these, steel or plastic coated steel is most often used. Stainless steel and titanium can be cleaned easily in the nitric acid, but are rarely used because of high cost and limited current carrying capability. The cost of copper racks is reasonable and current capacity is excellent. With copper, however, all submersed surface, except the contact points, should be coated to avoid copper contamination of the cleaning and plating solutions and to minimize stripping of the coating from the frame.

Because electrolytic steps are not required when processing aluminum alloys, plastics as well as metals can be used to support parts. The materials used for racks for aluminum alloys include polypropylene, CPVC, aluminum, and stainless steel. Polypropylene and CPVC are especially useful, because they are easily constructed, inexpensive, and highly resistant to plating. Iron, nickel, or copper alloys are not suitable, because they are rapidly attacked by the oxidizing and desmutting solutions used for aluminum alloys.

Coatings for racks and fixtures used in electroless nickel plating have only limited life. The high temperatures and harsh chemicals used during pretreatment and stripping can cause rapid degradation of vinyls, epoxies, and phenolics. Coatings, however, do reduce current requirements during cleaning and striking operations and can reduce unwanted deposition on the racks.

Fixturing. When fixturing and positioning a part, the following factors should be considered:

- *Hydrogen evolution:* During the deposition of electroless nickel, hydrogen gas is evolved at the surface of the part. As the hydrogen bubble grows and rises, it should be able to free itself from the part. If hydrogen becomes trapped in any area of the part, such as an inverted hole, it masks the surface and can reduce or prevent plating.
- *Electrical contact:* Good contact is needed between the support and the part to ensure adequate and uniform current for electrocleaning and striking. Proximity to anodes is not usually very important with these operations, although in extreme cases, such as deep holes, internal anodes may be required.
- *Rinsing:* Easy rinsing is necessary to minimize dragout of the pretreatment cleaners and to prevent drag-in of contaminants to the electroless nickel bath.

A rack should be designed to allow blind holes to drain easily or to allow holes to be rinsed thoroughly with a hose. Some racks are designed to be tipped or turned upside down to ensure rinsing and to control dragout. During plating, these holes must be positioned vertically to allow hydrogen gas to escape.

Reference cited in this section

48. C.P. Steinecker, Evaluation of PVC Tank Liners for Electroless Nickel Plating, *Met. Finish.*, Vol 90 (No. 5), May 1992

Bulk and Barrel Plating

The uniform plating thickness of electroless nickel coatings allows many parts that would have to be racked if they were finished electrolytically to be bulk plated. Because of the resulting labor savings, coatings such as chromium can sometimes be replaced with electroless nickel at a lower overall finished cost, although the chemical cost is higher. Four principal types of bulk plating are used:

- *Soldier-style racking:* Parts are placed so close together that complete coverage would be difficult, if not impossible, with an electrolytic process.
- *Baskets:* Many bulk plating jobs can be run efficiently in baskets made of polypropylene or stainless steel, especially in smaller electroless nickel tanks. Baskets occupy much less space than barrels and allow more loads to be run. When compared to using barrels, baskets have the disadvantage of not mechanically agitating parts during plating. Accordingly, baskets should be shaken and moved periodically to allow fresh plating solution to circulate around parts.
- *Trays:* Many jobs, such as small shafts and bars, can be run most easily using egg crate or test tube rack trays. In addition, many parts, because of their finish or design, must be separated during processing to keep them from touching or nesting. Separated trays accomplish this successfully and allow good solution transfer, minimizing the labor required for fixturing. Trays are most often constructed of polypropylene, steel, or stainless steel.
- *Barrels:* Where very large volumes of parts are to be plated or continuous mechanical agitation is necessary, barrels usually provide the most efficient and economical methods of processing.

Barrels for electroless nickel plating should be made from nonfilled, nonpigmented polypropylene. If added strength is required, glass-filled polypropylene construction is preferred. Polypropylene gears, rather than a belt drive, should be used to turn the barrel. Plastisol-coated steel barrels are not successful for electroless nickel plating, because they are prone to coating failures, plate out, possible contamination by bleedout of plasticizers or preplate preparation solutions, and occasional drive failures. For electroless nickel plating, the barrel speed should be 1 to 2 rev/min. Higher-speed barrels may be required, however, where the solution must be pumped through internal passages or holes in a part. The drive mechanism should allow the barrel to rotate, both in the processing tanks and in transfer stages, to ensure free rinsing and minimize dragout. To allow adequate solution transfer in and out of the barrel, the hole size should be as large as possible and should be just capable of containing parts.

All racks, baskets, trays, and barrels used for electroless nickel plating should be used exclusively for this operation. The use of equipment from other plating systems can result in contamination of the electroless nickel plating solution, in decomposition, or in reduced deposit quality.

Solution Control

To ensure a quality deposit and consistent plating rate, the composition of the plating solution must be kept relatively constant. This requires periodic analyses for the determination of pH, nickel content, and hypophosphite and orthophosphite concentrations, as well as careful temperature control. With modern premixed solutions, only checks of nickel content and pH are required. The frequency with which these analyses should be made depends on the quantity of work being plated and the volume and type of solution being used.

Hydrogen Embrittlement Relief

Hydrogen embrittlement is the failure that results from the absorption of hydrogen into metals. Hydrogen embrittlement usually occurs in combination with residual or applied stresses in a part, happening most frequently in high-strength steels and occasionally in other high-strength alloys.

Hydrogen can be introduced into a metal by processes such as pickling, electrocleaning, acid activation, electroplating, or electroless deposition. Although the hydrogen produced by electroless nickel plating is much less than that produced by an electrolytic process, such as cadmium or hard chrome plating, it can be enough to cause cracking of high-strength steels. To prevent this, components are baked at 200 ± 10 °C (390 ± 18 °F) to diffuse the absorbed hydrogen out of the steel. This usually restores the mechanical properties of the steel almost completely, helping to ensure against failure.

The time required to remove hydrogen from a steel and avoid embrittlement depends on the strength of the steel. Longer relief treatment periods or higher temperatures are needed as the strength of the steel increases. Recommendations for embrittlement relief of steels on different strength levels are summarized in Table 10. Longer times may be require for parts with deposit thickness greater than 1 mil. Deposits are amorphous, thus there are no grain boundaries for the hydrogen to follow. Shorter times may be used if unplated areas are present. Temperature ramp-up times should be longer than for hydrogen relief of other metal deposits. Hydrogen embrittlement relief treatment should begin within 4 h of the completion of electroless nickel plating (Ref 2, 49, 50).

Table 10 Heat treatment of steels to relieve hydrogen embrittlement

Maximum specified tensile strength		**Heat treatment at 190 to 210 °C (375 to 410 °F), h**
MPa	**ksi**	
≤ 1050	≤ 152	Not required
1051-1450	152-210	2
1451-1800	210-260	18

References cited in this section

2. G.G. Gawrilov, *Chemical (Electroless) Nickel Plating*, Portcullis Press, Redhill, England, 1979

49. *Metals Handbook*, 9th ed., Vol 1, American Society for Metals, 1978

50. "Autocatalytic Nickel-Phosphorus Coatings," ISO 4527, International Standards Organization

Applications

Electroless nickel is applied for five different applications: corrosion resistance, wear resistance, lubricity, solderability, or buildup of worn or overmachined surfaces. To varying degrees, these properties are used by all segments of industry, either separately or in combination. Applications of these coating are given in Table 11.

Table 11 Applications of electroless nickel plating

Application	Base metal	Coating thickness[(a)]		Reason for use
		μm	mils	
Automotive				
Heat sinks	Aluminum	10	0.4	Corrosion resistance, solderability, uniformity
Carburetor components	Steel	15	0.6	Corrosion resistance
Fuel injectors	Steel	25	1.0	Corrosion and wear resistance
Ball studs	Steel	25[(b)]	1.0[(b)]	Wear resistance
Differential pinion ball shafts	Steel	25[(b)]	1.0[(b)]	Wear resistance
Disc brake pistons and pad holders	Steel	25[(b)]	1.0[(b)]	Wear resistance
Transmission thrust washers	Steel	25[(b)]	1.0[(b)]	Wear resistance
Syncromesh gears	Brass	30	1.2	Wear resistance
Knuckle pins	Steel	38[(b)]	1.0[(b)]	Wear resistance
Exhaust manifolds and pipes and mufflers	Steel	25	1.0	Corrosion resistance
Shock absorbers	Steel	10	0.4	Corrosion resistance and lubricity
Lock components	Steel	10	0.4	Wear and corrosion resistance and lubricity
Hose couplings	Steel	5	0.2	Wear and corrosion resistance
Gears and gear assemblies	Carburized steel	25[(c)]	1.0[(c)]	Buildup of worn surfaces and wear resistance
Fuel pump motors	Steel	12	0.5	Corrosion, wear resistance
Aluminum wheels	Aluminum	25	1	Corrosion resistance
Water pump components	Steel	20	0.8	Corrosion resistance

Application	Base metal	Coating thickness[(a)]		Reason for use
		µm	mils	
Steering column tilt wheel components	Powdered metal	15	0.6	Ease of movement
Air bag hardware	Steel	10	0.4	Ease of movement
Air conditioning compressor components	Steel	25	1	Low friction
Decorative plastics	Plastics (ABS, etc)	2	0.1	Base coat
Slip yokes	Steel	15	0.6	. . .
Aircraft/aerospace				
Bearing journals	Aluminum	38[(d)]	1.5[(d)]	Wear resistance and uniformity
Servo valves	Steel	18	0.7	Corrosion resistance, uniformity and lubricity
Compressor blades	Alloy steel	25[(e)]	1.0[(e)]	. . .
Hot zone hardware	Alloy steel	25	1.0	Corrosion and wear resistance
Piston heads	Aluminum	25	1.0	Wear resistance
Engine main shafts and propellers	Steel	>38	>1.5	Buildup of worn surfaces and wear resistance
Hydraulic actuator splines	Steel	25[(b)]	1.0[(b)]	Wear resistance
Seal snaps and spacers	Steel	20[(e)]	0.8[(e)]	Wear and corrosion resistance
Landing gear components	Aluminum	>125	>5.0	Buildup of mis-machined surfaces
Struts	Stainless steel	>25	>1.0	Buildup of mis-machined or worn surfaces
Pitot tubes	Brass/stainless steel	12	0.5	Corrosion and wear resistance
Gyro parts	Steel	12	0.5	Wear resistance and lubricity

Application	Base metal	Coating thickness[(a)]		Reason for use
		µm	mils	
Engine mounts	4140 Steel	25	1.0	Wear and corrosion resistance
Oil nozzle components	Steel	25	1.0	Corrosion resistance and uniformity
Turbine front bearing cages	Alloy steel	25	1	Corrosion, wear resistance
Engine mount insulator housing	Alloy steel	25	1	Corrosion resistance
Flanges	Alloy steel	20	0.8	Corrosion, wear resistance
Sun gears	Alloy steel	25	1	Wear resistance
Breech caps	Alloy steel	15	0.6	Corrosion, wear resistance
Shear bolts	Alloy steel	50	2	Corrosion resistance
Engine oil feed tubes	Steel, stainless steel	10	0.4	Corrosion resistance
Flexible bearing supports	Steel	25	1	Corrosion resistance
Break attach bolts	Alloy steel	25	1	Corrosion resistance
Antirotational plates	Alloy steel	25	1	Wear resistance
Wing flap universal joints	Alloy steel	20	0.8	Corrosion, low friction
Titanium thruster tracks	Titanium	25	1	Wear and corrosion resistance, low friction
Printing				
Printing rolls	Steel/cast iron	38	1.5	Corrosion and wear resistance
Press beds	Steel/cast iron	38	1.5	Corrosion and wear resistance
Textiles				

Application	Base metal	Coating thickness[(a)]		Reason for use
		µm	mils	
Feeds and guides	Steel	50[(b)]	2.0[(b)]	Wear resistance
Fabric knives	Steel	12[(b)]	0.5[(b)]	Wear resistance
Spinnerettes	Stainless steel	25	1.0	Corrosion and wear resistance
Loom ratchets	Aluminum	25	1.0	Wear resistance
Knitting needles	Steel	12	0.5	Wear resistance
Molds and dies				
Zinc die cast dies	Alloy steel	25	1.0	Wear resistance and part release
Glass molds	Steel	50	2.0	Wear resistance and part release
Plastic injection molds	Alloy steel	15	0.6	Corrosion and wear resistance and part release
Plastic extrusion dies	Alloy steel	25	1.0	Corrosion and wear resistance and part release
Military				
Fuse assemblies	Steel	12	0.5	Corrosion resistance
Mortar detonators	Steel	10	0.4	Corrosion resistance
Tank turret bearings	Alloy steel	30	1.2	Wear and corrosion resistance
Radar wave guides	Aluminum	25	1.0	Corrosion resistance and uniformity
Mirrors	Aluminum/beryllium	>75	>3.0	Uniformity and reflectivity
Firearms				
Commercial and military firearms	Steel	8	0.3	Corrosion and wear resistance and lubricity

Application	Base metal	Coating thickness[(a)]		Reason for use
		µm	mils	
Marine				
Marine hardware	Brass	25	1.0	Corrosion resistance
Pumps and equipment	Steel/cast iron	50	2.0	Corrosion and wear resistance
Electronics				
Heat sinks	Aluminum	10	0.4	Corrosion resistance and solderability
Computer drive mechanisms	Aluminum	18	0.7	Corrosion and wear resistance
Memory drums and discs	Aluminum	25	1.0	Corrosion and wear resistance and uniformity
Terminals and lead wires	Alloy steel	2	0.1	Solderability
Chassis	Aluminum/steel	12	0.5	Corrosion resistance and solderability
Connectors	Steel/aluminum	25	1.0	Corrosion and wear resistance and solderability
Diode and transistor cans	Steel	5	0.2	Corrosion resistance and solderability
Interlocks	Steel/brass	12	0.5	Corrosion and wear resistance
Junction fittings	Aluminum/plastic	10	0.4	Corrosion and wear resistance, solderability and conductivity
Printed circuit boards	Plastic	5	0.2	Solderability and weldability
Railroad				
Tank cars	Steel	90[(f)]	3.5[(f)]	Corrosion resistance
Diesel engine shafts	Steel	>25	>1.0	Wear and fretting resistance and buildup of worn surfaces
Car hardware	Powder iron	20	0.8	Corrosion and wear resistance

Application	Base metal	Coating thickness[(a)]		Reason for use
		µm	mils	
Electrical				
Motor shafts	Steel	12	0.5	Wear and corrosion resistance
Rotor blades	Steel/aluminum	25[(b)]	1.0[(b)]	Wear and corrosion resistance
Stator rings	Steel/aluminum	25	1.0	Wear and corrosion resistance
Chemical and petroleum				
Pressure vessels	Steel	50	2.0	Corrosion resistance
Reactors	Steel	100[(f)]	4.0[(f)]	Corrosion resistance and product purity
Mixer shafts	Steel	38	1.5	Corrosion resistance
Pumps and impellers	Cast iron/steel	75	3.0	Corrosion and erosion resistance
Heat exchangers	Steel	75	3.0	Corrosion resistance
Filters and components	Steel	25	1.0	Corrosion and erosion resistance
Turbine blades and rotor assemblies	Steel	75	3.0	Corrosion and erosion resistance
Compressor blades and impellers	Steel/aluminum	125[(d)]	5.0[(d)]	Corrosion and erosion resistance
Spray nozzles	Brass/steel	12	0.5	Corrosion and wear resistance
Ball, gate, plug, check and butterfly valves	Steel	75	3.0	Corrosion resistance and lubricity
Valves	Stainless steel	25[(b)]	1.0[(b)]	Wear and galling resistance and protection against stress-corrosion cracking
Chokes and control valves	Steel/stainless steel	75	3.0	Corrosion and wear resistance and protection against stress-corrosion cracking

Application	Base metal	Coating thickness[(a)]		Reason for use
		µm	mils	
Oil field tools	Steel	75	3.0	Corrosion and wear resistance
Oil well packers and equipment	Alloy steel	75	3.0	Corrosion and erosion resistance
Oil well tubing and pumps	Steel	50	2.0	Corrosion and wear resistance
Drilling mud pumps	Alloy steel	75	3.0	Corrosion resistance and protection against stress-corrosion cracking
Hydraulic systems and actuators	Steel	75	3.0	Corrosion and wear resistance and lubricity
Blowout preventers	Alloy steel	75	3.0	Corrosion and wear resistance
Medical and pharmaceutical[(g)]				
Disposable surgical instruments and equipment	Steel/aluminum	12	0.5	Corrosion resistance and ease of operation
Sizing screens	Steel	20	0.8	Corrosion resistance and cleanliness
Pill sorters	Steel	20	0.8	Corrosion resistance and cleanliness
Feed screws and extruders	Steel	25	1.0	Corrosion and wear resistance and cleanliness
Food[(g)]				
Pneumatic canning machinery	Steel	25	1.0	Corrosion and wear resistance and cleanliness
Baking pans	Steel	25	1.0	High temperature resistance, cleanliness, and ease of release
Molds	Steel	12	0.5	Cleanliness, corrosion resistance and ease of release
Grills and fryers	Steel	12	0.5	Cleanliness, corrosion resistance and ease of release
Mixing bowls	Steel	25	1.0	Cleanliness and corrosion and wear resistance

Application	Base metal	Coating thickness[(a)]		Reason for use
		µm	mils	
Bun warmers	Steel	12	0.5	Cleanliness and ease of release
Feed screws and extruders	Steel	25	1.0	Cleanliness and corrosion and wear resistance
Material handling				
Hydraulic cylinders and shafts	Steel	25	1.0	Corrosion and wear resistance and lubricity
Extruders	Alloy steel	75[(b)]	3.0[(b)]	Wear and corrosion resistance
Link drive belts	Steel	12	0.5	Wear and corrosion resistance and lubricity
Gears and clutches	Steel	>25	>1.0	Wear resistance and buildup of worn surfaces
Mining				
Hydraulic systems	Steel	60	2.4	Corrosion and abrasion resistance
Jetting pump heads	Steel	60	2.4	Corrosion and erosion resistance
Mine engine components	Steel/cast iron	30	1.2	Corrosion and wear resistance
Piping connections	Steel	60	2.4	Corrosion resistance
Framing hardware	Steel	30	1.2	Corrosion resistance
Wood and paper				
Knife holder corer plates	Steel	30	1.2	Corrosion and abrasion resistance
Abrading plates	Steel	30	1.2	Corrosion and abrasion resistance
Chopping machine parts	Steel	30	1.2	Corrosion and abrasion resistance
Miscellaneous				

Application	Base metal	Coating thickness[a]		Reason for use
		µm	mils	
Chain saw engines	Aluminum	25	1.0	Wear and corrosion resistance
Drill and taps	Alloy steel	12[b]	0.5[b]	Wear resistance and ease of use
Precision tools	Alloy steel	12	0.5	Wear resistance and cleanliness
Shaver blades and heads	Steel	8	0.3	Wear resistance and smoothness
Pen tips	Brass	5	0.2	Corrosion resistance

(a) Many components are heat treated at 190 to 210 °C (375 to 410 °F) for 1 to 3 h to improve adhesion or to relieve hydrogen embrittlement.

(b) Heat treated for 1 h at 400 °C (750 °F) for maximum hardness.

(c) Heat treated for 6 h at 135 °C (275 °F) for hydrogen embrittlement relief.

(d) Heat treated for 10 h at 290 °C (550 °F) for maximum hardness.

(e) Cadmium plated after electroless nickel and then heat treated for 2 h at 340 °C (640 °F) to diffuse cadmium into the nickel.

(f) Heat treated for 1 h at 620 °C (1150 °F) to diffuse coating into basis metal.

(g) For medical, pharmaceutical, and food applications, coatings must be free of toxic heavy metals such as lead, cadmium, mercury, or thallium.

Applications for electroless nickel-boron deposits in the electronics industry include wire bonding for IC chips, soldering, brazing, laser welding, low electrical resistivity, and as a diffusion barrier.

Specifications

The published specifications for electroless nickel-phosphorus currently available in the United States include:

- AMS 2404, Electroless Nickel Plating (Ref 51)
- ASTM B 656, Autocatalytic Nickel Deposition on Metals for Engineering Use (Ref 43)
- Military Specification Requirements for Electroless Nickel Coatings (Ref 52)

In addition, an international standard has been drafted by the International Standards Organization (Ref 50). Published standards for electroless nickel-boron coatings for engineering purposes are not available.

Although these standards are good guidelines for testing and quality control, none include any real requirements for structural quality, corrosion resistance, or wear resistance. The standards consist primarily of a visual examination and simple tests for thickness and adhesion. Often this forces industrial users to develop their own internal specifications for coating quality. These in-house specifications can be relatively simple with requirements for only a few desired properties, or very detailed with requirements for substrate pretreatment, bath operation, equipment design, deposit chemistry, and properties.

References cited in this section

43. " Autocatalytic Nickel Deposition on Metals for Engineering Use," Part 9, B 656, *Annual Book of ASTM Standards,* ASTM, 1981
50. "Autocatalytic Nickel-Phosphorus Coatings," ISO 4527, International Standards Organization
51. "Electroless Nickel Plating," AMS 2404B, Society of Automotive Engineers, 1977
52. "Military Specification-Coatings, Electroless Nickel, Requirements for," MIL-C-26074B, U.S. Government Printing Office, 1959 and 1971

Electroless Nickel Composite Coatings

Composites are one of the most recently developed types of electroless nickel coatings. These cermet deposits consist of small particles of intermetallic compounds, fluorocarbons, or diamonds dispersed in an electroless nickel-phosphorus matrix. These coatings have a high apparent hardness and superior wear and abrasion resistance.

Chemistry. Most composite coatings are applied from proprietary baths. Typically, they consist of 20 to 30 vol% of particles entrapped in an electroless nickel containing 4 to 11% P. Most commonly silicon carbide, diamond particles, fluorinated carbon powders and PTFE are used, although calcium fluoride is also occasionally codeposited. The particles are carefully sized and are normally 1 to 3 μm in diameter (Ref 53, 54, 55) for silicon carbide and diamonds and 0.35 μm for PTFE. A micrograph of a typical silicon carbide composite coating is shown in Fig. 22 (Ref 56). The baths used for composite plating are conventional sodium hypophosphite reduced electroless nickel solutions, with the desired particles suspended in them. These baths, however, are heavily stabilized to overcome or inhibit the very high surface area produced by the particles. The baths otherwise are operated normally and the nickel-phosphorus matrix is produced by the traditional hypophosphite reduction of nickel. The particles are merely caught or trapped in the coating as it forms. Their bond to the coatings is purely mechanical.

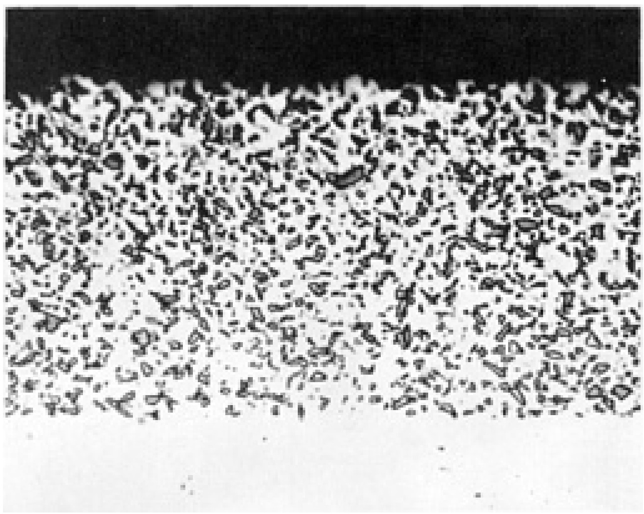

Fig. 22 Cross-sectional view of a typical silicon carbide composite coating.

Hardness and Wear. The primary use for electroless nickel composite coating is for applications requiring maximum resistance to wear and abrasion. The hardnesses of diamond and silicon carbide are 10,000 and 4500 HV, respectively. In addition, the coatings are normally heat treated to provide maximum hardness (1000 to 1100 HV_{100}) of the electroless nickel matrix. The resulting apparent surface hardness of the composite is 1300 HV_{100} or more (Ref 53, 56).

The wear surface of a composite coating consists of very hard mounds separated by lower areas of hard electroless nickel. During wear, the mating surface usually rides on the particles and slides over the matrix. Thus, the wear characteristics of these coatings approach that of the particle material (Ref 53). Typical wear test results for a silicon carbide composite coating are shown in Table 12 (Ref 56).

Table 12 Comparison of the Taber abraser resistance of silicon carbide composite coatings with other engineering materials

Material	Hardness	Taber wear index, Mg 11,000 cycles
400-C stainless steel	57 HRC	5.6
A2 tool steel	60-62 HRC	5.0
Electroless nickel (hardened)	900-1000 HV	3.7
Hard chromium	1000-1100 HV	3.0
Tungsten carbide	1300 HV	2.0
Electroless nickel and silicon carbide composite	1300 HV	0.18-0.22

Note: Taber wear index determined for an average of three 5000-cycle runs with 100 g load and CS17 abrasive test wheels

Frictional properties of composite coatings are similar to those of other electroless nickels. Typically, the coefficient of friction of these materials is about 0.13 in the lubricated condition and 0.3 to 0.4 in the unlubricated condition (Ref 53, 54).

Corrosion Resistance. In general, the corrosion resistance of composite coatings is significantly less than that of other electroless nickel coatings. The electroless nickel matrix contains large amounts of codeposited inhibitor, which reduces the alloy's passivity and corrosion resistance. Also, heat treated coatings are less protective than are as-applied coatings, both because of the conversion of the amorphous deposit to crystalline nickel and Ni_3P and because of cracking of the coating (Ref 53, 56). With composites, this problem is amplified because of the presence of the diamond or intermetallic particles. The mixture of phosphides, nickel, and particles creates a very strong galvanic couple accelerating attack. For applications requiring good corrosion resistance, electroless nickel composite coatings are not normally used.

References cited in this section

53. J.M. Scale, Wear Resistance of Silicon Carbide Composite Coatings, *Met. Prog.,* Vol 115 (No. 4), 1979, p 44
54. D.J. Kenton et al., "Development of Dual Particle Multifunction Electroless Nickel Composite Coatings," Electroless Plating Symposium, American Electroplaters' Society, 1982 (St. Louis, MO)
55. N. Feldstein et al., "The State of the Art in Electroless Composite Plating," Electroless Plating Symposium,

American Electroplaters' Society, 1982 (St. Louis, MO)

56. W.B. Martin et al., "Electroless Nickel Composites--The Second Generation of Chemical Plating," Electroless Nickel Conference, Nov 1979 (Cincinnati, OH)

Plating on Plastics

Except for ferrous alloys, plastics are probably the substrate most commonly electroless nickel plated. The coating is typically applied to nonmetallics as a conductive base for subsequent electroplating of both decorative and functional deposits. Occasionally, electroless nickel is used by itself for applications requiring resistance to abrasion or environmental attack (Ref 2). Because plastics are nonconductive and are not catalytic to the chemical reduction of nickel, special processing steps are required to ensure adequate adhesion and to initiate deposition. With synthetics, metallic bonds cannot form between the coating and the substrate. Thus, adhesion results only from mechanical bonding of the coating to the substrate surface. To improve adhesion, plastics are typically etched in acidic solutions or organic solvents to roughen their surface and to provide more bonding sites.

In order to initiate electroless nickel plating on plastics (or other nonmetals) their etched surfaces must first be catalyzed with stannous chloride and palladium chloride and then accelerated in acid. This produces palladium nucleation sites on the surface for deposition. A typical pretreatment sequence for plastics is:

- Degreasing
- Etching
- Neutralization
- Catalyzation
- Acceleration
- Electroless nickel deposition

Thorough rinsing after each processing step is essential. After the electroless nickel layer has been completed, the part may be plated conventionally with any desired electrolytic coating (Ref 2, 57).

Degreasing. When necessary, light soil or fingerprints can be removed from plastic parts by immersion in a mildly alkaline soak cleaner for 2 to 5 min. A typical degreasing solution contains 25 g/L each of sodium carbonate and trisodium phosphate and is operated at 50 to 70 °C (120 to 160 °F). Alkaline cleaning is not always required, provided the plastic is carefully handled after molding and is not allowed to become excessively soiled. Fingerprints and loose dust or dirt are normally removed by the etching solution.

Etching solutions for plastics are typically strongly oxidizing acids that cause a microscopic roughening of the part's surface. These solutions also alter the chemical character of the surface and cause it to become hydrophylic. Etching not only improves mechanical bonding and adhesion of the coating to the plastic substrate, but also improves access of subsequent processing solutions to the surface. Most commercially used etching solutions are formulated with either chromic acid or mixtures of sulfuric acid and chromic acid or dichromate salt. These solutions are typically operated at 50 to 70 °C (120 to 160 °F) with immersion times of 3 to 10 min. Chromic acid based solutions are particularly effective with ABS plastics, but are also used for polyethylene, polypropylene, PVC, polyesters, and other common polymers.

Neutralizing. After the plastic has been properly etched and rinsed, it should be neutralized to remove residual chromium ions, which may interfere with subsequent catalyzation. Neutralizers are rinsing aids and are typically dilute acid or alkaline solutions, often containing complexing and reducing agents. Ionic surfactants are sometimes added to increase the absorption of the catalyst on the surface. Neutralizing solutions are normally operated at 40 °C (105 °F) with immersion times of 1 to 2 min.

Catalyzing. In order to initiate deposition of the electroless nickel coating on plastics, their surfaces must be catalyzed. This is normally accomplished by chemically depositing small amounts of palladium. The original commercial catalyzing procedures required two processing steps. In the first step, stannous chloride was absorbed onto the surface from a solution of $SnCl_2$ and HCl. After rinsing, the part was immersed in a solution of $PdCl_2$ and HCl, and palladium chloride was absorbed onto the surface. The stannous ions then reduced the palladous ions leaving discrete sites of metallic palladium. Currently, a one-step catalyzing procedure is normally used. For this, a solution of stannous chloride and palladium chloride in hydrochloric acid is used. The solution consists of tin/palladium complexes and colloids stabilized by excess stannous chloride. The chloride content of the solution is critical and must be carefully controlled. During

immersion, globules of tin/palladium colloid absorb onto the plastic surface. After rinsing, nuclei of metallic palladium surrounded by hydrolyzed stannous hydroxide, are left attached to the surface.

Acceleration. With one-step catalyzation, a further step is required to remove excess stannous hydroxide from the surface and to expose the palladium nuclei. This step is called acceleration and is accomplished by immersing the part in a dilute solution of hydrochloric acid or an acid salt. The acid reacts with the insoluble stannous hydroxide forming soluble stannous and stannic chloride. After rinsing, there surface is free of tin and active catalytic sites are present. Acceleration solutions are typically operated at a temperature of 50 °C (120 °F) and are agitated with air. The parts are normally immersed for 30 to 60 s.

Electroless Nickel Deposition. Most electroless nickel solutions operate at too high a temperature for plastics. High temperatures may cause plastics to warp. In addition, the large difference in coefficient of thermal expansion between plastics and electroless nickel may cause adhesion failures during cooling from bath temperatures. Electroless nickel solutions for plating on plastics, thus, are formulated to operate at low temperatures--typically 20 to 50 °C (70 to 120 °F). These solutions are normally alkaline and reduced with sodium hypophosphite, although some DMAB solutions are also used. Ammonia-based plating baths are preferred because of their ability to complex excess palladium dragged in with the part and to avoid spontaneous decomposition. While most of these solutions are proprietary, some typical formulations (Ref 2) are:

Composition	Bath 1		Bath 2	
	g/L	oz/gal	g/L	oz/gal
Nickel chloride	119	15	. . .	. . .
Nickel sulfate	. . .	. . .	50	6.5
Sodium hypophosphite	106	14	50	6.5
Sodium pyrophosphate	. . .	. . .	100	13
Ammonium citrate	65	8	. . .	. . .
Ammonia, mL/L (fluid oz/gal)	. . .	. . .	45	5.8
Sodium hydroxide	To pH		. . .	. . .

Operating conditions	Bath 1	Bath 2
pH	10	10
Temperature, °C (°F)	30-50 (85-120)	25 (77)

Typical plating rate, μm/h (mils/h)	3-11 (0.12-0.44)	3 (0.12)

Plastic parts are normally immersed in the electroless nickel solution for 5 to 10 min to provide a uniform metal film about 0.25 to 0.50 μm thick. This coating is sufficient to cover the surface of the plastics and to make them conductive for subsequent electroplating. These deposits typically contain 2 to 6% P. After proper treatment the peel strength of 25 mm (1 in.) width strips of these coatings on plastics like ABS and polypropylene is on the order of 50 to 100 N (Ref 2, 57).

References cited in this section

2. G.G. Gawrilov, *Chemical (Electroless) Nickel Plating,* Portcullis Press, Redhill, England, 1979

57. J.K. Dennis and T.E. Such, *Nickel and Chromium Plating,* Newres-Butterworths, 1972, p 287

Electroless Copper Plating

Cheryl A. Deckert, Shipley Company, Inc.

Introduction

ELECTROLESS, OR AUTOCATALYTIC, METAL PLATING is a nonelectrolytic method of deposition from solution. The minimum necessary components of an electroless plating solution are a metal salt and an appropriate reducing agent. An additional requirement is that the solution, although thermodynamically unstable, is stable in practice until a suitable catalyzed surface is introduced. Plating is then initiated on the catalyzed surface, and the plating reaction is sustained by the catalytic nature of the plated metal surface itself. This definition of electroless plating thus eliminates both those solutions that spontaneously plate on all surfaces (homogeneous chemical reduction), such as silver mirroring solutions, and immersion plating solutions, which deposit by displacement a very thin film of a relatively noble metal onto the surface of a sacrificial, less noble metal.

The history of electroless plating began with the serendipitous discovery, by Brenner and Riddell, of electroless nickel-phosphorus, during a series of nickel electroplating experiments in 1946 (Ref 1). Electroless copper chemistry was first reported in the following year by Narcus (Ref 2). The first commercial applicability of electroless copper was reported in the mid-1950s with the development of plating solutions for plated-through-hole (PTH) printed wiring boards. Electroless copper solutions resembling today's technology were first reported in 1957 by Cahill (Ref 3) with the report of alkaline copper tartrate baths using formaldehyde as reducing agent. Copper baths of the 1950s were difficult to control and very susceptible to spontaneous decomposition. Over the years, continual advances in control and capabilities have taken place and continue to be recorded in a variety of reviews (Ref 4, 5). At present, not only are formulations extremely stable and predictable in behavior over long periods and under a wide variety of operating conditions, but they also provide copper deposits having excellent physical and metallurgical properties comparable with those of electrolytic deposits.

Electroless copper plates much more slowly, and is a much more expensive process, than electrolytic copper plating. However, electroless copper plating offers advantages over electrolytic plating that make it the method of choice in certain cases. Electroless copper plates uniformly over all surfaces, regardless of size and shape, demonstrating 100% throwing power; and it may be plated onto nonconductors, or onto conductive surfaces that do not share electrical continuity. The ability to plate large racks of substrates simultaneously is also an advantage in certain instances. These advantages have contributed to the choice of electroless copper in the applications to be discussed herein.

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References

1. A. Brenner and G.E. Riddell, *AES Proc.,* Vol 33, 1946, p 23
2. H. Narcus, *Met. Finish.,* Vol 45, Sept 1947, p 64
3. A.E. Cahill, *AES Proc.,* Vol 44, 1957, p 130
4. C.R. Shipley, *Plating,* Vol 71 (No. 6), 1984, p 94
5. G.O. Mallory and J.B. Hajdu, Ed., *Electroless Plating: Fundamentals and Applications,* American Electroplaters Society, 1990

Bath Chemistry

The theoretical basis of the electroless copper deposition process has been studied on numerous occasions and has recently been reviewed (Ref 6). As stated above, the minimum necessary components of an electroless plating solution are the metal salt and a reducing agent. The source of copper is a simple cupric salt, such as copper sulfate, chloride, or nitrate.

A number of common reducing agents have been suggested (Ref 7) for use in electroless copper baths: formaldehyde, dimethylamine borane, borohydride, hypophosphite (Ref 8), hydrazine, sugars (sucrose, glucose, etc.), and dithionite. In practice, however, virtually all commercial electroless copper solutions have used formaldehyde as reducing agent. This is due to the combination of cost, effectiveness, and ease of control of formaldehyde systems. It is particularly remarkable in view of the considerable and continual pressures exerted on the plating industry by environmental and regulatory agencies due to health concerns regarding formaldehyde exposure (see the section "Environmental and Safety Issues" in this article). Because of the overwhelming commercial importance, in this chapter we will confine discussion to formaldehyde-based systems.

For Cu(II), the relevant half-cell reaction for electroless deposition is:

$$Cu^{2+} + 2e^{-} \leftrightarrow Cu^{0} \quad E^{0} = +0.340V$$

For formaldehyde, the E^0 depends on the pH of the solution:

$$HCOOH + 2H^{+} + 2e^{-} \leftrightarrow HCHO + H_2O \quad pH = 0 \quad E^{0} = +0.056$$

$$HCOO^{-} + 2H_2 + 2e^{-} \leftrightarrow HCHO + 3OH^{-} \quad pH = 14 \quad E^{0} = -1.070$$

Therefore, electroless copper solutions using formaldehyde as reducing agent employ high pH, above pH 12 (typical NaOH concentration is >0.1 *N*; theoretically 0.1 *N* = pH 13).

Because simple copper salts are insoluble at pH above about 4, the use of alkaline plating media necessitates use of a complexing, or chelating, component. Historically, complexing agents for electroless copper baths have almost always fallen into one of the following groups of compounds:

- Tartrate salts
- Alkanol amines, such as quadrol (N,N,N',N' tetrakis(2-hydroxypropyl)ethylenediamine) or related compounds
- EDTA (ethylenediamine tetraacetic acid) or related compounds

Glycolic acids and other amines have also been reported (Ref 7).

Tartrates were used in the earliest baths and continue to be used, particularly for low-plating-rate ($\leq$0.5 μm/20 min), low-temperature (near ambient) applications. Tartrates are more easily waste-treatable than the other two classes of chelates, but they have not readily lent themselves to formulation of faster plating systems.

Alkanol amines came into wide use in electroless copper baths in the late 1960s, with the advent of faster plating systems. This type of chelate made it possible to achieve "high-build" (≥2 μm/20 min) electroless copper solutions, and it continues to have wide use even today. Because quadrol and its analogs are liquids, totally miscible with water, they are not easily removed from the waste solution, and hence they are resistant to many conventional waste treatment procedures.

EDTA salts are also widely used for complexing electroless copper solutions. EDTA has certain desirable characteristics versus those of quadrol, based on waste treatability. Specifically, EDTA can be more easily separated (precipitated) from waste solutions by pH adjustment. Starting in the late 1970s, bath additives for EDTA systems (see below) were developed that allowed excellent control of plating rate, grain structure, and other important factors. Because of the very high affinity of EDTA for any metal ions, even small residual amounts of dissolved EDTA can draw potentially toxic metals into the waste stream. This has led to increased legislative efforts (notably in Germany and Japan) against use of this chelate and its derivatives. However, at present, the most commonly used plating baths are based on EDTA.

Besides the copper salt, the reducing agent, the source of alkalinity, and the chelate, other important components are present in commercial electroless copper solutions. These components are generally considered the proprietary portion of the formulation, and they control such parameters as initiation and plating rate, stability (versus dragged-in catalyst; versus excessively high bath activity; versus long shutdown periods; versus Cu(I) oxide), deposit stress, color, ductility, and so on. Prior to development of well-characterized and controlled trace additives, electroless copper baths were prone to "triggering" (spontaneous decomposition of the bath), "plateout" (decomposition over a prolonged standing period), "second day startup" (inability to induce a controlled plating reaction when first stored after makeup), dark deposit color, rough deposit, coarse grain structure, and so on. Literally hundreds of papers and patents have been published relating to these additives. Useful summaries of this data are available (Ref 9, 10).

Additives that stabilize the bath against various manifestations of undesired plateout are referred to as *stabilizers.* Understanding their composition, mechanism, and optimal replenishment rate is key to successful operation of a bath. They are usually employed at low concentrations, typically 1 to 100 ppm. Principal among the materials reported are compounds such as mercaptobenzothiazole, thiourea, other sulfur compounds, cyanide or ferrocyanide salts, mercury compounds, molybdenum and tungsten, heterocyclic nitrogen compounds, methyl butynol, propionitrile, and so on. Pressure from environmental and regulatory groups over the years has led to near-elimination of cyanide- and mercury-type additives. It is noteworthy that perhaps the most common stabilizer for electroless copper baths is a steady stream of air (i.e., oxygen) bubbled through the solution.

Additives that increase the plating rate of the solution are variously referred to as *rate promoters, rate enhancers, exhaltants,* or *accelerators.* This last term is particularly unfortunate and confusing in view of the use of the term *accelerator* to describe a key process step in electroless copper processes (see the section "Processes" in this article). Materials that have been reported to function as rate promoters include ammonium salts, nitrates, chlorides, chlorates, perchlorates, molybdates, and tungstates. Rate promoters may be present in the electroless formulation at concentrations of 0.1 *M* or higher.

Other additives may also be incorporated in certain cases. For example, surfactants may be used to improve deposit characteristics (Ref 11), and incorporation of excess halide ion into the formulation permits elimination of the normal accelerator step (Ref 12) (see the section "Processes" in this article).

Typical examples of freshly made-up electroless copper baths are given in Table 1.

Table 1 Examples of electroless copper formulations

	Low build (tartrate)	**High build (quadrol)**	**High build (EDTA)**	**Full build (EDTA)**
Copper salt, as Cu(II)	1.8 g/L	2.2 g/L	2.0 g/L	3.0 g/L
	0.028 *M*	0.035 *M*	0.031 *M*	0.047 *M*

Chelate	Rochelle salt	Quadrol	Disodium EDTA dihydrate	Disodium EDTA dihydrate
	25 g/L	13 g/L	30 g/L	42 g/L
	0.089 *M*	0.044 *M*	0.080 *M*	0.11 *M*
Formaldehyde, as HCHO	10 g/L	3 g/L	3 g/L	1.5 g/L
Alkalinity, as NaOH	5 g/L	8 g/L	7 g/L	3 g/L
Additives[a]	<2 g/L	<2 g/L	<2 g/L	<2 g/L
Temperature, °C (°F)	20 (70)	43 (110)	45 (115)	70 (160)
Plating rate, μm/20 min	0.2	2.5	2	1

Note: The terms *low build, high build,* and *full build* are defined in the section "Deposit Properties" in this article.

(a) Examples of additives: 2-mercaptobenzothiazole, diethyldithiocarbamate, 2,2'-dipyridyl, potassium ferrocyanide, vanadium pentoxide, nickel chloride, polyethylene glycol

The overall electroless copper plating reaction is theoretically given as:

$$Cu^{2+} + 2HCHO + 4OH^- \rightarrow Cu^0 + H_2 + 2\,H_2O + 2\,HCO_2^-$$

This equation calls for the consumption of four hydroxide ions and two molecules of formaldehyde for each atom of copper deposited. However, certain side reactions may also take place, the most common being the Cannizzaro reaction, which consumes additional caustic and formaldehyde:

$$2HCHO + OH^- \leftrightarrow CH_3OH + HCOO^-$$

In addition, other side reactions also occur, consuming formaldehyde and producing unwanted byproducts such as cuprous oxide, which can lead to bath decomposition unless suitable stabilizers are present.

Once the bath begins to be used, copper, caustic, and formaldehyde are consumed and must be replenished. This is typically carried out by routine analysis, either manually or electronically, with back addition of appropriate replenishment chemistries (see the section "Controls" in this article). Ordinarily, some bailout of the plating solution must be done at this point, to allow for the volume of new chemistry to be added. Because the anion of the copper salt (usually sulfate or chloride) and the cation of the caustic component (usually sodium) are not consumed, a buildup of sodium sulfate or chloride occurs. This can cause deleterious effects such as "voiding" or high deposit stress over prolonged bath life, particularly when bailout volumes are very low. In addition, formate ion builds up as a byproduct of the plating reaction itself. The extent to which the Cannizzaro reaction takes place also contributes to the quantity of byproduct buildup. Byproduct buildup can cause deterioration of bath and deposit properties (Ref 13, 14), and it is now typically accounted for during the bath formulation. Steady-state performance is achieved after a specified number of bath turnovers (or "cycles"), depending on the recommended bailout volume, and is typically controlled through specific gravity.

References cited in this section

6. P. Bindra and J.R. White, *Electroless Plating: Fundamentals and Applications,* G.O. Mallory and J.B. Hajdu, Ed., American Electroplaters Society, 1990
7. E.B. Saubestre, *AES Proc.,* Vol 44, 1957, p 130
8. M. Gulla and O.B. Dutkewych, U.S. patent 4,482,596, 1984
9. J. McDermott, *Plating of Plastics with Metals,* Noyes Data, 1974
10. J. Bielinski and K. Kaminski, *Surf. Coat. Technol.,* Vol 31, 1987, p 223
11. R.M. Lukes, U.S. patent 2,996,408, 1961
12. G.M. Wilkinson, C.A. Deckert, and J.J. Doubrava, U.S. patent 4,751,106, 1988
13. C.I. Courduvelis and G. Sutcliffe, *Plat. Surf. Finish.,* Vol 67, Sept 1980, p 71
14. C.A. Deckert, G.E. Hutchins, and M. Abu-Moustafa, Paper T-2, *AES Proc.,* Vol 69, 1982

Deposit Properties

Plating Rate and Deposit Thickness. Not strictly a deposit property, plating rate is a key characteristic of an electroless copper plating bath. Plating rate and useful range of deposit thickness dictate the specific applicability of a formulation. Plating baths are typically categorized as *low build, high (heavy) build,* or *full build.*

Low build deposits about 0.5 μm (or less) in about 20 min and typically operates at ambient temperature. This was typical of the earliest stable bath formulations developed in the 1960s. These baths are traditionally tartrate-based; in fact, it has proven difficult to formulate stable, faster plating baths using a tartrate chelate system. These deposits are typically fine-grain and exhibit good deposit integrity. They are suitable for applications such as subtractive printed wiring boards, where an electrolytic plateup process follows immediately after copper deposition (see the section "Applications" in this article).

High (heavy) build deposits 2 to 3 μm in about 20 min and typically operates at elevated temperature (35 to 55 °C, or 95 to 130 °F), but room-temperature formulations are also available. These baths are usually based on EDTA or quadrol chemistry. Acceptable formulations of this type were first developed in the early 1970s. Earlier baths tended to give coarse-grain deposits and produced somewhat highly stressed deposits, especially at higher limits of deposit thickness. However, these formulations have been refined to a high degree and are readily controlled to give excellent deposit properties. Major applications for this type of bath are those where intervening process steps may occur prior to subsequent plateup, such as in pattern plate printed wiring boards (see the section "Applications" in this article).

Full build typically deposits 25 μm or more of copper over a more prolonged plating cycle of up to 15 h. (By comparison, a typical electroplating process would deposit 25 μm of copper in 35 to 50 min.) The typical temperature of operation is 55 to 80 °C (130 to 175 °F). A fundamental requirement in developing this type of bath has been the achievement and maintenance of deposit characteristics such as high ductility and tensile strength, fine grain structure, low intrinsic stress, and so on throughout the thick deposit. This type of bath was first reported in 1964 (Ref 15) and has been employed primarily for additive-type printed wiring board applications. EDTA has been the main chelate used. This deposit typically represents the full metal thickness required for the applications and hence eliminates the need for electroplating altogether (Fig. 1). The very high expense of building a thick copper deposit using an electroless versus electroplating process is warranted (or required) for certain applications, such as when absolutely uniform thickness is needed, when electrically discontinuous surfaces are to be plated, or when very high aspect ratio holes are to be plated. For example, processes for fabricating multichip modules require use of a full-build electroless copper (see the section "Applications" in this article). In this application the copper thickness requirement may be substantially less than 25 μm. A number of advances in the area of full-build copper plating have occurred over the past five years or so (Ref 15, 16, 17). The most critical deposit characteristics are ductility and tensile strength, particularly at the elevated temperatures (260 to 288 °C, or 500 to 550 °F) employed in the printed wiring board assembly processes. Current development activities in this area are aimed toward achievement of substantially higher plating rates without loss of deposit properties.

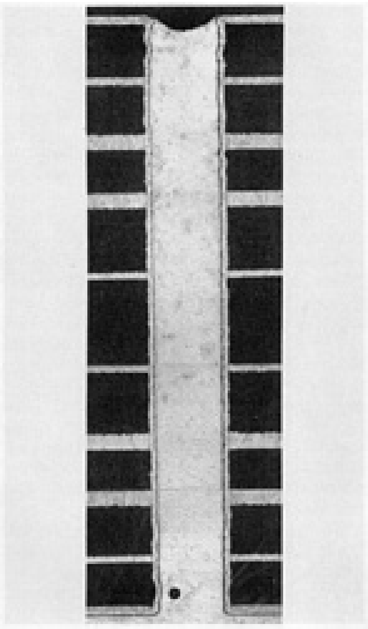

Fig. 1 Through-hole plated using full-build electroless copper

Other. Of course, intermediate thicknesses of copper are achievable by appropriate manipulation of the bath operating parameters. *Very slow* and *medium build* formulations are also applicable to some of the applications to be discussed.

Purity, Density, and Electrical Properties. Deposit purity of electroless copper films is somewhat lower than that of electrolytic films, due to codeposition of traces of electroless bath components. This affects several physical properties, including percent purity, density, and resistivity. Typical acid-copper electrolytic baths produce films of 99.9% purity, 8.92 g/cm^3 density, and 1.72 μΩ· cm volume resistivity (at 20 °C) (Ref 18), whereas the printed wiring board industry standard (Ref 19) for full-build electroless copper is 99.2% purity (min), 8.8 ±0.1 g/cm^3 density, and 1.90 μΩ· cm (at 20 °C) resistivity (max).

Grain Structure. Because electroless copper deposition is initiated on the randomly distributed catalyst particles on the substrate, initial grain structure is largely determined by that surface morphology. Bath formulation is of course a strongly determining factor as well, and it will control the grain structure as the deposit thickness increases. It is thought that fine-grain deposits, initiating at close proximity on the catalytic sites and coalescing to form a film early in the deposition process, offer superior copper quality in the early stages of film growth. Recently, full-build electroless copper grain structure was studied, correlated with etching rate in a variety of common copper foil etching solutions, and compared with typical electrolytic copper grain structure (Ref 17).

Tensile Strength and Ductility. Advances in electroless copper formulations, particularly for full-build applications in printed wiring board applications, have centered on achieving deposit mechanical properties, specifically tensile strength and ductility, that ensure the needed film reliability (Ref 20). Tensile strength of up to 490 MPa (70 ksi) and elongation of up to 15% can now be achieved (Ref 15), although these properties are not achieved from the same formulation. Improvement in the as-plated elongation values may be achieved with heat aging, at the expense of tensile strength. It has also been reported that ductility at thermal shock temperature (e.g., 260 to 288 °C, or 500 to 550 °F) may be significantly higher than as measured at ambient temperature. Some discussion is still in progress (Ref 15, 21) regarding the relative importance of these two properties in defining an ideal plated deposit.

Other Properties. Other deposit properties, such as hydrogen inclusion, are also of interest.

References cited in this section

15. D. Dinella and C. Mak, Paper B 5/1, Proc. Printed Circuit World Convention V (Glasgow, Scotland), 1990

16. K. Minten and J. Toth, Paper B 5/2, Proc. Printed Circuit World Convention V (Glasgow, Scotland), 1990; *Circuit World,* Vol 17, 1991, p 19
17. K. Minten, J. Seigo, and J. Cisson, *Circuit World,* Vol 18 (No. 4), 1992, p 5
18. F.E. Stone, *Electroless Plating: Fundamentals and Applications*, G.O. Mallory and J.B. Hajdu, Ed., American Electroplaters Society, 1990
19. IPC-AM-372, Institute for Interconnecting and Packaging Electronic Circuits, Lincolnwood, IL
20. V.A. Lamb, C.E. Johnson, and D.R. Valentine, *J. Electrochem. Soc.*, Vol 117, 1970, p 341c, 381c
21. A. Nakaso, K. Yamanoi, and T. Okamura, Paper WCIII-10, Proc. Printed Circuit World Convention III (Washington, D.C.), 1984

Applications

Printed Wiring Boards (PWBs)

By far the most important commercial application of electroless copper plating has been the PTH process for fabricating printed wiring boards (PWBs). Prior to the mid-1950s, mounting components onto PWBs relied on mechanical interlocking using inserted eyelets. The through-holes could not be electroplated directly because the base material of the circuit board (paper-phenolic, epoxy-glass, or other dielectric) did not provide the needed electrical conductivity. Development of electroless copper plating solutions (Ref 22), made practical by concurrent development of suitable selectively adsorbing catalytic materials (see the section "Processes" in this article), led to a dramatic improvement in the reliability of printed circuit boards and prompted the rapid growth of the PWB market during the 1960s through 1980s.

The vast majority of PWBs are made by a subtractive process using base material, typically epoxy-glass laminate, clad with electrolytic copper foil. The substrate is drilled, after which electroless copper is plated through the holes (and incidentally over the foil surface). Then electrolytic copper buildup and surface copper imaging (using dry film) take place; the order of these processes defines the fabrication process as either *panel* plating or *pattern* plating. In pattern plating, the plated areas are next overplated with a dissimilar metal (typically Sn/Pb), the dry film is removed, and all exposed copper is etched. In panel plating, no dissimilar metal plating is required; etching takes places immediately after imaging. The term *subtractive* processing arises from the fact that the circuitry is ultimately formed by removing base copper from the circuit board.

Although the basic overall process flow for fabricating a PWB has remained essentially constant for decades, the technology associated with every subprocess has undergone great improvement over that time period, and the electroless copper process is no exception. Improvements in electroless copper formulations, as discussed earlier, have greatly improved control of PWB processing and end product reliability. However, developments in PTH pretreatment have probably contributed even more greatly to end board reliability over that period. New hole preparation methods for multilayer boards provided such substantial benefits in terms of key criteria like copper coverage, adhesion (to laminate) and solderability (Ref 23) (see the section "Performance Criteria" in this article) that two-sided boards are now also frequently processed through these additional steps.

Careful integration of the steps immediately preceding catalyzation has also ensured that the optimal uniform, yet minimal, catalyst film is deposited in preparation for plating. This has provided the key to achieving interconnect bonds sufficiently strong (Ref 24) to withstand multiple thermal shocks, thus assuring very high end-product reliability (see the section "Performance Criteria" in this article). At present, the PWB market is under considerable environmental and cost pressure to replace electroless copper with a direct metallization process (see the section "Environmental and Safety Issues" in this article). Recent quality improvements, such as those described, present a formidable target for replacement technologies.

Additive processes for PWBs rely, as the name implies, on the buildup of the circuit copper over bare laminate. Variations on the fully additive process include semiadditive and partly additive processes. Description of these is documented in many published reports, which have been recently reviewed (Ref 25). Fully additive processes have been in use since 1964 and offer a number of advantages over conventional subtractive processing. Despite this, growth in the additive market has been slow; worldwide production in 1992 has been estimated at 2 to 5% of the world PWB production (Ref 26, 27). This slow growth is due partly to the more difficult adhesion and selectivity requirements and partly to the lack of adequate physical properties in the full-build electroless copper that is an integral component of the process. However, in recent years the quality of full-build electroless has become satisfactory, and this, coupled with

improved process control and new automatic bath controllers, provides support for future growth of the additive PWB market (see the section "Equipment" in this article).

Decorative Plating-on-Plastic (POP) (Ref 28)

Since the 1950s, plastics have been substituted for metals in a multitude of applications and for a variety of reasons, including weight advantages, cost advantages, and the relative ease of creating complexly shaped substrates through molding. These factors prompted the development of suitable decorative finishing processes, specifically plating processes, starting in the early 1960s. Electroless metal deposition as a base for a thicker, decorative electrolytic deposit has proven extremely reliable and commercially successful. For lower-performance applications, electroless nickel is a suitable choice. However, ever since the demonstration in the 1970s that electroless copper provides better resistance to environmental exposure (Ref 29, 30), it has become the material of choice in the majority of higher-performance applications, especially automotive. The molded substrate is chemically treated to improve adhesion of the copper film (see the section "Processes" in this article), then about 0.5 to 0.75 μm of electroless copper is applied. Typically an electrolytic copper or Watts nickel strike follows, and then a thicker (12 to 25 μm) electrolytic bright acid copper deposit. Finishing coats of electrolytic nickel and/or chromium plating are then applied.

Substrate materials (Ref 28) for decorative plating-on plastic include acrylonitrile-butadiene-styrene (ABS), ABS/polycarbonate, polyphenylene oxide, polycarbonate, polysulfone, polyester, nylon, and so on. There are many grades for any given plastic, and these may differ considerably in plateability. Certain grades of foamed plastics may also be used. For decorative POP, ABS is by far the most commonly used plastic. ABS is a thermoplastic alloy with an acrylonitrile-styrene matrix that has butadiene rubber dispersed throughout. The butadiene is selectively etched by the pretreatment chemistry, creating a uniformly roughened surface suitable for plating.

In all POP applications, control of the molding process is critical. Care must be taken to avoid introducing stresses or strains, to avoid troublesome mold-release agents, to limit use of "regrind" resin, to ensure a resin-rich surface (in cases where fillers are used), and so on. The use of complexly shaped parts necessitates close attention to such details as mold design and maintenance, melt and mold temperatures, fill speed, and many other parameters. In designing or troubleshooting a plating-on-plastic process, it is critical to use molded parts of the exact grade and design to be used, as there is high interdependence between molding and plating processes.

Functional POP (Electromagnetic Interference Shielding)

Another commercially important application for electroless copper is electromagnetic interference (EMI) shielding of electronic components. The need to reduce (attenuate) electromagnetic signals (Ref 31) generated either internally or externally to a packaged component leads to the need to provide EMI shielding to the component. EMI shielding capability is directly related to the conductivity of the component; hence, metal cases are highly effective in attenuating EMI. However, the same factors (cost and weight) that led to the use of plastics as base materials for decorative applications have also led to their implementation in electronic cabinetry. Because plastic enclosures are poor at attenuating EMI signals, a variety of coating methods have been developed to address this need. Methods that address the requirements of EMI shielding of plastic enclosures include electroless copper plating, as well as various types of metal-filled paints, zinc arc/flame spray, sputtered or evaporated metals, and conductive foils/tapes. Table 2 summarizes and updates published data (Ref 32, 33) on the most common methods of shielding. Key in choosing a method is the attenuation (measured in decibels) over a desired frequency range (Ref 34). Note that decibels of shielding is a logarithmic term, so a difference of 20 dB equals 100 times the shielding effectiveness.

Table 2 Methods of EMI shielding

Material/ method	Shielding capability[(a)]	Process cost[(b)]	Advantages	Disadvantages
Zinc arc spray	H	H	Good conductivity; hard, dense coat; very effective	Special equipment needed; prone to flaking; may distort housing
Conductive paints				

Silver	VH	VH	Good conductivity; conventional equipment; resists flaking; easy to apply	Expensive
Nickel	L	M	Conventional equipment	Multiple coats needed; effectiveness not high; thickness causes problems
Copper	M-H	M	Conventional equipment	Multiple coats needed; thickness causes problems
Evaporated metal	M	H	Familiar technology	Size limited by vacuum chamber; expensive equipment
Sputtered metal	M	M	Good conductivity	Expensive equipment; may distort housing
Conductive foils/tapes	H	VH	Good conductivity; good for experimentation	Complex parts are difficult; labor intensive
Conductive plastics	L	L	No secondary process	Material expensive; poor attenuation
Electroless plating				
Copper (two-sided)	VH	M	Uniform thickness; good for all shape parts; resists chipping; good conductivity	Limited to certain plastics; two-sided process usually requires paint finish; prone to oxidation
Nickel (two-sided)	M	H	Same as above, except conductivity	High thickness required for effective shielding
Copper/nickel (two-sided)	VH	M	Same as copper only, plus corrosion resistant	Same as copper only, except no oxidation
Copper/nickel (one-sided)	H	M	Same as Cu/Ni two-sided; fewer chemical steps; allows molded-in color	Same as Cu/Ni two-sided, except no finish coat

Source: Updated from Ref 32, 33

(a) Attenuation: VH (very high), 90 to 120 dB+; H (high), 60 to 90 dB; M (moderate), 30 to 60 dB; L (low), 10 to 30 dB; VL (very low), 0 to 10 dB.

(b) Cost: VH (very high), >\$3.25/ft^2; H (high), \$2.50 to \$3.25/ft^2; M (moderate), \$1.50 to \$2.50/ft^2; L (low), \$0.35 to \$1.50/ft^2; VL (very low), <\$0.35/ft^2.

Clearly, electroless copper is a very effective method of EMI shielding over a wide range of radio frequencies, having been first suggested in 1966 (Ref 35) and subsequently developed in the early 1980s (Ref 36). Considerable commercial activity has taken place, as several large computer manufacturers anticipated that higher "clock speeds" of electronic devices would require rapid conversion to the most effective methods of EMI shielding, such as electroless copper. However commercial activity using electroless copper for EMI shielding applications has lagged versus the rate

previously anticipated. Sustained growth in the use of electroless copper for EMI shielding is probable in the future, because the increased clock speeds of the devices emitting the signals accentuate the need for more effective shielding.

When electroless copper is employed for EMI shielding, the conductive film used typically consists of electroless copper plating to a thickness of about 0.7 to 2 μm, overplated with a thin film (0.25 to 0.5 μm) of electroless nickel. The parameter used to specify copper thickness is resistivity (Ref 37); normally less than 0.05 Ω/point-to-point over a set distance is readily achievable using electroless copper. The nickel contributes virtually nil to the shielding effectiveness (Ref 38), but it provides durability and corrosion resistance.

Specific substrate resins used in electronic enclosures include solid and/or foamed forms of ABS, polycarbonate, ABS/polycarbonate alloys, polyphenylene oxide, polystyrene, and polysulfone. A newly emerging, and potentially very large, market involves electroless copper for shielding fabric used in cable, military, and wall covering applications.

Electroless copper plating for EMI shielding may employ either a two-sided or single-sided process. In the two-sided process the entire cabinet is treated and plated; this approach generally requires a finish coat of paint. The single-sided process involves plating of the interior surface only; thus the molded plastic surface represents the final surface finish. These two processes involve totally different pretreatments, as discussed in the section "Processes" in this article.

Hybrid and Advanced Applications

Molded Interconnect Devices. Following advances in control and capability of imaging and plating technologies, and commercialization of high-performance injection molded plastics, a natural development was the molded circuit board, or molded interconnect device (MID). Adhesion promotion principles developed for the decorative POP industry have been applied to devising adhesion promotion processes for a variety of engineering thermoplastics (Ref 39), permitting deposition of adherent electroless copper deposits that could be built up in thickness and imaged similarly to conventional PWBs.

In certain cases, conventional plastics such as ABS have been used as MID substrates. However, in order to survive board assembly temperatures, more advanced plastics are often required. These include polyetherimide, polyethersulfone, polyarylsulfone, liquid crystal polymers, and so on. Molding requirements are even more critical than for decorative POP, due to the need for higher levels of adhesion (typically ≥1.1 kN/m, or 6 lb/in., peel strength, versus ~0.7 kN/m, or 4 lb/in., for decorative POP) and due to the stresses induced by plateup, imaging, and assembly processes. Certain of the plastics mentioned have proven more amenable than others to development of suitable adhesion promotion processes. Polyetherimide, in particular, has proven to be compatible with surface chemistry-altering pretreatments that produce very strongly adherent electroless copper (Ref 40), while not roughening the substrate surface excessively. The latter characteristic is particularly important when fine-line imaging processes are to be employed later in the process.

Depending on the MID design and process chosen, plateup of the initial electroless copper strike plate may employ either electrolytic copper or full-build additive copper (20 to 35 μmm). Imaging of three-dimensional substrates has necessitated development of inventive materials and processes (Ref 41). Electrodeposited photoresists, as well as novel methods of exposure and related equipment, have proven key in this effort.

At this time, the MID market has proven to be feasible and has achieved commercial success in several dedicated facilities. Many ingenious and cost-saving devices have been designed and are currently in production (Ref 39, 42). Figure 2 demonstrates a number of commercially produced MIDs. However, this market has not achieved the level of acceptance predicted in the late 1980s, due to the need for high volumes of a given design to amortize mold costs, the failure of materials costs to come down to required levels, and the tendency of electronic designers to employ more familiar methods, such as conventional PWBs, whenever possible.

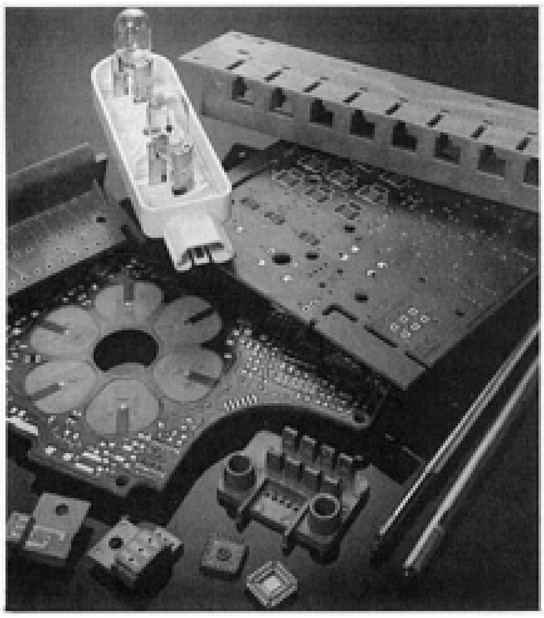

Fig. 2 Examples of commercially produced molded interconnect devices. Courtesy of Shipley Co.

Composite Connectors. The composite connector application is a hybrid of two-sided EMI shielding with molded interconnects. These parts are currently made of aluminum, and for all the usual reasons, considerable interest lies in replacing the aluminum with a lighter material such as plastic. The physical requirements of the connector are such that only advanced engineering plastics, such as those used in the MID market, are suitable. The parts must be plated, not to form circuitry but to provide EMI shielding. Fabrication of these devices employs the same plastics and pretreatments for electroless plating that are employed for molded interconnects. Due to the durability, lubricity, and hardness requirements of the finished parts, the electroless nickel overcoat is built up to a rather higher thickness (~5 μm) than for EMI shielding of electronic cabinetry. Examples of some plastic composite connectors, processed through electroless copper and nickel, are shown in Fig. 3.

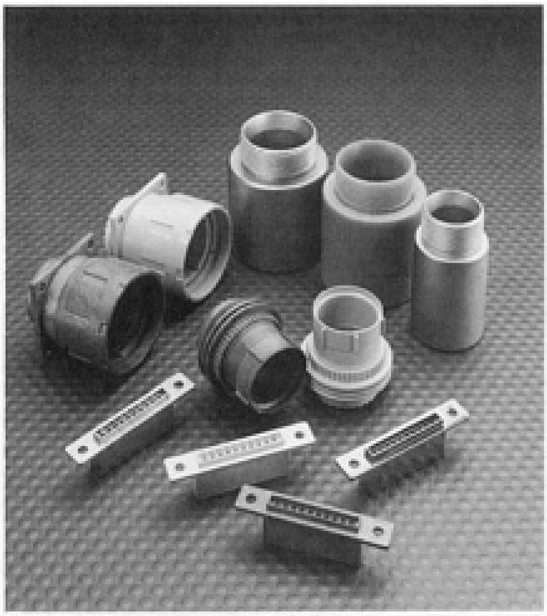

Fig. 3 Examples of plastic composite connectors plated with electroless copper and nickel. Courtesy of Shipley Co.

Multichip Modules. Progress in semiconductor technology continues to place increasing demands on interconnection and assembly technology. In the 1980s, the response to this demand on the PWB side was increasing numbers of layers and finer circuitry. However, this trend cannot be sustained at the needed rate (Ref 43), leading to the requirement for an intermediate level of interconnection onto which bare chips may be mounted (Ref 44). These devices, known as multichip modules (MCMs), may be fabricated using several approaches (Ref 45, 46, 47). However, a common feature is the use of full-build electroless copper (Ref 48) to build up the conductive traces.

An example of a fabrication process for an MCM is given in Fig. 4. The electroless copper subprocess generally follows along the lines of the PTH and POP processes (discussed in more detail in the section "Processes" in this article). Adhesion promotion for the metallization layer to the unique dielectric materials employed in MCMs can be a challenge in itself. Conventional "swell and etch" approaches are normally used; other approaches are also in development.

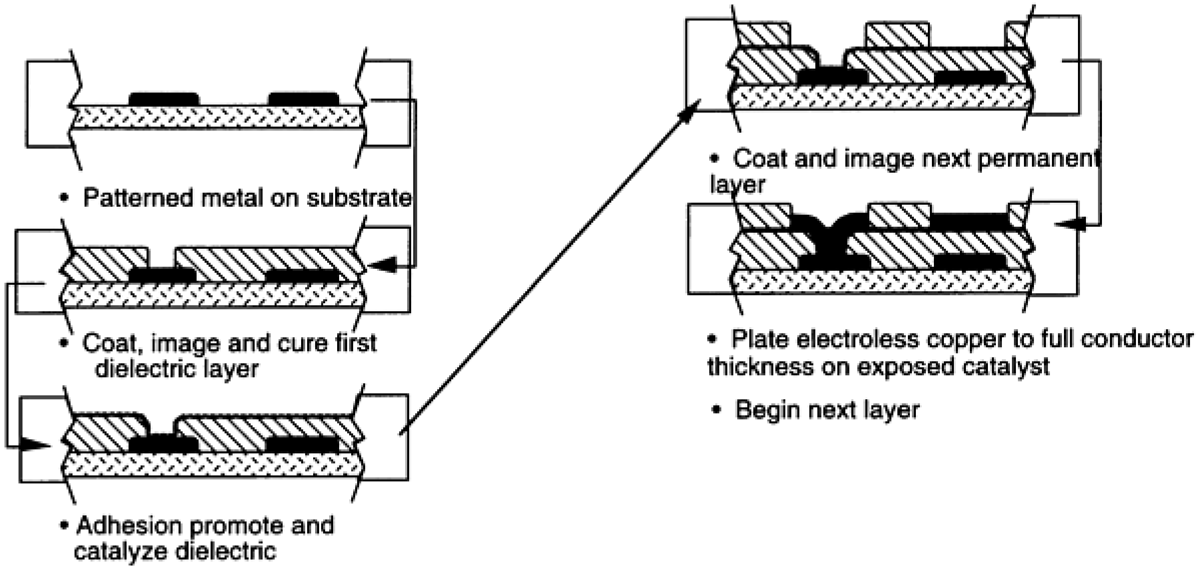

Fig. 4 A process flow chart for deposition of a multichip module on a conventional printed wiring board. Courtesy of Shipley Co.

Silicon Devices. Recently some interest has arisen in employing electroless copper for integrated circuit manufacture (Ref 49, 50, 51). It is felt that aluminum, which is used in providing the conductive path on chips, may not be sufficiently conductive at the very high resolutions required in future devices. Very thin films of electroless copper (~0.1 to 0.2 μm), deposited additively in channels between a photodefined temporary film, have been used.

References cited in this section

22. E.B. Saubestre, *AES Proc.,* Vol 46, 1959, p 264
23. C.A. Deckert, *Circuit World,* Vol 13 (No. 3), 1987, p 29
24. C.A. Deckert, IPC-TP-699, Institute for Interconnecting and Packaging Electronic Circuits, Lincolnwood, IL, 1988
25. H. Nakahara, *Printed Circuits Handbook,* 3rd ed., C.F. Coombs, Ed., McGraw-Hill, 1988, and references therein
26. K. Nargi-Toth and J. Wynschenk, Paper P-16, Proc. Printed Circuit World Convention VI (San Francisco), 1993
27. D. Dinella, Paper P-17, Proc. Printed Circuit World Convention VI (San Francisco), 1993
28. *Standards and Guidelines for Electroplated Plastics,* 3rd ed., American Society of Electroplated Plastics, Prentice-Hall, 1984

29. R.L. Coombes, Proc. 2nd Annual Mtg, American Society of Electroplated Plastics, 1969, *Plating,* Vol 57, 1970, p 675
30. R.G. Wedel, *Plating,* Vol 62, 1975, p 40, p 235; *Int. Met. Rev.,* Vol 22, 1977, p 97
31. J.L.N. Violette, D.R.J. White, and M.F. Violette, *Electromagnetic Compatibility Handbook,* Van Nostrand Reinhold, 1987
32. G.A. Krulik, *Prod. Finish.,* Oct 1983, p 49
33. J.J. Kuzmik, *Electroless Plating: Fundamentals and Applications,* G.O. Mallory and J.B. Hajdu, Ed., American Electroplaters Society, 1990
34. ES 7-83 and D 4935-89, ASTM
35. G.A. Lordi, *Plating,* Vol 54, 1967, p 382
36. J. Hajdu and G. Krulik, *Plat. and Surf. Finish.,* Vol 70, July 1983, p 42
37. F 390, ASTM
38. G.A. Krulik, *Plastics Finishing and Decoration,* D. Satas, Ed., Van Nostrand Reinhold, 1986
39. J. E. Rychwalski, Paper A 7/2, Proc. Printed Circuit World Convention V (Glasgow, Scotland), 1990
40. D.F. Foust and W.V. Dumas, U.S. patent 4,999,251, 1991
41. E.D. D'Ottavio, R.E. Hawkins, S.S. Rodriguez, and J.E. Rychwalski, U.S. patent 5,004,672, 1991
42. V.V. Zaderej, J. Mettler, R. McQueeney, and W. Kearney, Paper B 4/1, Proc. Printed Circuit World Convention V (Glasgow, Scotland), 1990
43. E. Clark, *Printed Circuit Fab.,* Vol 16 (No. 20), 1993, p 69
44. Y. Tsukada, *Proc. 42nd Electronic Components and Technology Conference,* 1992, p 22
45. G. Messner et al., *Thin Film Multichip Modules,* The International Society for Hybrid Microelectronics, 1992
46. T.G. Tessier and P.E. Garrou, *Proc. International Society for Hybrid Microelectronics,* 1992, p 235
47. P.D. Knudsen, R.L. Brainard, and K.T. Schell, Proc. Surface Mount International (San Jose, CA), 1993
48. R. Enomoto and M. Asai, U.S. patent 5,055,321, 1991
49. C.H. Ting and M. Paunovic, *J. Electrochem. Soc.,* Vol 136, 1989, p 456
50. Y. Shacham-Diamand, *J. Micromech. Microeng.,* Vol 1, 1991, p 66
51. J.S.H. Cho, H.-K. Kang, S.S. Wong, and Y. Shacham-Diamand, Bull. 31, Materials Research Society, June 1993

Processes

Properties of the electroless copper bath and deposit are highly dependent on the pretreatment (and, to a lesser degree, the post-treatment) system used. Although the plating bath is the most visible and complex-to-operate solution in the process line, a mistake commonly made is to blame any process problem on the plating chemistry itself. In a majority of cases, this is not the case. Lack of correct attention to the details of the preplate chemistry is more likely to have caused the problem.

This section concentrates on the main commercial processes for electroless copper, namely PTH, decorative POP, and EMI. Other applications employ similar processes, some of which are shown in the overall process flow summary given in Fig. 5. Note that rinse steps are not shown; unless stated otherwise it should be assumed that one or more rinse steps intervene between every two process steps. This is not to minimize the importance of adequate rinsing; the adage of "it's the water" has been proven true in many troubleshooting situations. Specific requirements of water quality for PWB plating processes have been published (Ref 52) (see also the section "Controls--Miscellaneous" in this article).

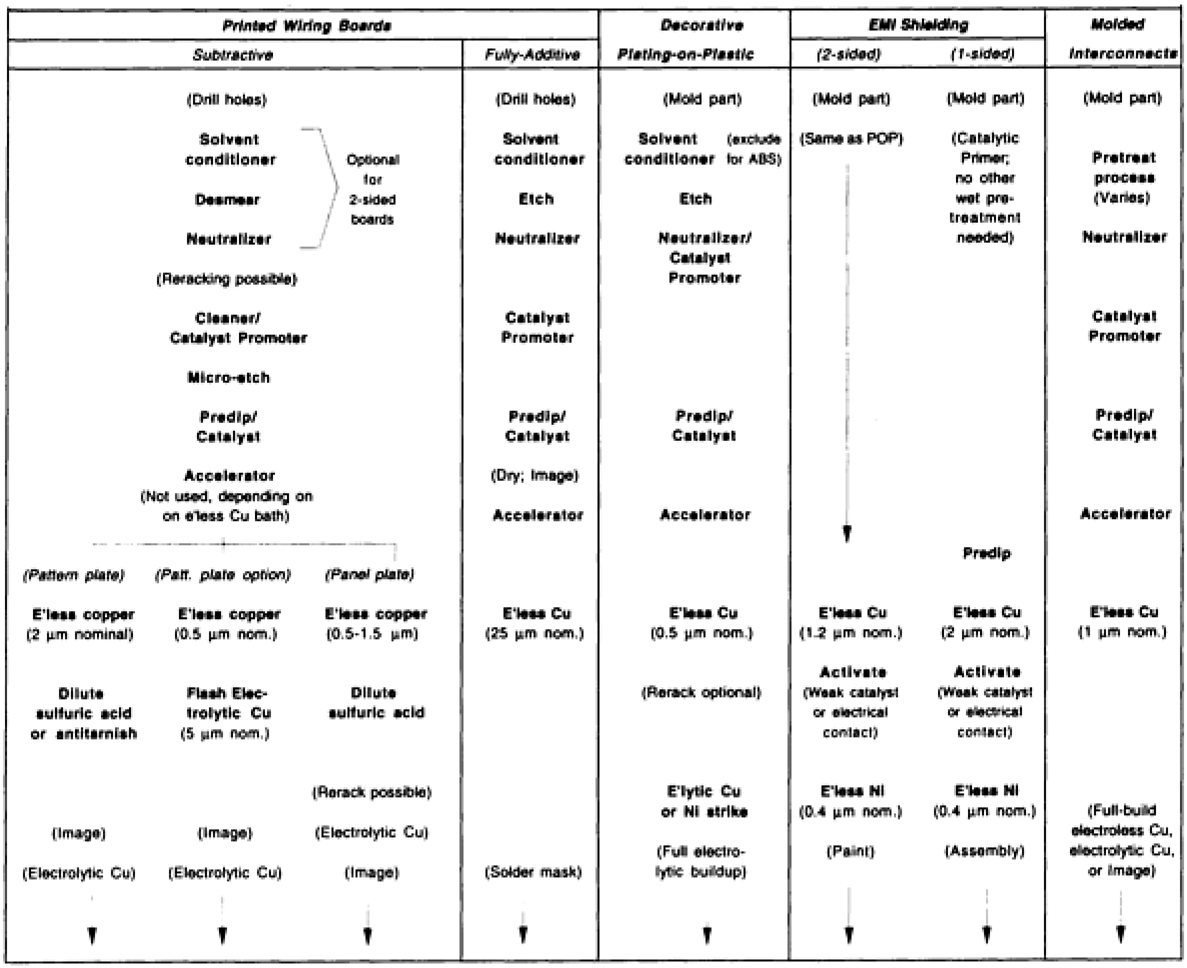

Fig. 5 Comparison of electroless copper processes. Unless otherwise stated, it should be assumed that one or more rinse steps intervene between each two process steps.

Pretreatment

Other than single-sided EMI, which will be discussed separately, electroless copper processes are similar in terms of functionality of pretreatment steps.

Gross Surface Preparation. The first steps of pretreatment, for either multilayer PWBs or bare plastic, employ fairly aggressive chemicals to remove debris and foreign matter from the substrate and etch the surface. These steps may change the topography and/or surface chemistry of the substrate significantly. The main objectives of this sequence of steps are to ensure good adhesion and eliminate the visible (gross) voiding that can result from a poorly prepared surface.

Printed Wiring Boards. This sequence of steps encompasses the desmear process for drilled holes in multilayer boards (MLBs). Drilling of the through-holes causes the laminate material (usually epoxy) to be smeared across hole wall surfaces. Reliable fabrication of multilayer boards requires that this drill smear be removed from the copper inner layers to ensure an effective copper-copper bond. The most common type of desmear process is based on a permanganate (Ref 53, 54, 55) oxidizing solution and involves three steps:

- *The MLB conditioner or pre-etch* is an aqueous-alkaline-oxygenated solvent solution that is operated at elevated temperatures (60 to 70 °C, or 140 to 160 °F) and penetrates slightly into the epoxy laminate so as to prepare it for optimal effect in the subsequent permanganate solution. Although analogous to the swell and etch system used in POP, this PWB analog does not penetrate deeply into the plastic; only surface layers (<5 µm) are thought to be affected. (Note that the term *conditioner* as used in this context must be differentiated from the PTH conditioner, or catalyst promoter, to be discussed below.)
- *The MLB etch or promoter* is a strongly alkaline permanganate solution that is operated hot (75 to 85

°C, or 165 to 185 °F) and actually dissolves a minute amount of epoxy, in particular removing any epoxy smeared on the copper inner layers. A microporous surface structure is also normally imparted to the resin. This results in an excellent surface upon which catalysis and plating can take place.

- *The neutralizer* is an acidic, mildly reducing solution that removes manganese (MnO_2) residues from all board surfaces. Typical chemistries include dilute sulfuric-peroxide solutions or acid solutions of hydroxylamine salts. It is noteworthy that, in contrast with the use of chromium-containing etchants, special care need not be taken to ensure total removal of all manganese residues, as manganese does not have a harmful effect on subsequent processing.

Figure 6 compares a typical multilayer board through-hole, after drilling, with a permanganate-desmeared through-hole that exhibits a clean hole wall and microroughened resin surface.

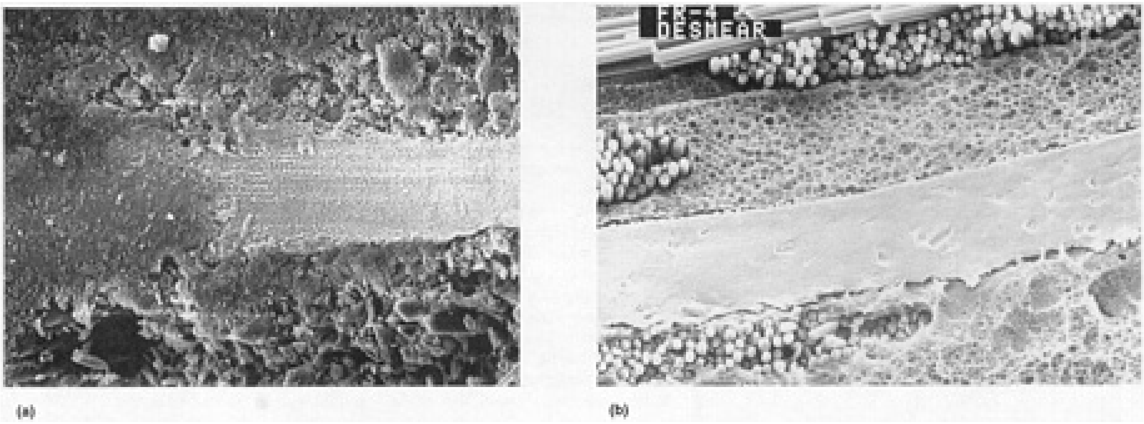

Fig. 6 Multilayer board through-holes. (a) After drilling. Note resin smear over copper inner layer surface, and loosely adherent debris covering surface. (b) After permanganate desmear. Note clean overall appearance and uniformly microroughened epoxy surface.

Chemistries alternative to permanganate that have been used for desmearing PWBs include chromic acid or concentrated sulfuric acid (each with appropriate pre- and/or post-treatment) or plasma treatment. These methods exhibit numerous shortcomings relative to permanganate in terms of safety, toxicity, reliability, cost, and/or control.

Following the desmear process, depending on the configuration of the plating equipment, it may be necessary to unrack the parts, and then rerack for treatment in the balance of the electroless process.

Plating-on-Plastic (Decorative and Two-Sided EMI Shielding). The corresponding process steps for POP applications also typically include three steps:

- *The conditioner or pre-etch* is an aqueous-organic solvent mixture. The specific solvent used will differ qualitatively depending on which plastic is being treated. In the case of ABS, this step is not needed.
- *The etch* is typically based on aqueous chromic acid (a sulfuric acid admixture is also commonly used).
- *The neutralizer* is a reducing solution that may be either acid or alkaline and which removes all hexavalent chromium residues. In comparison with the permanganate neutralizer used in PWB desmear, it is essential that every trace of hexavalent chromium be removed from the surface, as Cr(VI) is a poison for the subsequent catalyst step. The neutralizer chemistry may be modified to include in one step the catalyst promoter discussed below.

Immediate preparation for plating ensures the final cleanliness of the part (if necessary), ensures that the surface will be receptive to catalyst, deposits the catalytic film, and converts the catalyst to its active form, in preparation for electroless plating.

Cleaning (Optional). For substrates such as two-sided PWBs that do not require the gross surface preparation sequence above, a conventional cleaning step is needed. Also, in cases where equipment configuration forces a split between the gross surface preparation steps and the balance of the process, a cleaning step may be needed to remove any soils that were thereby introduced. It is common practice to incorporate this cleaning step together with the subsequent catalyst promotion step. A hot solution is typically used, ~55 to 70 °C (130 to 160 °F). The main constraints on the chemistry are that it be easily rinsable and that it be compatible with the rest of the process line. Waste treatment concerns are shifting cleaning chemistries away from the use of amine chelates and strongly acid or alkaline solutions.

Catalyst promotion (conditioning) imparts a uniform surface film to the substrate, which ensures uniform adsorption by the subsequent catalyst step and therefore promotes better plating. Because the most commonly used catalyst, the palladium-tin colloidal catalyst, is negatively charged, conditioning agents tend to bear a positive charge. The conditioning step may be combined with either the preceding cleaning step (two-sided PWBs) or the neutralizer (POP). The main issue is compatibility with subsequent steps. Specifically, in the case of PWBs, this means the ability to effectively remove any residual film from the copper during the intervening rinse and microetch steps. In the case of decorative POP, the need to achieve selectivity in the plating (i.e., no rack plating) favors the use of marginally effective catalyst promoters, whereas for PWB applications, the general difficulty of plating glass fibers in the laminate material leads to use of more effective conditioning chemistries, despite the resultant rack plating.

Microetching is required for PWBs only. It etches a thin film (0.75 to 2 μm) of the foil and inner-layer copper, thus ensuring cleanliness in preparation for plating. Any conditioning agent from the previous step is ideally removed from copper surfaces, as it could lead to a poor copper-copper bond if left in place. Normally either a mildly acidic sodium or potassium persulfate solution or a sulfuric acid-peroxide solution is used. If a persulfate solution is used, it may be followed by a dilute sulfuric acid dip.

A catalyst predip is normally employed just prior to the catalyst solution (no intervening rinses). This predip contains all components of the catalyst solution minus the catalyst itself. The purposes of the predip are to protect the expensive catalyst bath from contaminants and normalize the substrate surface chemistry prior to exposure to the catalytic species.

Catalyzation (Sensitization). Good catalyzation is the key to the entire electroless copper process. All the preceding steps are employed so as to optimize this step and ensure the uniformity and selectivity of the catalyst deposit. In theory, any of a wide range of metals, including copper, nickel, gold, silver, and all the other precious metals (Group VIIIB), may be used. In practice, because of a tradeoff between cost and selectivity (preferential adsorption of the catalyst to certain surfaces rather than others), only a few metals and physical/chemical forms of these have found acceptance in the electroless copper industry. These will be discussed roughly in chronological order of their development:

- *Binary precious metal salt:* Acidic solutions of simple precious metal salts, including $PdCl_2$, $PtCl_2$, and so on, may be used as catalyst for electroless plating in some instances. Because these salts are not tightly bound to the substrate surface, they may be removed by excessive rinsing. These solutions generally promote plating only on the most active surfaces, thus providing a good method of selectivity in certain applications.
- *Sequential tin, then palladium (so-called "two-step"):* An acidic Sn(II) solution, typically $SnCl_2$, dissolved in dilute hydrochloric acid, is first used to provide a uniform film of Sn^{2+} ions over the entire substrate surface. Because Sn(II) is inherently a strongly adherent material, the resultant film is tenaciously retained during rinsing. Then immersion in a dilute hydrochloric acid solution of $PdCl_2$ causes the more noble palladium ion to be reduced onto the substrate at the expense of the adsorbed Sn(II), which is oxidized to Sn(IV). This catalyst system was reported in 1955 (Ref 56) and has proven reliable and effective in metallizing nonconductive materials. However, a major disadvantage is the marked lack of selectivity: All exposed surfaces are heavily catalyzed. In the case of PWBs, use of the two-step catalyst often produces such a heavy catalyst film on the copper substrate that the resultant electroless copper deposit exhibits poor adhesion.
- *Palladium-tin colloid:* This type of catalyst system (Ref 57, 58) is by far the most prevalent type in commercial use. It is a stable reaction product of palladium and tin chlorides in acidic solution. The colloid is about 1 to 5 nm (10 to 50 Å) in size, consisting of a palladium-rich inner core and bearing hydrous Sn(IV) chlorides in the outer sphere. The overall colloid is negatively charged. Excess Sn(II) plays a key role in the stabilization of the catalyst solution. A high salt content is also present in modern versions of the colloidal catalyst. This system offers a number of advantages over earlier catalysts: it is

more stable, it is more active per unit of palladium, and it allows good selectivity. The catalyst as-deposited bears a high-tin-containing "sheath" surrounding the active catalytic species, and it is not optimally activated until the subsequent acceleration step.

- *Copper catalyst:* Because palladium is more expensive than the less noble metals (such as copper and nickel) that are known to be autocatalytic, there have been numerous attempts to develop a viable catalyst based on one of these metals. A copper-tin colloidal catalyst was first reported in 1976 (Ref 59) and has proven commercially successful in a number of installations. A major disadvantage is that because the catalyst is much less active catalytically, the accompanying electroless copper bath must be formulated as a much less stable solution than copper baths employed with the more active palladium-tin catalysts. This can result in process control problems.
- *Ionic (alkaline) complexed palladium:* In the mid-1970s an alkaline, ionic palladium catalyst system was developed (Ref 60) that demonstrated improved selectivity versus prior ionic palladium systems. This catalyst requires a subsequent activation step, namely immersion in a solution of a strong reducing agent such as dimethylamine borane, in order to become catalytically active. This catalyst system continues to have applicability (Ref 61) and is currently second in popularity to the colloidal palladium-tin catalyst system.

Acceleration (Activation). Discussion of this step will focus on the palladium-tin colloidal system, as it is the most commonly used catalyst. The tin-containing sheath surrounding the active palladium-rich catalytic core must be removed in order to initiate a strong plating reaction. Accelerating solutions typically are based on chemistries that dissolve and/or complex Sn(II) and Sn(IV) compounds. Commonly used formulations include dilute fluoboric acid or hydrochloric acid (or mixtures thereof), or other acidic or alkaline solutions. The catalyzation/acceleration process has been characterized in a number of studies (Ref 62). Proper control of accelerator parameters is needed to avoid an "overacceleration" condition wherein catalyst may actually be stripped, thus leading to voids in the electroless plating process. In recent years, particularly for PTH, the acceleration step has been eliminated altogether by incorporating excess chloride into the copper bath, thus causing it to be "self-accelerating" (Ref 12) without loss of stability.

Post-treatment

As Fig. 5 shows, post-treatments for electroless copper vary considerably, depending on the application.

Printed Wiring Boards. For conventional subtractive pattern plated boards, the panels may be treated in an antitarnish solution immediately after electroless copper. Afterward they are rinsed and dried, prior to unracking and going on to the imaging process. Antitarnish solutions are usually mildly acidic solutions, optionally containing a weakly chelating acid salt such as citrate or tartrate. Alternatively, a dilute solution of a specific antitarnish component such as benzotriazole may be used.

An optional pattern plate sequence, which employs very thin ($\leq$0.5 μm) electroless copper, uses a post-treatment step of thin (flash) electrolytic copper, ~5 μm thick, prior to unracking.

For subtractive panel plating processes, electrolytic copper plating is carried out immediately after the electroless copper process. The electroplating may be either in-line (thus necessitating use of a single flight-bar throughout the entire electroless process) or in separate equipment (allowing more flexibility in electroless equipment and racking, but involving additional handling steps).

Decorative Plating-on-Plastic. After electroless copper deposition, the parts are usually treated with an electrolytic copper or nickel strike about 2.5 μm thick. The purpose of this step is to build up the initial thin electroless film so as to facilitate the subsequent buildup. Following the strike, bright acid copper plating is usually carried out to a thickness of 12 to 25μm. Next, depending on the final finish and physical characteristics desired, one to three different electrolytic nickel treatments may be employed, totaling up to ~33 μm thickness. The final finish is usually electrolytic chromium, 0.12 to 0.25 μm thick; however, the final finish may also be brass, gold, silver, or other finishes.

Single-Sided EMI Process

In order to plate electroless copper on the inside (only) of a cabinet, so that the molded plastic substrate needs no other finish, special pretreatment methods have been developed and commercialized. These take the form of catalytic spray paints (Ref 63) that can be applied selectively onto the plastic surface and, following a defined bake or cure step, allow direct deposition of electroless copper. In theory, any of the metals that catalyze electroless deposition may be used; in practice, the choice of metal is a tradeoff of catalytic activity versus cost. Typically, the single-sided EMI process requires no chemical pretreatment other than the paint. Other mechanical steps required include masking of the surfaces not to be plated, drying/baking of the paint, and racking for the plating process.

References cited in this section

12. G.M. Wilkinson, C.A. Deckert, and J.J. Doubrava, U.S. patent 4,751,106, 1988
52. E.F. Duffek, *Printed Circuits Handbook,* 3rd ed., C.F. Coombs, Ed., McGraw-Hill, 1988
53. E.J. Leech, J. Polichette, and J.G. Branigan, U.S. patent 4,054,693, 1977
54. C.A. Deckert, E.C. Couble, and W.F. Bonetti, U.S. patent 4,515,829, 1985
55. A.R. Del Gobbo and C.I. Courduvelis, IPC-TA-721, Institute for Interconnecting and Packaging Electronic Circuits, Lincolnwood, IL
56. F. Pearlstein, *Met. Finish.,* Vol 53, Aug 1955, p 59
57. C.R. Shipley, U.S. patent 3,011,920, 1961
58. E.D'Ottavio, U.S. patent 3,532,518, 1970
59. N. Feldstein, U.S. patent 3,993,799, 1976
60. H.J. Ehrich, W. Clauss, and H. Mahlkow, U.S. patent 4,248,632, 1981
61. H.J. Ehrich, Paper WCIII-06, Proc. Printed Circuit World Convention III (Washington, D.C.), 1984
62. R.L. Meek, *J. Electrochem. Soc.,* Vol 122, 1975, p 1177, 1478
63. J. Chen and P.D. Knudsen, U.S. patent 5,076,841, 1991; U.S. patent 5,120,578, 1992

Controls

Electroless Copper Solution. The electroless copper solution requires a variety of controls, all aimed toward maintaining steady-state performance in terms of plating rate, deposit physical properties, and bath stability (both during operation and on storage). First and foremost, the principal chemical parameters (copper, formaldehyde, and caustic content) must be kept within specification. Normally, by following replenishment and bailout instructions with respect to these primary components, all other bath chemical components will remain within the recommended ranges. However, occasionally chelate and stabilizer levels will also need independent control. Other than the chemistry, operating temperature is the most critical operating parameter. Too low a temperature will shut the plating off; too high may cause excessive plating rate and instability. Other key operating parameters include specific gravity (a measure of byproduct buildup (see the section "Bath Chemistry" in this article), air agitation, filtration, circulation, panel loading, and others. Specific methods for maintaining bath stability during periods of shutdown are also specified: plating down to 70 to 80% copper content in the case of room-temperature operating baths, or simply reducing the temperature for storage in the case of heated baths. Air agitation is usually employed to improve storage stability.

In general, baths providing higher film thicknesses have tighter requirements in terms of equipment parameters such as heaters, air agitation, circulation, filtration, replenishment mode, and so on. Full-build baths in particular have stringent requirements for agitation, circulation, and filtration, and they require close control over plating rate consistency. The needed controls are well characterized for all current electroless formulations, and most plating facilities can readily maintain the required controls on a regular basis. For a discussion of automatic bath controllers, see the section "Equipment--Control Equipment" in this article.

Other Process Solutions. General controls for other process solutions include the temperature and concentration of critical components, as specified by the supplier. Immersion time may also be critical in certain cases (e.g., PTH microetch), but not so long as a specified minimum immersion is attained (e.g., catalyst promoter). Supplier recommendations should be followed. Due to interaction between various pretreatment chemistries, as well as with the electroless chemistry, it is strongly recommended that a single supplier be used for the entire process. This practice also facilitates prompt resolution in troubleshooting situations.

In the gross pretreatment sequence, certain general controls must be considered. For PWB desmear, the permanganate (Mn^{7+}) to manganate (Mn^{6+}) ratio must be maintained at a specified level. Similarly, for POP adhesion promotion, the (Cr^{3+}) level must be controlled as specified. In POP it is strongly recommended that the temperature of the neutralizing solution be higher than that of the etch, to ensure that all hexavalent chromium residues are leached from any porous surfaces.

Adherence to specified chemistry controls is also necessary in the direct pretreatment sequence. In the PTH microetch, deviation from the prescribed parameters can lead to over- or underetching. In the catalyst solution, important parameters include specific gravity (to control salt content, which helps maintain colloid stability), Sn(II) level (which protects the colloid from oxidation and sedimentation), and colloid content (to control catalytic activity). In addition, certain metallic contaminants that can poison the catalytic activity (such as iron and chromium) must be monitored and controlled. Attention must be paid to the temperature and immersion time of the accelerator solution, to avoid under- or overacceleration. In addition, especially in chloride-containing accelerators, the dissolved copper content must be controlled to avoid formation of a rough deposit (believed to be CuCl) on the panel surface.

Miscellaneous. The importance of adequate rinsing, using good-quality water, can hardly be overemphasized. Heated rinses may be recommended after the catalyst promotion step to aid in removal of excess surfactant film. Rinsing after catalyzation requires maintenance of slightly acidic water containing no multiply charged cations, in order to prevent agglomeration of the negative colloid and surface roughness on the panel. Thorough rinsing in clean water is a general requirement in electroless copper processes, to prevent both panel surface defects and shortened bath life due to contaminated solutions.

Performance Criteria

The critical performance criteria for electroless copper processes vary somewhat, depending on the application. Two primary criteria that relate to all applications are coverage and adhesion. Other criteria have become increasingly important over the past decade or so, especially for PTH.

Coverage relates to the uniform and complete deposition of copper over the substrate. Coverage defects may be referred to as *voiding* (PWBs) or *skip plating* (POP). Gross coverage defects that are easily discerned by the naked eye are typically caused by an improperly prepared surface or major abnormality in the overall plating process parameters. Pinpoint defects, which may also be detectable to the eye, have long been a recognized problem in the POP industry, due to the importance of the appearance of the final product. Since about the late 1970s, microscopy has been widely used to detect minute defects in PTH, due to increasing demands on circuit integrity. Typically a panel is sliced so that half the plated hole is visible for microscopic examination. Rather than incident light, backlighting is often used (Ref 64), which provides a very sensitive measure of assessing coverage. Figure 7 demonstrates levels of coverage that can be discriminated. (Both these through-holes would appear totally covered when viewed using incident light.) Some debate has taken place regarding whether "total" backlight coverage is necessary, or even advisable. The critical importance of deposit adhesion, for instance, requires that any mechanism employed to promote coverage, such as use of strong catalyst promoters, be carefully controlled so as not to introduce weak boundary layers in the plated composite.

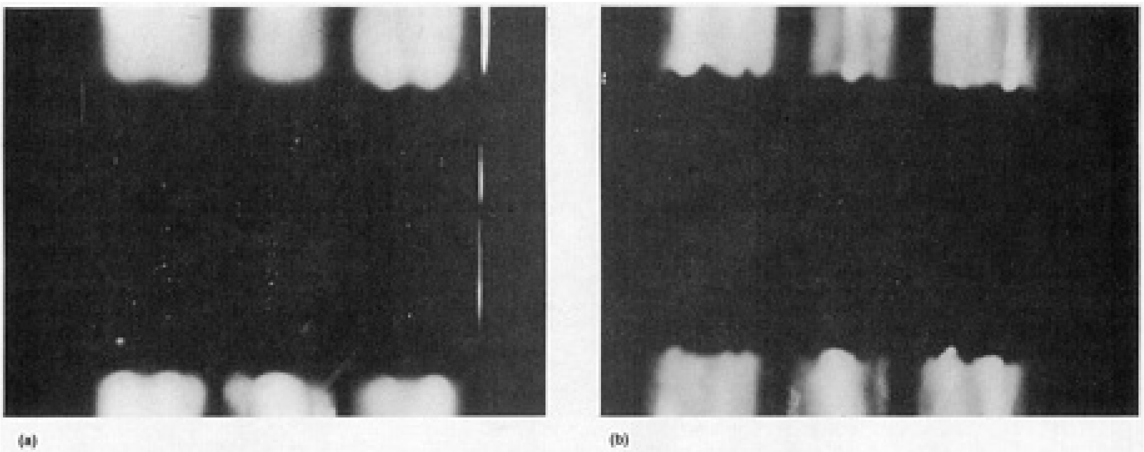
(a) (b)

Fig. 7 Backlight test cuopons. (a) Showing pinpoints voids. (b) Showing total electroless copper coverage

Adhesion of the copper deposit to the substrate is typically controlled by proper surface preparation. Typically the first two or three steps in the plating process prepare the surface in a gross manner. The subsequent steps of conditioning, microetch (for PWBs), catalyzation, and acceleration ensure that a complete, yet minimal, catalyst film is present, so as to maximize adhesion. Adhesion requirements vary, depending on the application. For POP the adhesion requirement is ~0.7 kN/m (4 lb/in.) peel strength, as measured by the Jacquet test (Ref 65), with good integrity to be maintained under a variety of environmental test conditions. The important factor is maintenance of a durable, cosmetic film over the lifetime of the part. The primary failure mode is blistering of the deposit. For conventional PWBs, peel strength per se is not usually measured. Adhesion is typically ascertained by cross-sectioning the board after electroplating, optionally subjecting the sample to high thermal stress that simulates or exceeds the expected stress to be induced during assembly, and then mounting and polishing prior to microscopic examination for failure between the electroless film and any of the other surfaces. Adhesion failure to the epoxy surface is commonly referred to as *hole wall pullaway;* adhesion failure to a copper inner layer is referred to as an *interconnect defect (ICD).* Detection and elimination of ICDs by improved electroless copper plating processes has led to significant improvement in PWB reliability over the past several years. Current industry standard electroless copper processes stand up to significantly more severe test conditions than those defined in the industry specification (Ref 66) (Fig. 8). In EMI shielding, the standard adhesion test involves scratching a cross-hatch pattern into the metallized film, then applying a tape test under prescribed conditions (Ref 67). This test is often used following a variety of environmental storage conditions.

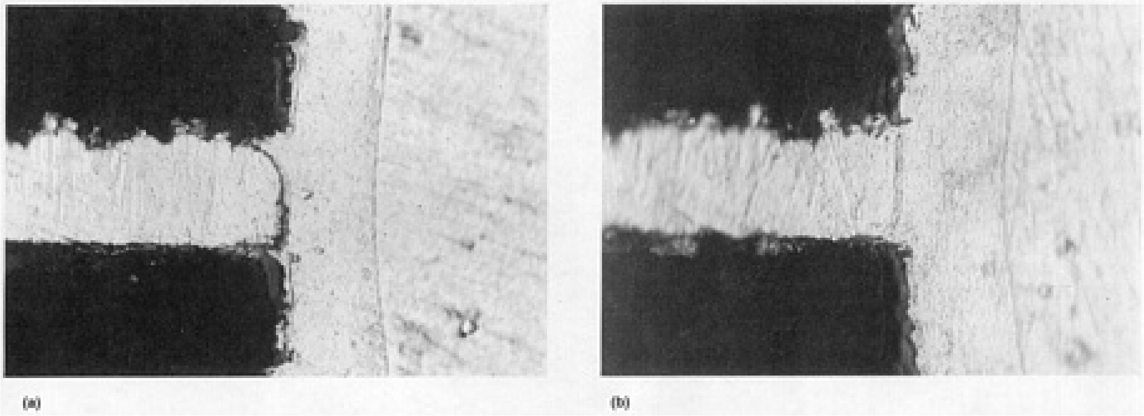

Fig. 8 Solder shock test coupons. (a) Showing interconnect defect. (b) Showing strong interconnect bond after multiple solder shock exposure. Courtesy of Shipley Co.

Deposit quality has become increasingly important over the past ten years. Controlled grain size, low intrinsic stress, and low electrical resistivity are some of the most important qualities sought. A method of PWB reliability testing using elevated-temperature fluid bed media has been employed to rapidly assess the long-term reliability of the copper deposit in through-holes (Ref 16).

Control of the copper bath is now routinely achieved, in contrast with the unstable and unpredictable formulations of the 1960s and 1970s. Plating rate, rate of depletion, deposit characteristics, and so on are all maintained consistently throughout the lifetime of the bath, allowing statistical control procedures to be readily implemented.

Solderability. The effect of the through-hole copper plating bath and process on solderability has been the subject of several studies (Ref 68), because outgassing or "blow holes" (Fig. 9) occurring during the assembly process can significantly affect PWB end-product reliability. It has been shown that outgassing is dramatically reduced by a permanganate-based surface preparation treatment used for desmearing multilayer boards in combination with a fine-grain, low-stressed copper deposit (Ref 24).

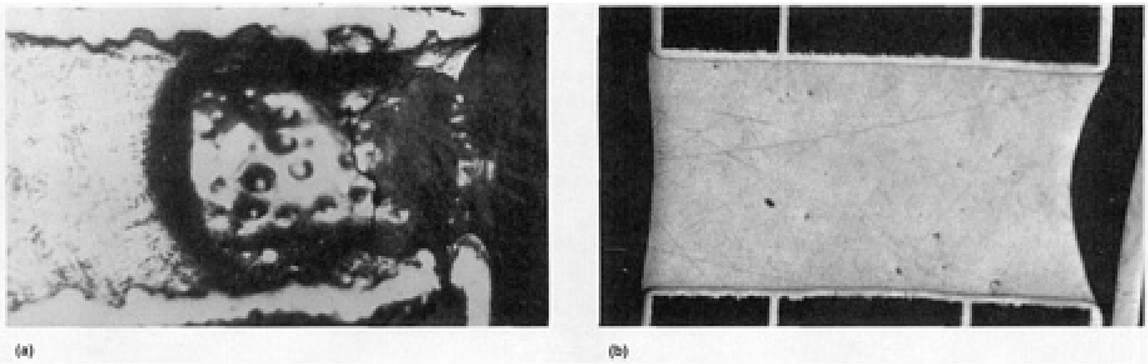

Fig. 9 (a) Solder blow hole induced during solder shock testing. (b) Through-hole showing good solder fill after solder shock testing

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References cited in this section

16. K. Minten and J. Toth, Paper B 5/2, Proc. Printed Circuit World Convention V (Glasgow, Scotland), 1990; *Circuit World,* Vol 17, 1991, p 19
24. C.A. Deckert, IPC-TP-699, Institute for Interconnecting and Packaging Electronic Circuits, Lincolnwood, IL, 1988
64. H.-J. Grapentin and J. Wolff, *Galvanotechnik,* Vol 70, 1979, p 958
65. B-533, ASTM
66. MIL-P-55110D, U.S. Government Printing Office
67. D3359-78B, ASTM
68. C. Lea et al, *Circuit World,* Vol 11 (No. 3), 1985, p 5; Vol 12 (No. 4), 1986, p 14, 20, 26; Vol 13 (No. 1), 1986, p 28, 43

Equipment

Processing Equipment

Printed Wiring Boards. Electroless copper process equipment consists essentially of a juxtaposed series of tanks, typically 380 to 1135 L (100 to 300 gal) in size (or as high as 3800 L, or 1000 gal), including process chemistry tanks, rinse tanks, and load/unload stations, with all associated heaters, chillers, air spargers, and so on. The panels are transported vertically through the system in a rack that typically holds panels representing a surface area of 25 to 735 cm^2/L (0.1 to 3 ft^2/gal) of copper bath. (Other process tanks may be sized appropriately to most efficiently hold the rack.) An automatic hoist system is used, except in the smallest installations.

In the past, electroless lines were designed for two-sided boards only. The multilayer desmear process was entirely separate, thus requiring additional unracking and reracking between segments. Most electroless copper plating lines now being built include tanks for the desmear process as well.

Recently, considerable interest has developed in applying conveyorized horizontal processing to part, or all, of the electroless copper process, as there are a number of technical and operational benefits to this approach. At present, horizontal desmear is being used in select facilities worldwide, and several facilities are also successfully operating in production using horizontal equipment for electroless copper itself (Ref 69).

Plating-on-Plastic. Plating equipment for POP typically involves tank volumes of about 3800 L (1000 gal), but tanks of up to 26,500 L (7000 gal) have been used. The plating process in decorative POP is carried out in one of two modes: designated straight-through or semibulk. Straight-through processing is carried out in a continuous system, where the preplate, electroless, and electroplating steps are carried out with no interruption for reracking. In semibulk processing, two separate fixtures are used, one for the pretreatment/electroless steps and the other for electroplating. There are

numerous advantages for each type of system (Ref 28). Advantages of straight-through processing are evident: only one piece of equipment, fewer processing steps, less handling, and so on. Semibulk processing, however, offers a number of advantages, including much higher capacity, more degrees of freedom in choosing racking systems and chemicals, and flexibility in processing sequences.

Control Equipment

Due to rapid changes in the chemistry of an operating electroless plating bath, frequent analysis and replenishment are required. Hence, automatic control equipment has been of interest (Ref 70) almost since the baths were first commercially employed. A benchmark controller, developed in about 1980, measured and controlled copper, hydroxide, and formaldehyde contents. Copper content was determined by an optical absorbance method, hydroxide and formaldehyde contents by a titration method. Over the years, the simplicity and reliability of such equipment have undergone great improvement, but the basic techniques of analysis have remained essentially the same (Ref 71). Today these control systems are commonplace in all but the very smallest installations and are used to automatically replenish all bath components, as well as for bailout. Recently, to address the added control requirements of full-build electroless copper baths, a new, more accurate method of copper analysis and control has been developed and commercialized. This method is based on vibration of a quartz crystal that acts as a microbalance (Ref 72), thus measuring the mass of copper plated on its surface and providing real-time measurement and control of thickness.

References cited in this section

28. *Standards and Guidelines for Electroplated Plastics,* 3rd ed., American Society of Electroplated Plastics, Prentice-Hall, 1984
69. G. Allardyce, J. Bladon, S. Hirst, and J. Rasch, Paper P-18, Proc. Printed Circuit World Convention VI (San Francisco), 1993
70. H. Hirohata, M. Oita, and K. Honjo, U.S. patent 3,532,519, 1970
71. J.E. Harris and W.H. Rees, U.S. patent 4,774,101, 1988
72. K. Minten and J. Cisson, *Circuit World,* Vol 19 (No. 2), 1993, p 4

Environmental and Safety Issues

The electroless copper plating industry has come under increasing legislative control in recent years, due to a variety of environmental and safety concerns relative to the chemistry and processes. The main issues are quality of waste water discharged, volatile components discharged, and health and safety concerns about handling of the various chemicals.

Waste Water. Regulations regarding effluent vary dramatically, both globally and within single countries. This factor has probably contributed significantly to the relocation of numerous plating facilities to areas having less stringent regulations. Copper itself is probably the main concern; waste treatment equipment designed to plate residual copper from discarded plating solutions will normally reduce Cu^{2+} below the legal limit (typically 1 ppm). Strong chelates have become a concern recently due to their tendency to dissolve any metallic surfaces encountered, either before or after discharge. Certain plating bath additives used in the past, including mercury and cyanide compounds, have been virtually eliminated from use due to waste water restrictions. Adjustment of waste water pH to a neutral range is also usually required. Chromium, used in POP pretreatment, is particularly toxic to the environment, but virtually all current users recycle their chromic acid etchants internally, thus avoiding any discharge. Discharge of strong oxidizing or reducing agents is also typically regulated closely. The issue of waste water treatment is so key to operating a successful plating operation that considerable literature on designing and implementing waste treatment systems is available (Ref 73).

Handling of individual chemicals in the plating process presents a number of concerns. A significant concern is the use of formaldehyde, which has been shown to be a carcinogen for certain laboratory animals, although no direct link with cancer in humans has been demonstrated at this time. Limits by the Occupational Health and Safety Administration on airborne formaldehyde have recently been reduced from 1 to 0.075 ppm (8-h time-weighed average permissible exposure in air). Concerns about formaldehyde, as well as concerns about waste treatment of electroless copper, have contributed to ongoing development of direct electroplating (Ref 26, 69, 74, 75), which could eliminate the need for electroless copper, particularly in portions of the PWB market.

References cited in this section

26. K. Nargi-Toth and J. Wynschenk, Paper P-16, Proc. Printed Circuit World Convention VI (San Francisco), 1993
69. G. Allardyce, J. Bladon, S. Hirst, and J. Rasch, Paper P-18, Proc. Printed Circuit World Convention VI (San Francisco), 1993
73. P.G. Moleux, *Printed Circuits Handbook*, 3rd ed., C.F. Coombs, Ed., McGraw-Hill, 1988, and references therein
74. K.L. Minten and G. Pismennaya, U.S. patent 4,619,741, 1986
75. B. Bressl, H. Meyer, and L. Stamp, Paper P-20, Proc. Printed Circuit World Convention VI (San Francisco), 1993

Electroless Gold Plating

Jean W. Chevalier, Technic, Inc.

Introduction

THE DEPOSITION of a metal on a given substrate can be achieved by numerous conventional methods. Electrodeposition is extensively used because it is technically convenient to operate and is cost efficient. Other techniques, such as chemical vapor deposition and sputtering, are also used, but they require sophisticated equipment and are more expensive to operate. In recent years, an unconventional technique, electroless deposition, has become increasingly attractive, particularly in the electronics industry where the use of nonconductive substrates and the miniaturization of the circuitry presents difficulties in using conventional techniques.

By definition, electroless deposition is the controlled autocatalytic reduction of a dissolved metal by a dissolved reducing agent at an interface. This process requires a reducing agent to provide the electrons for the reduction of the metal ion to the metal to be deposited on the metal substrate. Chemical deposition can also be accomplished by galvanic reaction between a less noble metal and a more noble metal ion. The noble metal is deposited via this reaction. This form of the process is known as *immersion plating*.

Several metals can be deposited using the electroless plating technique. Electroless copper and electroless nickel are widely used (see the articles "Electroless Nickel Plating" and "Electroless Copper Plating" in this Volume). There is a growing interest in the electroless plating of gold and, to some extent, other precious metals such as palladium and silver. This article describes the electroless gold plating technique in terms of its advantages and limitations, applications, processing, and the properties of the plated deposits.

Advantages of electroless deposition of gold include the following:

- Uniform, thin gold films can be deposited over electrically isolated tracks and bonding pads.
- Gold can be uniformly deposited on complex shaped and hollow articles, provided there is adequate agitation of the solution and/or the articles to be coated.
- Gold can be deposited on nonconducting substrates such as glass, ceramics, polymeric materials, etc., provided the substrate is activated.
- Gold films resulting from electroless deposition are 99.9% pure; therefore, they have excellent electrical, soldering, and bonding properties.

Limitations of the process include:

- The electroless gold deposition rate is generally slow. The typical rate is 2 to 3 μm/h, compared to 10 or more μm/h for electroplating baths.
- The chemistry of electroless gold baths is complex; the baths require tight control because they are very sensitive to operating conditions as well as to organic and inorganic contaminants. Consequently, they have a shorter

lifetime and are more expensive to operate than conventional baths.

Applications. Electroless gold finds its application primarily in the electronics industry, where it is used for the metallization of conductors and insulators in printed circuit boards (Ref 1). It is particularly appropriate to use electroless gold on electrically isolated tracks and bonding pads that require uniform gold films, which are difficult to achieve by electrolytic gold deposition. Electroless gold is also recommended to achieve good ohmic contacts on III-V semiconductor materials such as n-GaAs, InP, etc. (Ref 2, 3). It can also be used in the fabrication of multilayer ceramic packages (Ref 4) to improve their brazing, soldering, and wire bonding properties. Another major application for electroless gold is for uniformly plating hollow articles that cannot be successfully plated by electrolytic deposition because their shape results in bad electric field distribution.

Properties of Electroless Gold Films. Depending on bath chemistry, the color of electroless gold films varies from pale yellow to dark brown; the surface texture can be matte, semibright, or reflective. The purity of electroless gold deposits is 99.9% or better. This results in a soft gold film of less than 90 Knoop hardness, suitable for soldering and bonding. The density of the deposited metal is about 19.3 g/cm^3. The grain structure, as observed by scanning electron microscopy (Fig. 1) exhibits a relatively tight distribution of fine particles. The porosity of such gold films depends on the thickness, but above 1.5 μm the deposit is generally pore-free.

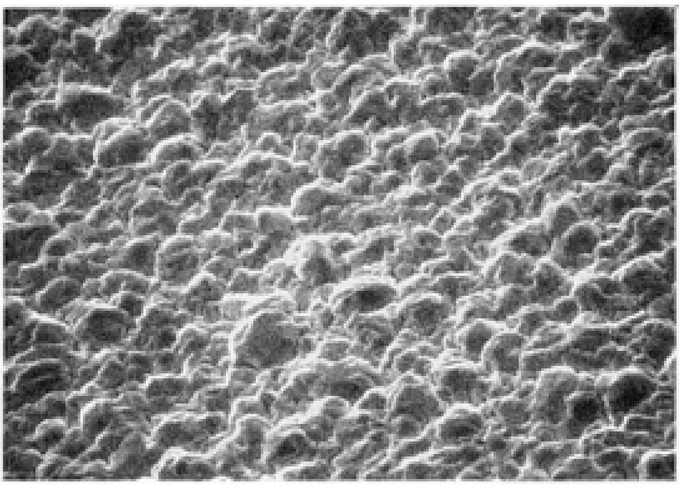

Fig. 1 SEM micrograph of an electroless gold film deposit obtained using a cyanide-base system with potassium borohydride as the reducing agent. Deposit thickness, 1.5 μm. 5000×

References

1. G.O. Mallory and J.B. Hajdu, Ed., *Electroless Plating: Fundamentals and Applications,* American Electroplaters and Surface Finishers Society, 1990
2. G. Stremsdoerfer, H. Perrot, J.R. Martin, and P. Clechet, *Proc. Electrochem. Soc.,* Vol 88 (No. 12), 1988, p 61
3. L. D'Asaro and Y. Okinaka, U.S. Patent 4,162,337, 1979
4. M.F. El-Shazly, U.S. Patent 4,374,876, 1983

Process Description

As mentioned earlier, the deposition of gold without an external source of current can occur by a simple displacement reaction between two metals:

$$\begin{array}{l} M_1^0 \rightarrow M_1^{n+} + ne^- \\ M_2^{n+} + ne^- \rightarrow M_2^0 \\ \hline M_1^0 + M_2^{n+} \rightarrow M_1^{n+} + M_2^0 \end{array} \quad \textbf{(Eq 1)}$$

A typical immersion plating process is the displacement reaction between a less noble metal (nickel) and a more noble metal (gold) in an immersion gold bath:

$$\begin{array}{l} Ni \rightarrow Ni^{2+} 2e^- \\ 2Au^+ + 2e^- \rightarrow 2Au \\ \hline Ni + 2Au^+ \rightarrow Ni^2 + + 2Au \end{array} \quad \textbf{(Eq 2)}$$

The immersion gold process is relatively slow, and it is limited by the decreasing availability of the nickel substrate as the thickness of deposited gold increases. A maximum gold bath thickness of 0.25 μm can be obtained (Fig. 2).

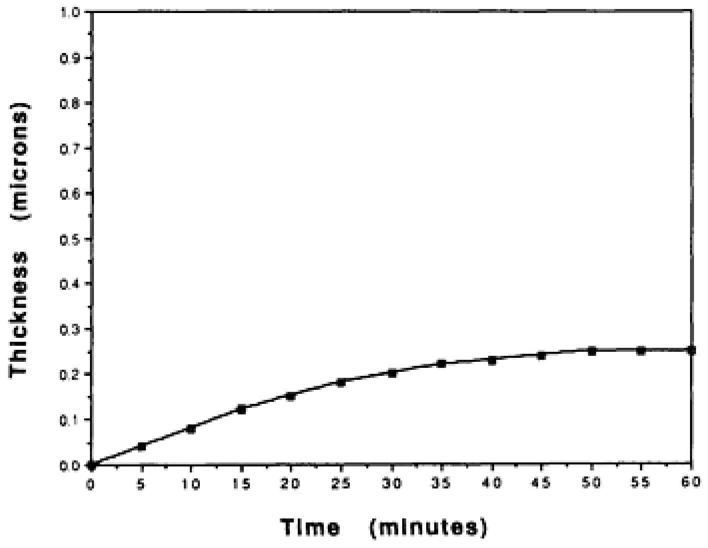

Fig. 2 Thickness of gold as a function of time for an immersion electroless gold plating bath

In order to achieve thicker gold deposits, the use of a true electroless gold bath is required. Such baths are based on a reducing agent that provides the electrons necessary for the reduction of gold ions absorbed on a gold substrate. The catalytic effect of metallic gold promotes the process. This deposition reaction is called an *autocatalytic* process:

$$\begin{array}{l} M^{n+} + ne^- \rightarrow M^0 \\ Red \rightarrow O_x + ne^- \\ \hline M^{n+} + Red \rightarrow M^0 + O_x \end{array} \quad \textbf{(Eq 3)}$$

By definition, an autocatalytic system is substrate catalyzed. Consequently, there are no theoretical limitations to the thickness of gold that can be achieved with an electroless gold bath (Fig. 3).

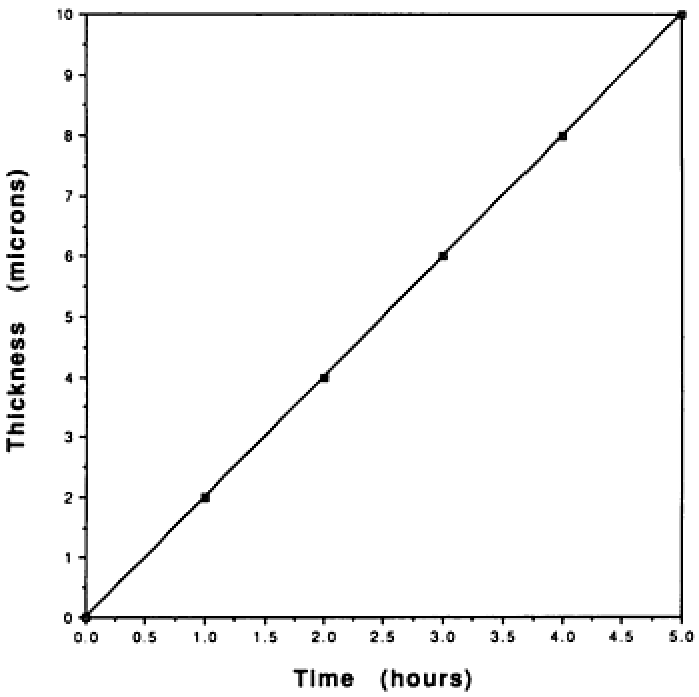

Fig. 3 Thickness of gold as a function of time for an autocatalytic electroless gold plating bath. Theoretical curve at optimum conditions

Many electroless gold bath compositions have been reported in the literature. A typical system, developed by Y. Okinaka (Ref 1), uses potassium gold cyanide as the source of gold and sodium borohydride or dimethylamine borane as reducing agents (Table 1). These baths operate in strongly alkaline media; the strong alkalinity is necessary for the activity of the reducing agent. The suggested reaction mechanism (Ref 5) for the electroless deposition of gold in the presence of sodium or potassium borohydride is:

$$\begin{gathered} BH_4^- - H_2O \rightarrow BH_3OH^- + H_2 \\ BH_3OH^- + 3OH^- \rightarrow BO_2^- + 3/2H_2 + 2H_2O + 3e^- \\ \underline{3Au(CN)_2^- + 3_e^- \rightarrow 3Au + 6CN^-} \\ BH_4^- + 3OH^- + 3Au(CN)_2^- \rightarrow BO_2^- + 5/2H_2 + H_2O \\ + 3Au + 6CN^- \end{gathered} \quad \text{(Eq 4)}$$

In fact, according to this mechanism, the hydrolysis of potassium or sodium borohydride leads to the formation of BH_3OH^- species, which ultimately provide the electrons for the reduction of the gold complex.

Table 1 Compositions and operating conditions for cyanide-base electroless gold plating baths

Reported by Y. Okinaka (Ref 1)

Constituent or condition	Bath A	Bath B
Potassium gold cyanide	0.003 *M*	0.02 *M*
Potassium cyanide	0.10 *M*	0.10 *M*

Potassium hydroxide	0.20 *M*	0.20 *M*
Potassium borohydride	0.20 *M*	0.20 *M*
Temperature °C (°F)	70 (158)	70 (158)
Rate of deposition μm/h	1.5	0.5

A number of different gold salts are used in the formulation of electroless gold baths. In addition to the most commonly used--for example, potassium gold cyanide, $KAu(CN)_2$, and potassium chloroaurate, $KAuCl_4$--there is a growing interest in using sodium gold sulfite in the formulation of cyanide-free systems. Different reducing agents can also be used, and their activity influences both the rate of deposition and the stability of the bath. Other components of electroless gold baths include some chelating agents, stabilizers, buffers, accelerators, and wetting agents. Gold plating baths reported by H. Okudaira et al. (Ref 6) and C.D. Yacovangelo (Ref 7) are listed in Table 2 and Table 3, respectively.

Table 2 Composition and operating conditions for a sulfite-base electroless gold plating bath

Reported by H. Okudaira (Ref 6)

Constituent or condition	**Amount**
Sodium chloroaurate	0.20 *M*
Sodium thiosulfate	0.50 *M*
Sodium sulfite	0.05 *M*
N-Methylthiourea	0.0001 *M*
Pyrogallol	0.09 *M*
Ammonium chloride	0.20 *M*
Temperature, °C (°F)	70 (158)
pH	6.0
Rate of deposition, μm/h	1.8

Table 3 Composition and operating conditions for a cyanide-base electroless gold plating bath

Reported by C.D. Yacovangelo (Ref 7)

Constituent or condition	**Amount**
Potassium gold cyanide	0.005 *M*

Potassium cyanide	0.035 *M*
Potassium hydroxide	0.80 *M*
Potassium carbonate	0.45 *M*
Dimethylamine borane	0.05 *M*
Hydrazine	0.25 *M*
Lead acetate, ppm	15
Temperature, °C (°F)	80 (176)
Rate of deposition, μm/h	≤ 7.8

Process Variables and Parameters. Electroless gold baths are very sensitive to operating conditions; therefore, it is important to control all of the variables that can affect both the rate of deposition and the stability of these systems.

Gold Concentration. As the gold concentration decreases, the rate of deposition also decreases. In order to keep the rate of deposition constant, periodic addition of gold should be made in the form of a gold salt. Replenishment can be made based on analysis data and/or close monitoring of the quantity of metal deposited on the substrate.

Reducing Agent. The concentration of the reducing agent is almost as critical as the concentration of gold. The decrease in the reducing agent concentration is not only a function of the reduction of gold, but also is affected by possible degradation reactions, such as those that occur with sodium borohydride. The concentration level should be frequently analyzed and adjusted.

Stabilizers. The presence of stabilizers is necessary to the operation of most electroless gold baths. Free cyanide seems to have a beneficial effect on the stability of most cyanide-base electroless gold baths. However, excess amounts will overstabilize the bath and inhibit the deposition of gold. Other stabilizers can also be used to prevent the formation of gold particles and their accelerated growth, which can result in a significant drop in the ionic gold remaining in the solution.

Contaminants. Organic and inorganic contaminants can have very deleterious effects on electroless gold baths. For example, trace amounts of nickel ions are sufficient to cause a rapid decomposition of the borohydride bath reported by Okinaka. Because of the effects of nickel, the use of an immersion gold coating of about 0.25 μm over a nickel substrate is often recommended prior to electroless gold deposition. Some electroless gold baths (such as that given in Table 3) can deposit gold directly over nickel by combining an immersion process with a catalytic process. Traces of tin are also detrimental, whereas copper has no negative effect on bath stability.

Temperature. All electroless gold baths are temperature-dependent. In general, the higher the temperature, the faster the speed of deposition. An adverse effect of high temperature is bath decomposition. High temperatures also cause rapid consumption of reducing agents, creating the need for frequent replenishment.

Agitation. The rate of deposition of gold as well as the uniformity of the gold film will be influenced by the agitation. Both the solution and the workpiece can be moved to ensure good uniformity. Agitation is also required to prevent localized heating and possible decomposition of the solution.

The effect of pH is particularly important when plating on pH-sensitive substrates. For example, degradation of polyimide substrates will occur in very alkaline baths. Alumina-ceramic substrates are also incompatible with highly alkaline systems, and they should be treated in electroless gold baths operating at neutral pH (such as sulfite gold baths, which have a pH of 8.0).

Surface preparation is a key issue in any deposition process. Cleaning and activation of the gold substrate are necessary prior to plating in order to prevent contamination and to enhance adhesion. When plating gold directly over nickel or copper, the removal of the oxide layer is essential for achieving excellent adherence of the gold film. In this respect, a flash of nickel (electroless or electrolytic) may be beneficial.

Processing Equipment. Because of their sensitivity to high temperature and to contamination, electroless gold baths should be run in carefully controlled equipment. For operating very small units (3 gal or less), pyrex jars or jacketed beakers are practical. For larger units, polypropylene tanks or Teflon-coated stainless steel tanks are recommended.

The heat source plays a major role in controlling the stability and the performance of an electroless gold bath. Small water baths with thermostatic control are very practical for small-scale operations. For larger operations, heat-exchanger coil systems made of Teflon and operating with hot water or with steam are recommended. Teflon-coated immersion heaters can also be used, but care should be taken to prevent localized heating by vigorously circulating the solution in the vicinity of the heating coils.

In large-scale operations, pumping and filtration systems are also necessary. All pumps and filters should be made of chemically resistant materials, such as polypropylene or Teflon.

Environmental Considerations. Spent electroless gold baths should be treated both for environmental reasons and for gold recovery. All major suppliers of plating chemicals offer waste treatment guidelines that should be followed by their customers, particularly those operating the cyanide systems. In California, only cyanide solutions and IX resins are accepted by gold reclaimers. Aqua regia solutions are not accepted.

Health and Safety Considerations. All electroless gold baths contain chemicals that can be harmful to the user's health if not handled safely. The use of protective goggles, gloves, and lab coats is strongly recommended. The plating solutions should not be swallowed. They should be stored in cool and well-ventilated rooms and used under well-ventilated hoods. The Material Safety Data Sheets provided by the manufacturer should be read carefully before using any plating products.

References cited in this section

1. G.O. Mallory and J.B. Hajdu, Ed., *Electroless Plating: Fundamentals and Applications,* American Electroplaters and Surface Finishers Society, 1990
5. Y. Okinaka, *Plating and Surface Finishing,* Vol 57, 1970, p 914
6. H. Okudaira, T. Shimakazi, and H. Yokono, European Patent 0,418,715A2, 1990
7. C.D. Yacovangelo, *J. Electrochem. Soc.,* Vol 138 (No. 4), 1991, p 976

Electroless Alloy Deposition

Phillip D. Stapleton, Stapleton Technologies

Introduction

METALLIC NONELECTROLYTIC ALLOY COATINGS produced from aqueous solutions are commercially used in several industries, including electronics, aerospace, medical, oil and gas production, chemical processing, and automotive. These coatings provide unique material properties that expand the physical properties beyond those of pure metal coating systems. Table 1 lists many of the properties and the coatings capable of providing these properties.

Table 1 Features and types of metallic nonelectrolytic alloy coatings

Property or use	**Alloy types**	**Thickness range, μm**
Corrosion protection	Ni-P, Ni-P-Mo, Ni-Sn-P, Co-P, Co-P-Mo, Ni-Cu-P	12-125
Wear resistance	Ni-B, Ni-B-Tl, Ni-B-Mo, Ni-B-Sn, Co-P, Co-P-W, Co-B	30-120
	Ni-P + SiC, Ni-P + WC (dispersion)	30-125
	Au-Ni, Au-Co	0.5-3
Magnetic	Ni-Co-P, Ni-Co-B, Ni-Fe-P	<0.1
Catalyzation	Pd-Rh	<0.05
Solderability	Sn-Pb, Ni-P	0.5-10
Bondability	Ni-P	2-5
High temperature	Co-W-B, Ni-Re-P	1-125
Diffusion barrier	Ni-P	12-30

Nonelectrolytic coating systems use two types of reactions to deposit metal onto a part: electroless and displacement. The electroless or autocatalytic process uses reducing agents to convert the metal from its metal salt. Displacement reactions use oxidation and reduction of the base metal to deposit a thin coating of metal.

The advantage of using nonelectrolytic alloy coating systems over electrolytic is the uniformity of deposit in alloy composition and thickness, the ability to perform bulk processing, and the ability to produce unique catalytic coatings. These coatings are produced from aqueous chemical processes by conventional aqueous pretreatment procedures.

Nonelectrolytic processes can be used to deposit binary or ternary alloy coatings. The chemistries of ternary alloy plating can be very complex and involve several chelation and secondary reactions. The typical ternary system operates by having the primary metal reaction at the surface produce an electropotential greater than the half-wave potential of the complexed secondary metal. This induced surface potential is called an *overvoltage potential.* This causes the secondary metal to be included with the primary metal along with the cation portion of the reducing agent. Examples of this type of ternary system are alloys of nickel-copper-phosphorus or nickel-thallium-boron.

Nonelectrolytic processes generally operate at slightly elevated temperatures up to the temperature of boiling. These processing solutions contain the primary element and may contain other alloying metals. The operating parameters for pH can range from strong acid to strong base, depending on the metal system and the type of chelation and reducing agent being used.

With some processes, a secondary reducer is used to increase the efficiency and quantity of alloying metal incorporated. The secondary metals that are being galvanically plated at their overvoltage may limit the deposition of the primary metal. The secondary metals will generally be consumed at a high rate and require replenishment. Reducing agents may also be consumed at a higher rate than the primary metal and require more frequent replenishment.

Electroless (Autocatalytic) Alloy Coatings. Electrolessly produced metallic alloy coatings use a reducing agent to cause the metal salts to be reduced onto an oxide-free part surface. This reduction reaction proceeds until the part is removed from the process. During the reaction, metal and reducing agents are depleted and require replacement to continue the processing. The process is called *electroless* because no external electrical power is applied. The term *autocatalytic* is the technical term for the process.

The electroless process can be complex and involve several simultaneous reactions producing hydrogen and electrical charge at the interface. Through experience and good operating techniques the plating operation can produce a uniform alloy with specific phase structures and compositions.

Electroless dispersion alloy coatings use the conventional electroless reduction reaction process with a suspension of particles to produce a deposit with unique macroproperties. These particles fall into two categories: lubricants or hard load bearing particles. The soft particles contain powders of polytetrafluoroethylene (PTFE), fluorinated carbons (CF_x), and fluoride salts, whereas hard particles consist of carbides, ceramics, insoluble powders, and diamonds. Dispersion coatings contain particles in the concentration range of 5 to 30%, depending on the particle and wear system. These alloy coatings are used in applications in which significant wear is present or repair and service are difficult.

Displacement (immersion) alloy coatings use the corrosion (oxidation) of the base material to produce a galvanic (reduction) reaction producing a thin alloy coating. This process is self-limiting and will stop when the oxidation reaction of the base metal stops. Generally these coatings are very thin and contain elements of the base material. These coatings are used primarily in electronic applications.

Immersion alloy deposition processes are easy to control and require little metal replacement because of the very thin deposits produced. Displacement tin-lead solder processes are the exception, producing thicker deposits requiring more frequent additions.

Types of Electroless Alloy Plating Systems

Most electroless alloy systems are based on nickel alloys and have been developed from basic electroless nickel-plating technology. Many alloy systems are documented in the literature and several are commercially available. In the following section each coating type is summarized and its availability is indicated as either "production" or "laboratory."

Nickel-Phosphorus. Electroless nickel-phosphorus is the most common nonelectrolytic alloy coating system. Electroless nickel has been used since the early 1950s and continues to show the most growth and development.

These coatings are widely used for control of wear and corrosion. An important property is the amorphous structure in the as-plated condition and the ability to heat treat the deposit by precipitation hardening to produce a crystalline structure.

There are three nonequilibrium phases for the as-plated electroless nickel deposit: beta, beta + gamma, and gamma. The beta phase is present up to a phosphorus content of 4%; above 4%, there is a mix of beta and gamma. When the deposit has more than 11.2% P, the deposit is gamma-phase. Upon heat treating the deposit containing nickel and phosphorus, a precipitation occurs, producing an equilibrium mix of nickel phosphide and alpha-nickel. A coating of unique mechanical and physical qualities can be produced by controlling the phase of metal being deposited, the alloy of phosphorus, and the postheat treatment.

To help classify the different nickel-phosphorus coatings, a system has been developed that groups them into types. This system has been incorporated into national and international draft specifications. The scheme presented in Table 2 follows the current industry convention.

Table 2 Electroless nickel-phosphorus plating systems

Alloy	Hardness, HK_{100}	Environments in which plating has demonstrated corrosion resistance	Significant properties and applications	Availability

Type II: 1-3% P, bal Ni	435-680	Alkali, brine, strong caustics	Solderability, electrical conductivity[(a)], wire bonding	Production
Type III: 2-4% P, bal Ni	700-800	Alkali, brine, strong caustics	High as-plated hardness for wear application on aluminum, beryllium, copper, and other base materials that cannot be precipitation hardened	Production
Type IV: 5-9% P, bal Ni	520-650	Alkali, brine, caustic solutions	General wear and corrosion resistance applications, including application in industrial interior and exterior nonmarine environments, undercoatings. Thicknesses for these applications range from 1 to 125 μm (0.03 to 5 μin.).	Production
Type V: 10-14% P, bal Ni	430-530	Alkali, brine, mildly acidic solutions, marine environments	Wear and corrosion resistance applications in marine and corrosive industrial environments; nonmagnetic undercoating in memory discs; oil and gas environments	Production

(a) Conductivity, 10-30 $\mu\Omega \cdot cm^2$

Procedures for the electroless deposition of nickel, nickel-phosphorus, and nickel-boron are described in detail in the article "Electroless Nickel Plating" in this Volume.

Nickel-Boron. Another family of nonelectrolytic alloy coatings uses boron-based reducing agents (Table 3). These are classified by boron alloy content. Generally the low-boron coatings are used in electronic applications as a replacement for gold. The higher-boron coatings are used to provide a hard surface to prevent galling in iron and nickel wear applications.

Table 3 Electroless nickel-boron plating systems

Alloy	Hardness, HK_{100}	Significant properties and applications	Availability
0.1-1% B, bal Ni	520-620	Electronic applications, replacement for gold in microelectronic equipment and printed wire circuit boards	Production
2-4.5% B, bal Ni	750-800	Aircraft engines, landing gear, valves, and pumps; resistance to galling, fretting, and erosion wear	Production

In general, high-boron coatings use sodium borohydride as the reducing agent and operate at a pH of 12.5 and above. Low-boron coatings use dimethyl amino borane (DMAB) as the reducing agent and operate in a neutral pH of 5.5 to 7. These systems are commercially available and provide the chemical basis for many of the nonelectrolytic ternary alloy systems. Both DMAB and sodium borohydride are powerful reducing agents and provide energy to reduce many elements.

Hypophosphite-Reduced Cobalt Alloy Coatings. Nonelectrolytically produced cobalt alloy coatings have been used in a limited number of magnetic and wear applications. These coatings are produced from sodium hypophosphite-based solutions at a slightly alkaline pH range at elevated temperatures. Table 4 lists property and application information for a hypophosphite-reduced cobalt-phosphorus coating.

Table 4 Electroless cobalt alloy plating systems

Alloy	Hardness, HK_{100}	Environments in which plating has demonstrated corrosion resistance	Significant properties and applications	Availability
Hypophosphite-reduced cobalt-phosphorus (3-6% P, bal Co)	550-650	Alkali, brine solutions	Magnetic and medical applications	Production
Boron-reduced cobalt-boron (3-4% B, bal Co)	350-500[(a)]	. . .	Wear resistance in high-temperature applications	Laboratory; limited application

(a) As-plated; 800-1000 HK_{100} after 30 min at 400 °C (750 °F)

Boron-reduced cobalt alloy coatings (Table 4) are produced by a reduction reaction of sodium borohydride or DMAB reducing agents. The deposits are harder and have higher melting points than those alloyed with phosphorus. These coatings have not been commercially available. They could be used in wear applications where service at higher temperatures is required.

Ternary alloy coatings are used to provide higher performance in specific properties over conventional electroless coating systems. By incorporating a third element in significant or trace levels, the basic structure and physical properties of the coating can be altered. There are many possibilities and systems that have been investigated and are available (Table 5).

Table 5 Electroless ternary alloy plating systems

Alloy	Hardness, HK_{100}	Environments in which plating has demonstrated corrosion resistance	Significant properties and applications	Availability
Hypophosphite-reduced alloys				
Nickel-phosphorus-molybdenum (5-9% P, 0.5-1% Mo, bal Ni)	550-650	Alkali, brine, caustics, weak acid solutions	Pitting corrosion protection	Laboratory
Nickel-copper-phosphorus (4-8% P, 1-3% Cu, bal Ni)	430-520	Alkali, brine, caustic solutions	Nonmagnetic, conductive, high modulus	Production
Nickel-cobalt-phosphorus (15-40% Co, 3-8% P, bal Ni)	. . .	. . .	High-coercivity coating for use in magnetic memory applications	Laboratory, limited production
Nickel-iron-phosphorus (1-4% Fe, 2-4% P, bal Ni)	. . .	. . .	Magnetic applications in electronics	Laboratory
Nickel-rhenium-phosphorus (1-45% Re, 3-8% P, bal Ni)	. . .	. . .	High melting point (1700 °C, or 3090 °F); high-temperature wear resistance	Laboratory

Nickel-tungsten-phosphorus (4-8% P, 1-4% W, bal Ni)	550-620	. . .	High melting point (1550 °C, or 2820 °F); high-temperature wear resistance	Laboratory
Cobalt-tungsten-phosphorus (4-8% P, 1-5% W, bal Co)	570-640	. . .	High-temperature wear resistance	Production
Boron-reduced alloys				
Nickel-thallium-boron (3-5% Tl, 3-5% B, bal Ni)	650-850	. . .	Wear applications requiring resistance to galling, fretting, and erosion; coating is self-lubricating in contact with ferrous materials	Production
Nickel-tin-boron (3-5% B, 1-3% Sn, bal Ni)	650-850	. . .	Wear applications requiring resistance to galling, fretting, and erosion; this coating is also self-lubricating	Production
Cobalt-tungsten-boron (3-5% B, 1-5% W, bal Co)	750-850	. . .	Wear applications requiring resistance to galling; can be used at higher temperatures than phosphorus systems	Laboratory

Boron-reduced ternary alloy coatings are produced by a reduction reaction of sodium borohydride or DMAB reducing agents. The deposits are harder and have higher melting points than those alloyed with phosphorus. Some of these coatings have not been commercially available. Figure 1 shows the microstructure of an electroless nickel-thallium-boron plating deposit.

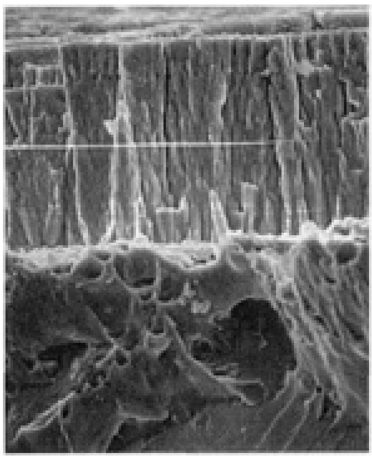

Fig. 1 Electroless nickel-thallium-boron deposit. The hard columnar structure increases resistance to fretting wear and the ability of the deposit to retain oil. Additional lubrication is provided with the presence of thallium, which interferes with the galling process between nickel and iron.

Types of Dispersion Alloy Coating Systems

Dispersion alloy coatings combine the finite microstructure of a dispersed particle into a macrostructure. These coatings can be categorized as composites containing lubricant particles or those containing hard particles. These dispersed particles are incorporated into a metal matrix of nickel phosphorus or cobalt phosphorus. In most applications an

undercoat is used to increase the corrosion resistance and improve the coverage of the dispersion coating. An overplate is also used to seal particles into the surface and produce a more consistent initial wear.

Nonelectrolytic solid-lubricant dispersion alloys are produced from solutions that use lubricant powders suspended in an aqueous electroless nickel or cobalt system. The powders are sensitized by cationic surface agents and dispersed by other surfactants.

There are commercial processes that use PTFE and CF_x as well as fluorinated carbon and fluoride salts of lithium, calcium, and magnesium. Each of these lubricant particle systems has specific advantages. Generally PTFE is used where the loads are low. Fluorinated carbon powders can operate at higher temperatures and greater loads. Fluoride salts provide lubrication at temperatures near the melting point of the coating.

Nonelectrolytic Hard-Particle Dispersion Alloys. A wide range of hard particles can be incorporated into the deposits, including diamonds, silicon carbide, tungsten carbide, titanium carbide, silicon nitride, and others. The basic requirement for the process is that the particles remain passive while deposit is proceeding and at the same time come to rest on the surface and become incorporated into the coating. These particles are generally between 0.4 and 3 μm in diameter and are loaded into the deposit from between 15% and 25% by weight. Coatings using these particles are generally designed to support moderate to high loads.

Silicon carbide in a nickel phosphorus matrix is the most common of the dispersed particle coating systems. These coatings provide abrasion resistance in mining and chemical processing applications and are used in internal combustion engines because the deposit provides for the retention of oil on the surface. Deposits containing dispersed diamond particles have provided significant improvement in the performance of textile-weaving equipment by reducing abrasive wear caused by textile fibers.

Nonelectrolytic Displacement Alloys

Displacement alloys are applied without the use of a reducing agent and are deposited by a combination of oxidation and reduction reactions that occur as the base metal corrodes. The result of this chemical reaction is the formation of an alloy of two elements.

The displacement alloy coating is self-limiting in thickness, and the reaction will stop when the density of the corroding metal on the surface drops below the reduction potential of the primary metal. There are two coating systems used in electronic applications that incorporate this technique.

Displacement tin-lead alloys are available for limited use as solder deposits. Process control is critical in producing a consistent alloy and melting point in this system. The other system, which is also used on a limited basis, is an alloy of palladium and ruthenium used in the activation of copper for subsequent electroless nickel plating in printed circuit board applications. The addition of ruthenium reduces the number of palladium atoms on the surface and improves the adhesion of the nickel to the copper.

Processing of Parts

The electroless alloy coatings discussed in this article are produced from aqueous solutions following a specific base-metal-dependent cleaning and activation procedure. These procedures are generally similar to those employed for the electroless deposition of unalloyed nickel; see the article "Electroless Nickel Plating" in this Volume for more information.

Process Control. Nonelectrolytic alloy processes require more frequent sampling and analysis than conventional electrolytic plating processes. This is caused by metal salt consumption without the advantage of an anode to replace the metal, oxidation of reducing agents, lower metal concentrations, and the consumption of the alloying agent at a rate different from that of the primary metal.

The process control requires that the operator know the rate of consumption of all ingredients. After initial adjustment to optimum concentrations, the operator must replenish each of the ingredients at their individual rate of consumption.

Two types of control tests determine this replenishment on-line and off-line. On-line tests are performed during the process by analyzing for trace metals, alloying elements, reducing agents, and organics. By selecting specific organic

chemistries that produce consistent alloys, maintaining these chemicals in balance, and controlling the conditions of the process, a consistent alloy can be produced. Off-line testing is performed on the alloy specimens after the plating process and is used to verify that the process control is valid.

By combined use of these control systems and scheduled replenishment during the plating process, uniform deposit properties can be achieved.

Deposit Analysis. There are several tests which can be performed on the alloy to determine its quality. They should be selected to measure a specific property in the application.

Composition is generally measured by inductively coupled plasma or atomic absorption for the major constituents. Alloys of dispersed particles require more complex procedures to ensure that the alloy as well as the percentage weight of the included particle is within specification.

Wear resistance is sometimes used to measure the quality of the deposit. The Taber abraser has been used to test abrasion resistance on dispersed hard-particle alloys. Other methods include the Falex pin-on-vee-block and LFW1 block-on-ring apparatus for testing adhesive wear. Other test methods for fretting and erosion wear are sometimes used. An important consideration in evaluating the wear rate is the number of samples required to produce statistically accurate results. Generally the most relevant test is in the field, where the parts are subjected to the actual wear system and the wear rate or service life is the measure of performance.

Uniformity of dispersed particles within the alloy may be measured to ensure consistent wear resistance. This is generally measured by examination of a metallographic cross section of a specimen processed with the parts.

Equipment for Nonelectrolytic Alloy Plating

Nonelectrolytic alloy plating processes use a variety of chemicals in their formulations. Some of the processes have high pH conditions, whereas others operate in the acid pH range. Still others are corrosive to polyvinylidene fluoride (PVDF) and other plastics. Because of this variability of chemistry a number of different materials are used in making the tanks and piping, including polypropylene, polyethylene, polyvinyl chloride, PVDF, PTFE, and stainless steel.

Nonelectrolytic alloy plating equipment is shown in Fig. 2. The plating solution is removed from the bottom of the tank and circulated through a pump, heat exchanger, and filter and then returned to the plating tank through an agitation manifold. Processes using dispersed particles require special fixturing and manifolds to ensure that the particles are distributed uniformly.

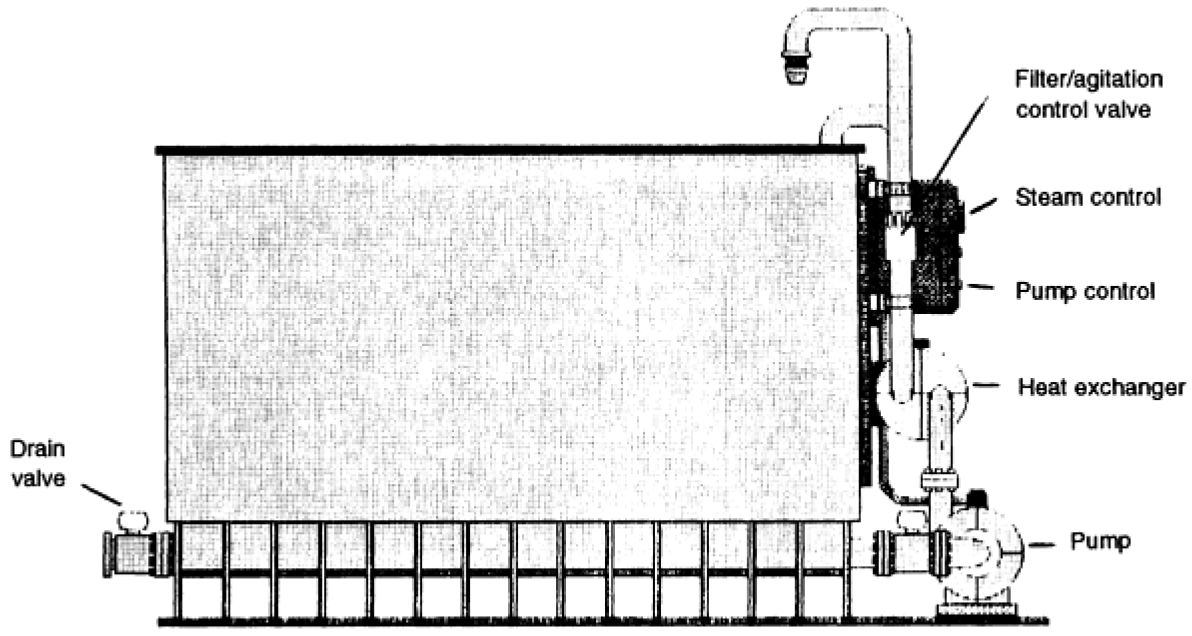

Fig. 2 Tank system for electroless alloy plating

In Fig. 2, the solution is heated with hot water or steam by a heat exchanger. A double mechanical, water-sealed pump is used to circulate the solution from a trough bottom tank that is constructed from natural, stress-relieved polypropylene and welded with inert gas. The piping is made of PVDF and is fuse welded to ensure years of leak-free service. Automatic equipment is used to add replenishment chemicals to maintain a consistent alloy by reducing variations in the process chemistry. Some processes require constant additions to ensure that the processes remain stable. For process volumes of less than 500 L, small chemical-feed pumps that deliver 10 to 20 L/h should be used. Racks, barrels, and baskets are used in the operations to move the parts through the processes. These items should be made of materials compatible with the system.

Safety and Environmental Concerns

Nonelectrolytic deposition processes contain metals that are generally considered toxic. Nickel is regulated in the sewer and ground water and should be controlled. Metals other than nickel may also be regulated and must therefore be controlled.

Processes should have secondary containment, ventilation, and exhaust blowers and recovery and recycling equipment to contain the metals and eliminate hazardous waste. Recycling equipment to remove the byproducts and return the metals to the process is available, thereby extending the operational life of the process.

Good finishing hygiene requires operators to use gloves, goggles, and aprons when mixing and handling chemicals used in these processes. The use of a mask is required on some processes, and careful study of the material safety data sheet is required.

Mechanical Plating

Arnold Satow, McGean-Rohco, Inc.

Introduction

MECHANICAL PLATING is a method for coating ferrous metals, copper alloys, lead, stainless steel, and certain types of castings. The process applies a malleable, metallic, corrosion-resistant coating of zinc, cadmium, tin, copper, or aluminum; combinations of metals can be applied as codeposits or as "sandwich" layered deposits. Mechanical plating has been used internationally for over 40 years and is referred to by a variety of names, including *peen plating, impact plating,* and *mechanical galvanizing.* Mechanical plating often can solve engineering, economic, and pollution-related plating problems. It offers a straightforward alternative method for achieving desired mechanical and galvanic properties with an extremely low risk of hydrogen embrittlement. In some circumstances, it offers a potential cost advantage over electroplating (Fig. 1).

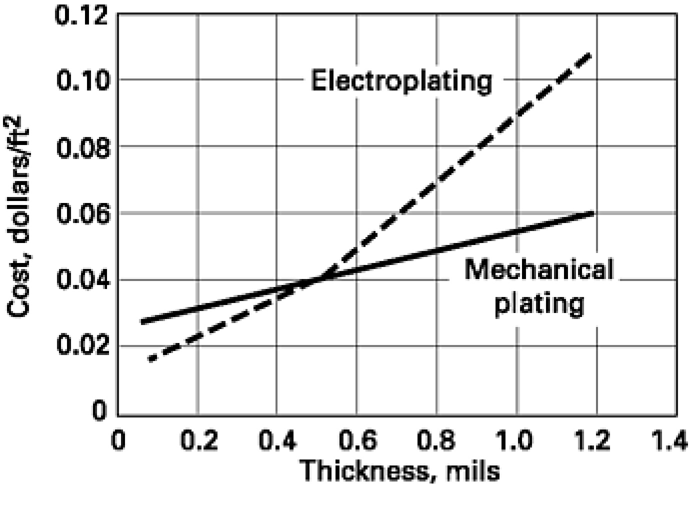

Fig. 1 Cost comparison of mechanical plating and electroplating. Approximate costs shown are for chemicals only and do not include labor or overhead.

Mechanical plating is accomplished at room temperature, without the electrical charge passing through the plating medium that is necessary with electroplating or electrocoating. The metallic coating is produced by tumbling the parts in a mixture of glass beads, metallic dust or powder, "promoter" or "accelerator" chemicals, and water. The glass beads provide impacting and hammering energy, which serves to pound the metallic particles against the surfaces of the parts. The result is a tight, adherent metallic coating produced by "cold welding" fine, powdered metallic particles to the surfaces of parts.

Recent improvements in deposit quality, cost-effectiveness, and ease of application have induced many finishing engineers to investigate and adopt mechanical plating for certain applications. Special advantages of the mechanical plating and galvanizing process are that it:

- Greatly reduces part susceptibility to hydrogen embrittlement
- Can be used to deposit a wide variety of metals in a broad range of coating thicknesses
- Consumes comparatively low amounts of energy
- Does not require the use of toxic chemicals
- Simplifies waste treatment
- Does not require baking in most cases
- Provides greater uniformity of coatings (when used for galvanizing)

Hydrogen Embrittlement

The need to prevent hydrogen embrittlement was one of the major reasons for the creation and use of mechanical plating. A critical concern in electroplating and other coating processes used on ferrous parts is the embrittling effects of hydrogen absorbed by the part. The current used in electroplating acts to enhance the possibility of hydrogen embrittlement--both because most electroplating generates hydrogen at the cathode and because the negative charge acts to pull hydrogen into the part. Hydrogen embrittlement can cause sudden development of breaks or cracks in highly stressed areas, with subsequent total rupture of the part or the assembly. The risk increases for parts that have high hardness from cold working or heat treating, especially those made of high-carbon steels.

In the normal electroplating process, an important source of hydrogen gas is the reaction between acids and metals present in the plating solution. The hydrogen migrates through the metallic substrate and concentrates at high stress points and grain boundaries. The trapped hydrogen builds internal pressures that can lower the tolerance to stresses applied in actual use. Dangerous failures in critical applications can result.

Other atmospheres that can potentially cause or contribute to hydrogen embrittlement include heat-treating furnaces, cleaning solutions, and pickling baths.

Advantage of Mechanical Plating in Avoiding Embrittlement. Mechanical plating deposits metals while eliminating or at least minimizing the risk of embrittlement caused by the coating process itself. A hydrogen-producing reaction does occur in mechanical plating:

$$\text{Zn metal} + 2H^{+} \rightarrow H_2\text{(gas)} + Zn^{++}\text{(ion)} \qquad \textbf{(Eq 1)}$$

However, this reaction occurs essentially on the surface of the powdered zinc particles, which are approximately 5 to 10 μm in diameter. The reaction proceeds at a relatively slow rate and within a more porous, less oriented metallic grain structure than that produced by electroplating. Therefore, the hydrogen gas is not likely to be trapped or occluded within or under the metal particles in the coating. The effusion or escape of hydrogen gas through the deposit and away from the substrate is more likely than diffusion into the base metal. A substantial portion of the mechanical plating performed today is done on parts and metals that are predisposed to hydrogen embrittlement. These include spring steels, parts heat treated to 42 HRC or higher, cold-headed parts, or any part for which service application or structural integrity is highly critical.

Mechanical Plating Equipment

Mechanical plating is accomplished in mild steel or stainless steel variable-speed tumbling barrels. Because the entire process takes place at low (1 to 2) pH, the barrels must be lined with an inert, abrasion-resistant protective coating such as neoprene, polypropylene, polybutylene, or urethane. The lining is usually applied at a thickness of 19 to 25 mm (0.75 to 1 in.); thicker linings may be used in high wear areas such as the inner base of the barrel.

Typical tumbling barrels have capacities of 0.04 to 1.13 m^3 (1.5 to 40 ft^3), where *capacity* is the total available working volume, which is typically about 25 to 35% of the total volume. For example, a 0.57 m^3 (20 ft^3) plating barrel will hold approximately 910 kg (2000 lb) of 25 mm (1 in.) long steel threaded fasteners or about 680 kg (1500 lb) of 8d common nails. After the parts are loaded in the barrel, approximately 1000 kg (2200 lb) of glass beads are added with sufficient water to form a slurry.

The tumbling of part on part and glass bead on part creates kinetic energy that serves to cold weld the spheroidal metal particles to the substrate. The diameters of the most commonly used glass beads are nominally 5 mm (0.187 in.), 1.5 mm (0.056 in.), 0.7 mm (0.028 in.), and 0.25 mm (0.010 in.). The ratio of glass beads to parts is about 1.5:1 by weight, but varies depending on the part mass and geometry and on the coating thickness required (greater thicknesses sometimes require a higher ratio of beads to parts and the use of larger beads). The barrels rotate at a surface speed of 43 to 75 m/min (140 to 250 ft/min) and at a tilt angle of about 30° from horizontal.

The glass plating beads perform a number of functions. They:

- Assist cleaning and oxide removal through a mildly abrasive scrubbing action
- Facilitate mixing and displacement of the chemicals
- Consolidate the metallic coating
- Protect and separate parts from one another, thereby preventing edge damage and tangling
- Help push the plating metal into corners, recesses, and blind areas

Glass beads are constantly reused and recycled through a glass bead recovery and pumping system, which is part of the standard mechanical plating equipment package.

Process Steps

The mechanical plating process requires a series of chemical additions. The quantity depends on the total area of part surface. The total area must be determined prior to each cycle. All of the plating steps are performed in the same barrel, normally without rinsing or stopping the rotation. The only exception is removal of heavy oil or scale; these contaminants should be removed before parts enter the plating barrel.

The first process steps include a series of chemical and metal additions designed to mildly acid clean and activate the substrate and then to apply a thin, uniform copper strike. The copper strike provides a clean, galvanically receptive part surface. The next step involves adding an "accelerator" or "promoter" agent, which creates a chemical environment that controls the rate of deposition and subsequent bonding of the plating metals. A defoaming agent is used during the process to control foaming and to prevent any associated loss of plating solution.

The plating metal is added as a dry, fine powder or a water slurry containing the powder. Platers add metal in a series of steps and in amounts proportional to the coating thickness desired. Commercial plating thicknesses of 5 to 12.5 μm (0.0002 to 0.0005 in.) usually require two to three additions of metal, while greater thicknesses or "galvanized" coatings can demand eight or more.

The following represents a typical sequence of operations for mechanical plating:

1. Alkaline or acid preclean (if necessary)
2. Prepare surface
3. Copper strike

4. Add accelerator/promoter
5. Add plating metal
6. Add plating metal
7. Add plating metal

The plating cycle is carried out at temperatures between 15 and 32 °C (60 and 90 °F). A pH between 1 and 2 is required at all times to ensure proper adhesion and a high plating efficiency. The low pH level acts to maintain an oxide-free condition at all times on both the part surface and the surface of the plating metal particles. These temperature and pH conditions facilitate mechanical bonding ("cold welding"). The process has an efficiency of about 92%; that is, approximately 92% of the plating metal added is actually plated on the parts.

The mechanical plating process usually takes about 45 min. At the conclusion of the cycle, the slurry of glass beads, coated parts, and water discharges into a vibrating *surge hopper* under the plating barrel. The capacity of this hopper should be large enough to accept the entire load, thereby freeing the barrel to begin plating the next load. The slurry dumps onto a vibrating screen or magnetic separator. Water sprays are used to wash and remove glass beads from the parts. A glass bead handling system consisting of a sump, a double-diaphragm pump, and an overhead conical storage reservoir with a pinch valve at the bottom is used to recycle the beads. More than one batch of glass beads can be used to speed production.

As described above, the mechanical plating process can be used to apply a variety of metals and codeposits with varying coating thicknesses, all with the same equipment. This capability offers advantages in equipment cost and space utilization over other forms of plating.

Process Capabilities

Plating Thickness. The thickness of mechanical plating deposits ranges from 5 to 75 μm (0.2 to 3 mils). The heavier coatings are referred to as *mechanical galvanizing* or *cold-impact galvanizing* coatings. Because the coating thickness is somewhat independent of cycle time and is controlled by the plating metal additions, a heavy "galvanized" coating thickness can be applied in almost as little time as thinner commercial coating thicknesses. Mechanical galvanizing provides uniform, smooth, and adherent coatings, and the coated parts require no thread chasing. Extensive exposure and salt spray testing have confirmed that the corrosion resistance of mechanical galvanized parts is comparable to that of hot-dip galvanized parts and parts coated with other types of zinc deposits at equivalent coating weights (Table 1).

Table 1 Corrosion resistance of threaded bolts with various coatings

Coating	Coating thickness, μm	Hours to red rust[(a)]
Zinc-aluminum	50 25	5000 2200
Zinc galvanized	50	490
Cadmium plated	25	1100
Dacromet	. . .	1250
Zinc electroplated	12.5	144

Note: All parts except Dacromet were mechanically plated. Dacromet is a zinc flake/chromate dispersion coating applied like dip/spin paint with a double cure.

(a) ASTM B 117 salt spray test

Applicable Parts. Many parts for which coating options were formerly limited to electroplating or hot-dip galvanizing are now successfully being mechanically plated. Part types now universally accepted as candidates for mechanical plating or galvanizing include nails; chain and wire forms of all types; bolts, nuts, and washers; offshore drilling hardware; pole-line hardware for telephone and cable television lines; certain marine fasteners; ASTM A 325 structural bolts; aircraft hardware; and automotive hardware of all types.

Whether or not parts can be successfully coated using mechanical plating or galvanizing depends on their size, weight, and geometry. Parts that would tend not to withstand the vigorous tumbling action of the process are not suitable. Parts heavier than 1 to 2 kg (2.2 to 4.4 lb) or longer than 0.5 m (1.64 ft) are not usually coated using mechanical plating.

Specific Characteristics, Advantages, and Limitations. Because of the dust or powder form in which metals are deposited, the surfaces of mechanical coatings will have matte to medium-bright luster. It is possible to achieve very smooth surfaces, but the mirrorlike surfaces typical of electroplated parts cannot be obtained. For this reason, mechanical plating finishes are considered to be functional rather than decorative.

Parts with holes and recesses that are difficult to electroplate to the desired thickness usually can be properly plated via mechanical plating. Parts with hole diameters as small as 0.78 mm (0.03 in.)--even where the depth of the hole is greater than the diameter--frequently can be plated successfully. Mechanical plating is often more economical and more flexible for parts that require special racking or special anode configurations to electroplate recessed areas.

Powder metallurgy parts can be coated by mechanical plating without prior sealing of their surfaces. Because mechanical plating solutions are generally chemically consumed, little excess is available to be entrapped in the pores of the substrate. The initial galvanically deposited copper strike will permeate such pores, and the metal powder will fill and bridge them. Also, because the potential for hydrogen embrittlement is extremely low, any pores in the part should not accumulate significant amounts of hydrogen.

Quality Control. In order to ensure the quality of the mechanically plated parts, the operator must pay constant attention to the coating adhesion, weight and thickness, consolidation, uniformity, and general appearance and brightness. The main causes of nonuniform appearance include:

- Use of glass media in poor condition
- Insufficient cleanliness of parts prior to plating
- Insufficient burnishing time at the end of the plating cycle
- Wet parts kept in surge hopper too long
- Conductivity of water too high
- Zinc added to cycle too quickly or in incorrect amounts

Applicable Specifications. ASTM B 635, B 695, and B 696 are standard specifications for mechanical plating. The military standard is covered by MIL C 81562. Many large original equipment manufacturers have their own specifications, as do many state highway departments. Mechanical galvanizing conforms to the coating weight and general requirements specified in ASTM A 153, which is widely used in the hot-dip galvanizing industry.

Post Treatments

Mechanical plating post treatments are similar to those used in electroplating. The coating is most receptive to post treatment immediately after plating, while it is still wet. A mild acid dip (e.g., 1% nitric acid) will reactivate parts that have already been dried. Conversion coatings such as clear or blue, yellow, olive drab, or black chromates can be applied. Mechanically plated parts can also be painted. A chromate coating pretreatment will improve paint adhesion.

The color, luster, and iridescence obtained with colored or clear chromates are somewhat different than those obtained on electroplated surfaces, but are well within the normal range of acceptable appearance and performance. Waxes, lacquers,

and silicates will satisfactorily adhere to the coating and will enhance the lubricity, durability, appearance, and corrosion resistance of the surface. No baking for embrittlement relief is required prior to or after supplementary treatment.

Waste Treatment

Before choosing a wastewater treatment system for mechanical plating, engineering and analytical data must be gathered. The preliminary work should determine:

- Treatment options for the metals in solution
- Present and future flow rates, and batch collection volume requirements
- Water conservation possibilities
- What is required to meet discharge limits
- Availability and type of treatment chemicals
- How sludge will be dewatered, dried, and disposed

In most cases, removal of heavy metals from mechanical plating effluent is accomplished by precipitating metal hydroxides. This is done routinely as long as the metal ions in the effluent are not complexed and the pH is high enough to ensure optimum precipitation. Zinc, for example, reaches minimum solubility at a pH between 9 and 10. A pH of 9.5 provides satisfactory precipitation in about 30 min. Although other metals reach minimum solubility at different pH levels, a pH of 9 to 10 will precipitate other residual metals associated with the process, such as copper, tin, iron, cadmium, and aluminum (but not the chromium present in certain post-treatment chromates). The chemical most commonly used in precipitation is 50% liquid sodium hydroxide. Magnesium hydroxide and lime slurry also can be used as a source of alkalinity. Lime tends to be less expensive but increases the precipitation time.

Chromium presents a special problem when present as a chromate (hexavalent state). Hexavalent chromium must first be reduced to the trivalent state before standard precipitation can proceed. Sodium metabisulfite or ferrous sulfate added at a pH of about 2 will reduce the hexavalent chromium and allow the resultant trivalent chromium to be combined with other wastes for regular precipitation.

Most mechanical plating systems capable of plating 1000 kg (2200 lb) of parts will discharge 22 to 45 1/min (6 to 12 gal/min) of solution; therefore, a batch system with a minimum of two collection tanks should be satisfactory. Each tank should be capable of holding the effluent from one shift, allowing one to fill while the other is being treated.

Flocculation is an important consideration. After pH adjustment of the effluent, it should flow to a tank for flocculation of the suspended metal hydroxides. Addition of a polyelectrolyte causes the small particles to agglomerate into larger, heavier particles, with improved settling characteristics.

After being flocculated and settled, the suspended solids enter a sludge dewatering device such as a filter press. Sludge drying further reduces the volume (by up to 75%) of the solid wastes released from the filter press. A standard mechanical plating and galvanizing system will produce approximately 0.028 m^3 (1 ft^3) of dewatered and dried sludge per 1000 to 2000 kg (2200 to 4400 lb) of plated parts.

Surface Preparation for Continuously Applied Coatings

Curtiss Dunbar, LTV Steel Company

Introduction

METALLURGICALLY CLEAN SURFACES are necessary to promote the proper bonding of continuously applied dip, barrier, and chemical conversion coatings on steel substrates. Surface preparation removes contaminants on the substrate that would prevent the optimal metallurgical bonding of the coating.

There are two basic types of contaminants. Carbonaceous materials, which include oils, represent one type. These materials are actually applied to the steel strip during the cold-reduction process to facilitate rolling. Normal, unavoidable surface oxidation is the other type. The surface of every processed steel strip has one or both of these contaminants, which

must be removed before dip, barrier, or conversion coatings can be applied. These contaminants can be removed by using wet cleaning methods, furnace-atmosphere techniques, fluxes and other specialized methods, or a combination of these.

Although this article primarily describes techniques that prepare steel surfaces for hot-dip coatings, the same techniques can be used for electroplated and chemical conversion coatings. Modern continuous annealing lines use similar methods to clean steel strip before heat treatment. The term "line" refers to the sequenced operations in the coating process.

Surface preparation usually comprises separate cleaning steps, which can be used either alone or in combination, depending on the amount of soil on the incoming steel strip and the design layout for the coating line. Modern lines usually include several of these cleaning steps to meet the demanding quality requirements of the market in the 1990s.

A good example of modern surface-cleaning techniques, shown in Fig. 1, combines both wet and furnace surface-preparation methods in order to produce a clean steel strip. The incoming strip first contacts a dip alkaline cleaner and then a brush scrubber. The strip next contacts an electrolytic alkaline cleaner and then a second brush scrubber. The strip is then rinsed and dried. After this wet section of the process, the strip enters an unfired, or waste gas, preheater before entering a high-gradient, direct-fired furnace. Finally, it enters a high-temperature, radiant-tube, reducing/annealing furnace with a hydrogen-nitrogen atmosphere.

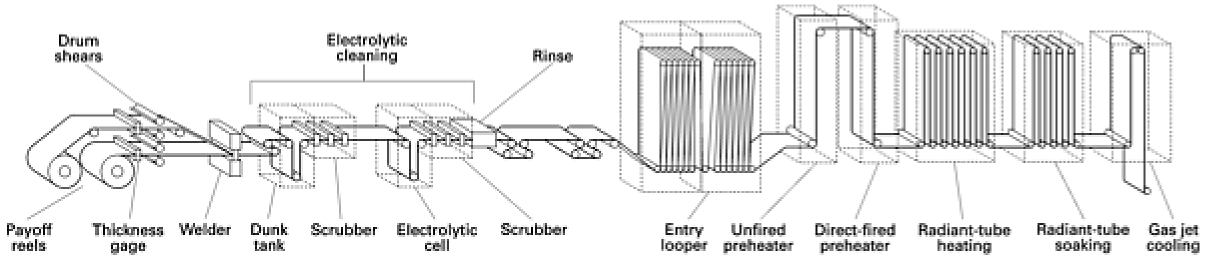

Fig. 1 Schematic of cleaning section of modern coating line that provides both wet and furnace types of surface preparation

Wet Cleaning Methods

Wet cleaning is a generic term that means aqueous solutions are used to prepare the surface of the strip. This term incorporates both alkaline and acid processes. The wet cleaning section of a coating line has a relatively low initial cost, compared with the cost of large, gas-fired furnaces, but requires a high degree of maintenance. In addition, the cost of the chemicals and of the disposal of spent chemicals results in high operating expenses.

Alkaline Cleaning. In the dip operation of continuous strip coating lines, alkaline cleaning is used to remove protective oils, soil, and the residues of rolling oils. Although it is possible to remove thin oxide layers using alkaline cleaning, these layers are usually removed during subsequent pickling operations.

Alkaline cleaners are blends of various inorganic salts with small amounts of inhibitors and surfactants to promote different cleaning mechanisms, such as saponification and emulsification.

Saponification refers to the chemical action whereby an oil is converted to a water-soluble soap. This reaction depends on concentration, temperature, pH, and time of immersion. This mechanism will clean the majority of light rolling oils and rust-preventative oils that are common on flat, rolled steel strip. Care must be taken to ensure that the soil level in the cleaner does not become high enough to cause redeposition of the soil or to interfere with proper rinsing.

Emulsification is the process whereby surfactants penetrate soils and break them into sufficiently small particles to allow dispersion and suspension in the cleaning solution.

The capabilities of the alkaline cleaner can be augmented by adding brushes to the continuous strip coating line in order to mechanically loosen and remove surface soil. An abrasive material can be bonded to these brushes to enhance their scouring or scrubbing action. The brushes are usually placed in the processing line with a steel roll on the opposite side of the strip. This arrangement allows the contact pressure of the brush to be increased without deflecting the pass-line of the

strip. The cleaner is often applied through the brush to provide cooling at the contact area and to act as a medium for floating the loosened soil away and preventing its redeposition.

Electrolytic Cleaning. Cleaners can be designed to work with electric current. The strip can be either cathodic or anodic. The recommended practice for continuous lines is either the anodic configuration or a switching current, where the strip is switched between being positively and negatively charged. In anodic electrocleaning, the strip is positively charged and oxygen is discharged at the strip surface to create a mechanical scrubbing action. One disadvantage of anodic cleaning is the tendency to build up sludge on the electrodes. In cathodic electrocleaning, the strip is negatively charged, producing the release of a much larger volume of hydrogen and better mechanical scrubbing at the strip surface. This condition also increases the possibility of hydrogen being charged into the strip and the unwanted plating out of metallic contaminants onto the strip surface, which can cause quality problems with the subsequent coating operation. Periodic reversing, or switching, electrocleaning is a combination of both anodic and cathodic methods that produces a better cleaning of the strip surface without excessive contamination, hydrogen charging, or electrode buildup.

Maintenance. The concentration of the cleaner must be maintained and any additives that tend to be used up at a faster rate than the basic caustic components must be controlled in terms of proportion. The cleaner system should allow for the periodic settling and removal of solid soils, especially metallic particles such as the iron fines that form during cold rolling. Oil needs to be cleaned from the system by frequent or continuous skimming. Magnetic separators and other devices are effective in removing soil burden and prolonging the useful life of the cleaner.

Chemical Pickling. Most pickling operations use an acid to dissolve metal oxides. The resulting reactions are affected by concentration, temperature, and agitation. These reactions will naturally slow down as the acid solution becomes more concentrated in the metal being dissolved.

Sulfuric acid is the most common acid used in pickling iron-base materials because of its low cost. After the acid has removed the oxide scale, it will begin to attack the steel substrate. Therefore, inhibitors are commonly used to retard the attack of the base metal without affecting oxide scale removal. As with most chemical reactions, an increase in temperature increases the pickling rate. As the acid is consumed, the pickling time must be increased to achieve the same level of descaling. In continuous coating lines, it is not possible to simply increase the pickling time to compensate for the reduced effectiveness of the acid pickling. Pickling effectiveness is also decreased as iron builds up in the pickling bath. Therefore, both acid and iron contents must be adjusted by replenishment.

Hydrochloric acid is an excellent pickling agent for the removal of oxides from steel strip. Although it is more expensive and its fumes much more corrosive than sulfuric acid, it has a longer useful life, can be operated at lower temperatures, and is not affected by the iron concentration to the same degree experienced in sulfuric acid pickling.

Electrolytic Pickling. Electrolytic action can be used to increase the speed of pickling, which is a very important aspect of continuous coating lines (Fig. 2). The electric current can be either alternating or direct, and the strip can be either anodic or cathodic. Cathodic pickling is faster than anodic, but this advantage decreases with increasing concentration and bath temperature. Cathodic pickling charges the steel with hydrogen much faster than straight chemical pickling does. In modern continuous coating lines, the current is often switched, which makes the strip cathodic and then anodic.

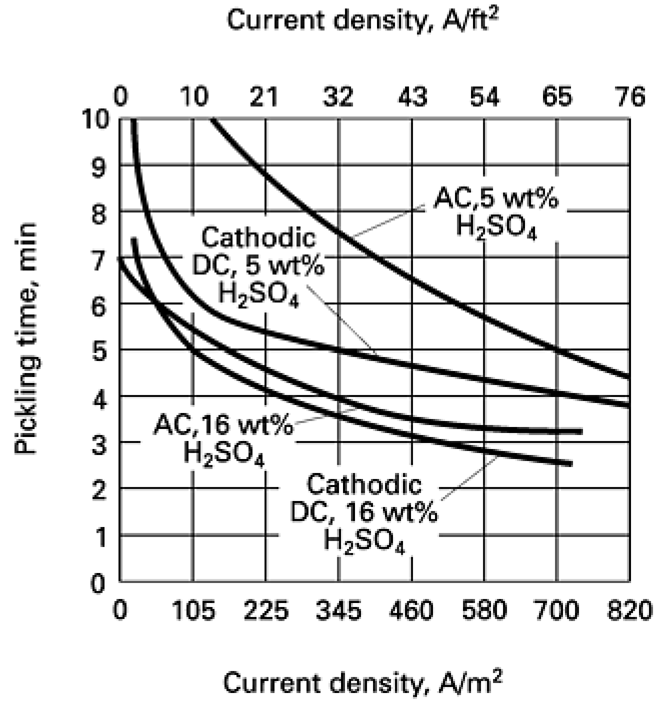

Fig. 2 Effect of current density on pickling time for anodic, cathodic, and alternating current electrolytic pickling. AC, alternating current; DC, direct current. Source: National Electric Products Corp.

Flame Cleaning and Furnace Preparation

Sendzimir Oxidation/Reduction Method. The original method for flame cleaning was proposed by Tadeusz Sendzimir in the 1930s. His invention involved heating a steel strip in a direct oxidizing flame to burn off the rolling oils and other contaminants. This step left an oxide on the steel surface, which was then cleaned by heating to a much higher temperature in a reducing furnace with a hydrogen-nitrogen atmosphere. This two-furnace cleaning method was converted into a coating line by cooling the strip and immersing it in molten zinc while it was still under the protective hydrogen-nitrogen atmosphere. An additional benefit was that the strip could be annealed while it was being cleaned for coating.

Oxidizing Furnace. In general, both the oxidizing furnace and the newer, nonoxidizing, direct-fired furnace can perform the same job. Both types of furnace configurations preheat the strip before it enters the radiant-tube furnace, and both flash off the volatile materials and oxidize the carbon compounds that are on the surface of the strip.

The role of the oxidizing furnace is to oxidize all of the carbonaceous products without leaving too thick an oxide layer for the reducing furnace to convert back to pure iron. All oxide that forms in the oxidizer *must* be reduced in the reducing furnace in order to prepare the strip for coating. Unreduced oxide is brittle and, if left on the strip, will result in poor coating adherence.

Oxidizing furnaces usually preheat the strip to approximately 480 °C (900 °F). This temperature, which is somewhat arbitrary, depends on the uniformity of heating and the reducing capability of the radiant-tube furnace that follows. Care should be exercised to avoid overheating the edges of the strip. Because the oxidizing furnace is not sealed, air can be drawn into the furnace, making the atmosphere within this furnace oxidizing to the steel strip, regardless of burner combustion practices. Burners are usually adjusted to perfect combustion for efficiency. If the combustion ratio of the burners is too rich, then carbon deposits (soot) can form on the strip and completely negate the cleaning purpose of the oxidizer. Carbon cannot be removed with a hydrogen atmosphere, and uncoated spots and poor coating adhesion will result.

Direct-Fired Furnace. The use of a nonoxidizing, high-gradient, direct-fired furnace is preferred for strip preparation. The direct-fired furnace is so named because there is direct flame impingement of the combustion products on the strip. This type of furnace is connected directly to a reducing or radiant-tube furnace. The large volume of combustion products

that is produced in the direct-fired furnace acts as either a barrier or a seal to pressurize the rest of the reducing furnace, which minimizes the consequences of small furnace leaks.

Direct-fired furnaces usually have zones, or segments, that can be turned off to adjust for lighter-gage strip or lower annealing-temperature requirements. These zones are usually connected to a common flue near the entry of the furnace. This flue usually contains a damper that controls the furnace pressure to a predetermined value. Pressure that is too high can force combustion products into the reducing zones and contaminate the hydrogen-nitrogen atmosphere. The flue must be large enough and the pressure such that all combustion products will flow out of the flue.

The advantages of this type of furnace are that it preheats, removes volatiles and carbon without oxidizing the strip, and provides a much higher preheat temperature than an oxidizing furnace.

Although the direct-fired furnace is in many ways superior to the original oxidizing furnace, it does have negative aspects. Its major disadvantage is that it is expensive to operate and maintain. It also has a high initial cost because of the sophistication of the burners and burner controls, and because of the refractory requirements to operate at high temperatures. In addition, high operating temperatures and thermal shock can cause problems with the maintenance of the refractories. Controls for the fuel-to-air ratio and the furnace pressure are very critical and cannot be neglected. Because the gas feed on the individual burners can easily become plugged, it needs to be checked and cleaned. The ability of the positive pressure to overcome furnace leaks is not a cure-all for poor maintenance practices. Air can be aspirated into the furnace, even with positive furnace pressure.

Combustion Ratios. Because the furnace must rapidly heat a steel strip without oxidizing it, the correct ratio of air to gas must be ensured. Although the optimal amount will vary with the coating line, it should be in the 4 to 5% range for excess combustibles in the last zone of the direct-fired furnace, where the strip temperature is the highest. This ratio should be set without having the strip or any hydrogen in the furnace. This combustion ratio will increase when the coating line is running because of the addition of the hydrogen atmosphere to the furnace. After exiting from the furnace, the strip should be bright and oxide-free. Minor adjustments are often made using strip appearance only as a guide.

If the amount of excess combustibles are greater than 7 to 8%, then carbon can be deposited on the strip surface, resulting in uncoated spots and poor adhesion. In many mills, it is common practice to set the combustion ratios progressively leaner (closer to perfect combustion and, in some cases, excess air) in the zones closest to the furnace entry, where the strip temperatures are lower. Output will be increased and some of the wasted energy will be recovered by burning the hydrogen furnace atmosphere and the excess fuel from the preheater zones.

Strip Exit Temperature. If strip exit temperatures from the direct-fired furnace are too high, then the strip will be oxidized. Usually, the maximum indicated temperature without oxidation is approximately 730 °C (1350 °F). Higher temperatures almost always produce an oxide, regardless of burner ratios. Lower temperatures do not produce an oxide, but they defeat the powerful cleaning capability and lose the advantage of the rapid preheating. The maximum allowable temperature is also very dependent on furnace design, combustion ratios, and dwell time in the furnace.

Zone Temperature. If the zone temperatures of the direct-fired furnace are too low, then the strip will be oxidized. Usually, these zone temperatures are maintained at a minimum of 1100 °C (2000 °F). Control of the direct-fired furnace is best accomplished by turning zones off, rather than by turning them down. It is best to leave the last zone (the one next to the radiant-tube furnace) on full fire and then add or turn off the other zones in order, as needed. A relationship between strip exit temperature and zone temperature is critical to ensure proper cleaning.

Dwell Time. Even under perfect nonoxidizing conditions within a direct-fired furnace, strip will become oxidized if the residence time, or *dwell time,* is excessive. For any given coating line, the line speeds (dwell time in the direct-fired furnace) for each gage width and grade are predetermined to achieve the highest production rates consistent with producing the desired physical and mechanical properties. This virtually eliminates the possibility that well times will be used that are long enough to oxidize the strip.

A waste-gas preheater is an unfired section of furnace that is put ahead of the direct-fired furnace in the coating line. The exit gases pass through this furnace section before being exhausted through a damper. The incoming strip can be heated to approximately 200 °C (400 °F), just by contacting the very hot exhaust gases of the direct-fired furnace. Because this section of the furnace can be oxidizing if strip temperatures get too high, it is important not to make this section too large. Too much strip preheat will either oxidize or bake on the oils and carbonaceous material, which will seriously affect the ability of the direct-fired furnace to clean the strip. Direct-fired furnaces with waste-gas preheaters

produce a tremendous amount of strip heating and cleaning in a relatively small amount of floor space. In addition to their cleaning capability, they produce a means to pressurize the rest of the furnace to negate the problem of small furnace leaks.

Radiant-Tube Furnace. Gas-phase surface preparation in a radiant-tube furnace allows surface iron oxide to be converted to pure iron, using heat and a hydrogen atmosphere. The radiant-tube furnace is so named because the insides of tubes that are positioned throughout the furnace are heated by external burners. These hot tubes radiate heat to the inside of the furnace without exposing the furnace to either air or combustion products.

Radiant-tube furnaces usually operate with an atmosphere mixture of hydrogen and nitrogen. The steel strip that enters the reducing, or radiant-tube, furnace will be heated under this reducing atmosphere. Hydrogen reacts with surface oxides to produce pure, nascent iron and water vapor (dew point). After the strip is cleaned and annealed to achieve the desired properties, its temperature is adjusted (cooled) to a level close to that of the molten coating bath. This is accomplished by passing the strip through an unheated furnace with cooling tubes that are similar to the radiant tubes, except that only air is blown through them.

A more efficient method of cooling the strip is to use gas-jet coolers, which remove the hot furnace atmosphere and pass it over a heat exchanger to cool, before returning the atmosphere to the furnace, where it contacts and cools the hot strip.

Process Variables. The atmosphere of the radiant-tube furnace must be maintained as reducing to steel, in order to achieve the desired surface preparation. This condition is controlled by the amount of hydrogen, the temperature of the strip, and the amount of water vapor in the furnace. Figure 3 shows the relationship of these variables as a function of temperature versus the water/hydrogen ratio.

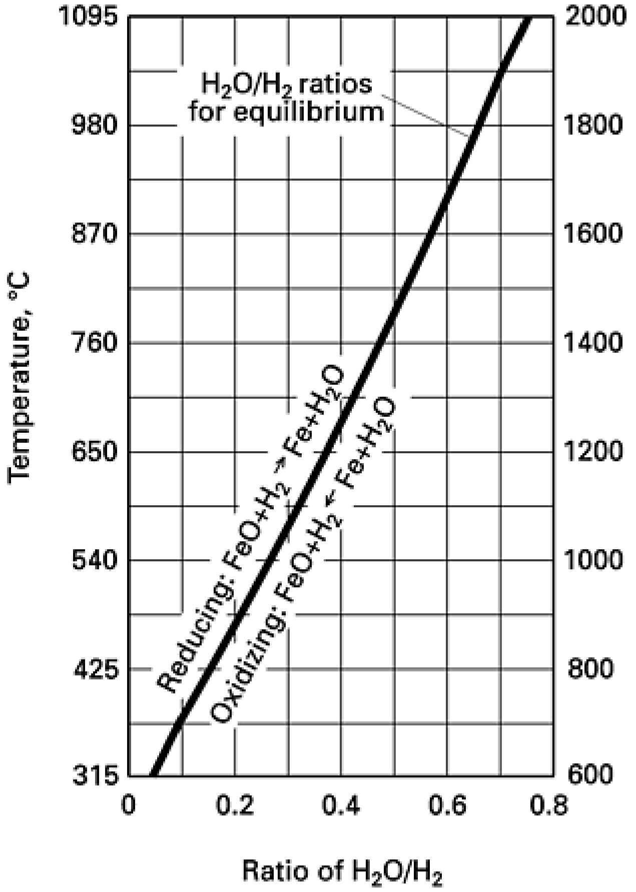

Fig. 3 Theoretical equilibrium relationship between iron, iron oxide, hydrogen, and water vapor

Another concern is the infiltration of free oxygen into this atmosphere. Oxygen levels between 50 and 100 ppm have been shown to be detrimental to proper surface preparation for hot-dip coatings.

Wet chemical precleaning and strip heating in a hydrogen-nitrogen atmosphere has certain advantages. The mechanical properties of the final product can be predetermined before coating, and then a low-temperature cycle can be used during coating to preserve these properties. This practice does have higher production costs than the in-line annealing processes. Advantages are that less furnace refractory maintenance is required and that there are many skilled builders of radiant-tube furnaces.

The relatively low-gradient heating that characterizes this method requires a long overall furnace length. Wet chemical precleaning requires higher overall maintenance of equipment and solutions. The cleaning section of the coating line must provide a properly dried and rinsed strip, or else problems can develop with alkaline carryover to ceramic-coated hearth rolls.

The maintenance of a radiant-tube furnace is higher, because tubes are fired harder than they are in a direct-fired furnace. There is greater vulnerability to furnace leaks, because it is difficult to maintain significant positive pressure of the hydrogen-nitrogen atmosphere.

The direct-fired preheating method provides positive and consistent thermal cleaning of cold-rolled strip. It is therefore the preferred combination for most modern coating lines. Direct-fired preheaters provide rapid, high-gradient heating, which requires a much shorter furnace length than radiant-tube furnaces with a wet cleaning capability. This system is less sensitive to furnace leaks, because a high positive furnace pressure is maintained by the controlled discharge of combustion products. Fewer radiant tubes are required, which is a factor that reduces the possibility of furnace leaks. In-line annealing is more economical and produces equivalent mechanical properties when modern stabilized substrates are used.

Refractory maintenance is much greater in a direct-fired section than in a radiant-tube furnace. The direct-fired section lends itself to both horizontal and vertical configurations. The steel strip is heated in the direct-fired section to temperatures that are high enough to effect positive shape correction by stretching before tracking difficulty can occur.

Other Specialized Cleaning Methods

Fluxes. One of the earliest methods of coating one metal with another incorporated the use of a flux. In modern methods, fluxing involves coating an incoming strip with a material that will chemically break down, thereby producing conditions that remove surface oxides. Modern continuous flux lines usually incorporate alkaline and acid wet cleaning steps ahead of the flux operation.

Fluxes are mixtures of acid salts with surfactants and other inert materials that float on the surface of the coating metal bath, helping to prevent oxidation. The most common fluxes are the zinc chloride plus ammonium chloride mixes that are used in the production of terne (92% Pb and 8% Sn) coatings and in Cook-Norteman continuous galvanizing lines. Ammonium chloride has the stronger fluxing action, whereas zinc chloride provides preheat thermal stability and acts as an inhibitor for steel surface oxidation. Steel strip is cleaned, pickled, and, as a final step, coated with an aqueous solution of the zinc and ammonium chloride flux. In the Cook-Norteman lines, the strip is then dried and preheated to minimize the impact of the cold, incoming strip in cooling the molten zinc bath. Because productivity is very important, it is desirable to preheat the strip to the maximum temperature possible without damaging the flux coating and oxidizing the strip. Upon entering the zinc bath, the flux breaks down, releasing a hydrogen chloride gas that acts as a chemical surface preparation. The balance of the spent flux floats to the surface of the bath, where it is removed. Under proper conditions, the flux will completely release from the strip surface and be replaced by a wetted layer of the coating metal.

Mechanical Cleaning. Other methods of cleaning also have been tried and used successfully in certain applications. These methods include mechanical alteration of the surface of a material, such as shot/grit blasting or abrasive/wire brushing, in order to remove particles before the surface is coated. Grit blasting can include sand, glass, and steel grit or shot. Brushes with embedded abrasive materials are commonly used as a surface preparation step in coil paint lines and in brush alkaline cleaners. Although these brushes appear to uniformly alter the strip surface, microstructural examination of a mechanically cleaned surface shows that a large portion of it never contacts the abrasive materials.

Ultrasonic cleaning methods loosen surface material by using ultrasonic energy to alternately compress and expand the cleaning solution. This pressure can "tear" the solution apart, producing cavitation bubbles. These bubbles have the effect of blasting solid soil away from the surface. Ultrasonic energy can be used with any of the standard cleaners if proper adjustments are made. The major disadvantage of using ultrasonic energy in a continuous line is the high cost associated with processing strip at high speeds.

Continuous Hot Dip Coatings

Herbert E. Townsend, Bethlehem Steel Corporation

Introduction

OWING TO its many favorable characteristics, steel is well suited and widely used for a broad range of engineering applications. It has a variety of excellent mechanical properties, such as strength, toughness, ductility, and dent resistance. Steel also offers good manufacturability, including formability, weldability, and paintability. Other positive factors include its availability, ferromagnetic properties, recyclability, and cost. Because steel is susceptible to corrosion in the presence of moisture, and to oxidation at elevated temperatures, successful use of these favorable characteristics generally requires some form of protection.

Methods of corrosion protection employed to protect steel include: altering the metal by alloying, changing the environment by desiccation or use of inhibitors, controlling electrochemical potential by application of cathodic or anodic currents, and applying organic and metallic coatings. Application of a metallic coating by a continuous hot dip process is one of the most widely used means of protecting steel. In continuous hot dip coating, long strands of sheet, wire, or tubing are fed through a bath of molten coating metal in a continuous process. In batch hot dip coating, fabricated parts, such as fasteners, poles, or beams, are dipped into a molten bath either individually or in discrete batches.

Metals and alloys that can be applied as coatings to steel in a continuous hot dip process are limited to those with a melting point low enough to allow steel to be pulled through a coating bath without tearing. These include the coatings described below, namely, zinc, zinc-iron alloy, aluminum, aluminum-silicon alloy, Zn-5Al alloy, 55Al-Zn alloy, and lead-tin alloy. Metals such as chromium and titanium cannot be applied to steel by hot dipping because of their high melting points. Tin, which prior to 1937 was applied only by hot dipping, is now almost always electrodeposited. This is because it is very difficult to produce the thin and uniform coatings required for tinplate by means of hot dipping.

Coating thickness is a key factor in determining coated product performance. In general, thicker coatings provide greater corrosion protection, whereas thinner coatings tend to give better formability and weldability. The amount of coating can also be expressed in terms of mass per unit area. This is determined by weighing a section of the coated product, stripping the coating in an acid solution, and weighing again. Tables 1 and 2 summarize coating thickness and mass called for by ASTM specifications for continuous hot dip coatings for sheet and wire (Ref 1, 2, 3, 4, 5, 6, 7, 8, 9). In the case of sheet, the coating thickness is usually expressed in terms of the coating on one side, whereas the mass is usually given as the sum of the coating on both sides.

Table 1 Nominal coating mass and thickness for continuous hot dip coatings on steel sheet

Type of coating[(a)]	Designation	Coating mass[(b)], g/m^2	Coating thickness[(c)], μm
Zinc (A 525)	Z1100	1100	78
	900	900	64
	700	700	50
	600	600	42
	450	450	32
	350	350	25

	275	275	19
	180	180	13
	90	90	6
	001	(d)	(d)
Zinc-iron (A 525)	ZF180	180	11
	120	120	9
	100	100	7
	75	75	5
	001	(d)	(d)
Aluminum (A 463) type 1	T1 40	120	20
	25	75	12
Aluminum (A 463) type 2	T2 100	305	48
	65	195	30
	LC	(d)	(d)
Zn-5Al (A 575)	ZGF 700	700	48
	600	600	41
	450	450	31
	350	350	24
	275	275	19
	225	225	15
	180	180	12

	135	135	9
	90	90	6
	001	(d)	(d)
Zn-55Al (A 792)	AZ 180	180	24
	165	165	22
	150	150	20
Lead-tin (A 308)	LT 110	336	15
	85	259	12
	55	168	8
	40	122	6
	35	107	5
	25	76	3
	01	(d)	(d)

Note: All values are based on specified triple-spot minima.

(a) ASTM specifications as given in *Coated Steel Products,* Vol 01.06, *Annual Book of ASTM Standards,* ASTM, 1993.

(b) Two sides.

(c) One side. Calculated from densities in g/cm^3 as follows: zinc and zinc-iron, 7.07; aluminum type 1, 3.017; aluminum type 2, 3.21; Zn-5Al, 6.87; Zn-55Al, 3.70; lead-tin, 11.08.

(d) No minimum

Table 2 Minimum coating mass and thickness ranges for continuous hot dip coatings on steel wire

Type of coating(b)	**Coating class**	**Range of minima(a)**	
		Coating mass(c), g/m^2	**Coating thickness(d), µm**

Zinc (A 641)	1	45-190	6-27
	A	180-300	25-42
	B	360-600	51-85
	C	540-900	76-127
Aluminum (A 809)	. . .	92-122	29-38
Zn-5Al (A 856)	1	45-190	7-28
	A	180-300	26-44
	B	360-600	52-87
	C	540-900	79-131

(a) Minimum coating increases with increasing wire diameter.

(b) ASTM specifications as given in *Coated Steel Products,* Vol 01.06, *Annual Book of ASTM Standards,* ASTM, 1993.

(c) Two sides.

(d) Calculated from densities in g/cm^3 as follows: zinc, 7.07; aluminum, 3.21; Al-5Zn, 6.87

Typical applications for hot-dip-coated steel sheet, wire, and tubing cover a wide range in the construction, automobile, utility, and appliance industries (Table 3). As the cost of lumber increases, additional large-scale applications of hot-dip-coated steel sheet are expected to develop in the residential construction markets for roofing, siding, and framing. Compared to conventional home building materials, steel has obvious advantages, such as price stability, dimensional stability, and better resistance to fire, earthquakes, hurricanes, and insects.

Table 3 Typical applications of continuous hot-dip-coated steel sheet, wire, and tubing

Coating	**Product**		
	Sheet	**Wire**	**Tubing**
Zinc and Zn-5Al	Roofing, siding, doors, culvert, ductwork, housings, appliances, autobody panels and structural components	Nails, staples, guy wires, strand, tension members, rope, utility wire, fencing	Electrical conduit

Zinc-iron	Autobody panels and structural components	. . .	. . .
Aluminum type 1	Mufflers, tailpipes, heat shields, ovens, toasters, flues, chimneys	Guy wires, strand, rope, utility wire, fencing	. . .
Aluminum type 2	Roofing, siding, ductwork, culvert, silo roofs	Guy wires, strand, rope, utility wire, fencing	. . .
Zn-55Al	Roofing, siding, ductwork, culvert, mufflers, tailpipes, heat shields, ovens, toasters, flues, chimneys, silo roofs	. . .	. . .
Lead-tin	Fuel tanks, radiator components, valve covers, air-filter housings	. . .	Fuel lines, hydraulic lines

Among all coated products, continuous hot-dip-coated steel sheet is the biggest in terms of tons produced and consumed. As shown in Fig. 1, over 9 million U.S. tons (8.2 million metric tons) of hot-dip-coated steel sheet were shipped in the United States in 1992 (Ref 10). This amounts to almost 12% of all steel products shipped in the United States.

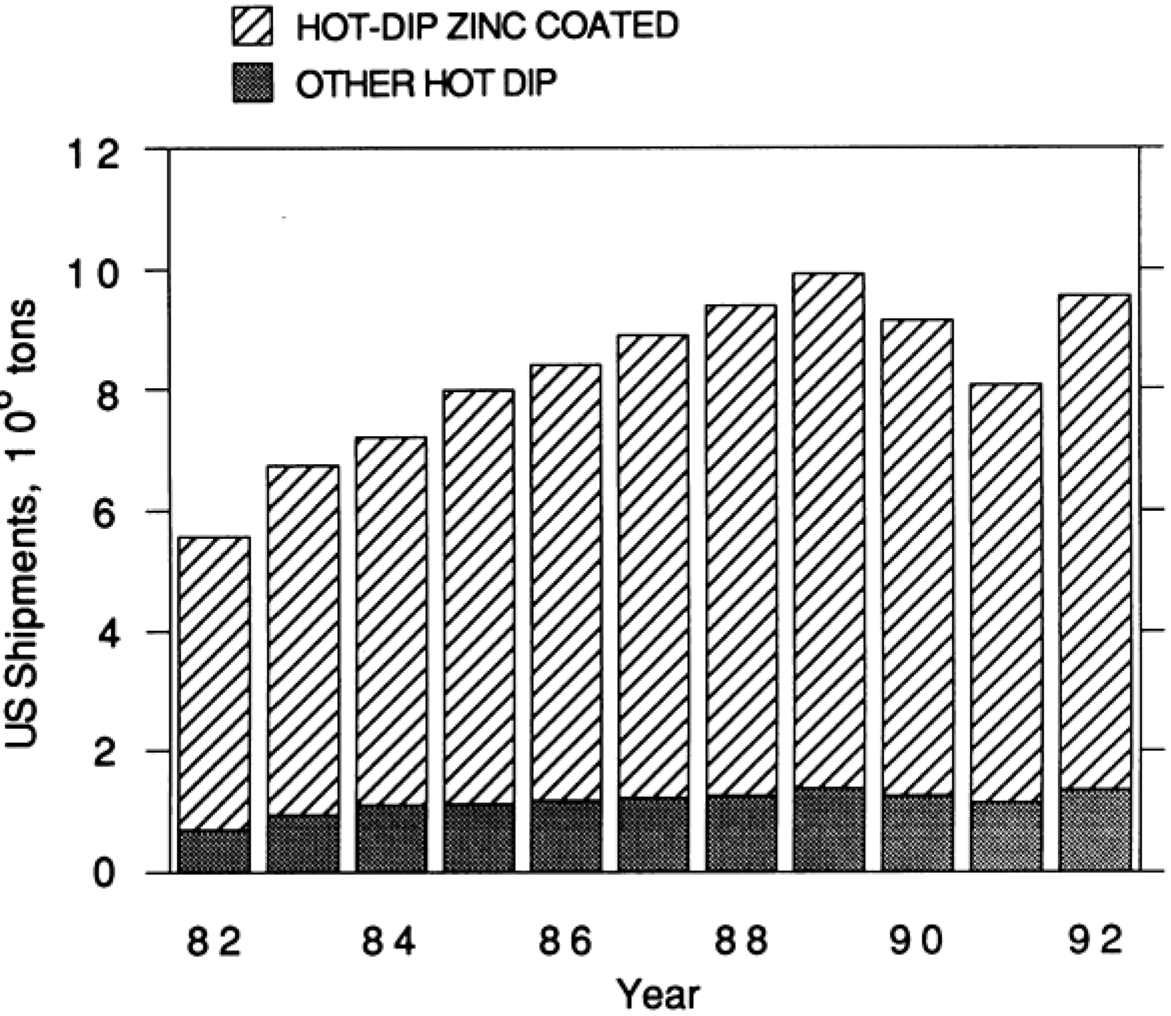

Fig. 1 U.S. shipments of coated steel sheet. Source: Ref 10

This chapter deals mainly with the processes and coatings used for the continuous hot-dip coating of steel sheet. Much of this information is also applicable to steel wire and tubing. Additional details can be found in a number of earlier reviews (Ref 11, 12, 13, 14, 15, 16).

Notwithstanding a lapse due to a sluggish economy during 1990-1991, hot-dip-coated steel sheet has shown substantial growth over the 11-year period shown in Fig. 1. This growth occurred largely because coated steel is replacing uncoated steel in order to satisfy consumer demands for improved durability, particularly in the automobile industry. In order to meet this increasing demand, producers in the United States and around the world are investing in more hot dip coating facilities. It is estimated that from 1990 to 1995, the total hot dip sheet-coating capacity of the Western World will grow from 49 to 63 million metric tons per year. Most of this capacity will be located in Japan (35%), North America (28%), and Europe (30%).

Hot-dip-coated, low-carbon steel sheet is available with a broad range of mechanical properties. As shown in Table 4, it can be produced with yield strengths in the range of 241 to 620 MPa (35 to 90 ksi). Compared to uncoated steel, hot-dip-coated, low-carbon steel sheet has slightly less ductility because of the thermal effects of the coating process on the precipitation of carbon in the steel and associated age hardening. Extra-deep-drawing-quality grades are made with steel that has been vacuum degassed to very low carbon levels and stabilized with additions of titanium and/or niobium. The stabilized substrates are relatively immune to the thermal effects of hot dipping and provide excellent formability. Low-alloy grades are also galvanized to meet the requirements of specific applications.

Table 4 Typical mechanical properties of continuous hot-dip-coated steel sheet

Grade	Yield strength		Tensile strength		Elongation in 5 cm (2 in.), %
	MPa	ksi	MPa	ksi	
Full hard	620	90	634	92	5
Commercial quality	255	37	338	49	35
Drawing quality	248	36	324	47	37
Drawing quality special killed	241	35	332	48	38

References

1. "Standard Test Method for Weight of Coating on Zinc-Coated (Galvanized) Iron or Steel Articles," ASTM A 90, *Annual Book of ASTM Standards,* Vol 01.06, ASTM, 1993
2. "Standard Specification for Steel Sheet, Zinc-Coated (Galvanized) by the Hot-Dip Process," ASTM A 525, *Annual Book of ASTM Standards,* Vol 01.06, ASTM, 1993
3. "Standard Specification for Zinc-Coated (Galvanized) Carbon Steel Wire," ASTM A 641, *Annual Book of ASTM Standards,* Vol 01.06, ASTM, 1993
4. "Standard Specification for Steel Sheet, Cold-Rolled, Aluminum-Coated, Type 1 and Type 2," ASTM A 463, *Annual Book of ASTM Standards,* ASTM, 1993
5. "Standard Specification for Aluminum-Coated Carbon Steel Wire," ASTM A 809, *Annual Book of ASTM Standards,* Vol 01.06, ASTM, 1993
6. "Standard Specification for Steel Sheet, Zinc-5% Aluminum Alloy Metallic-Coated by the Hot-Dip Process," ASTM 875, Vol 01.06, ASTM, 1993

7. "Standard Specification for Zinc-5% Aluminum-Mischmetal Alloy-Coated Carbon Steel Wire," ASTM A856, *Annual Book of ASTM Standards,* Vol 01.06, ASTM, 1993
8. "Standard Specification for Steel Sheet, Aluminum-Zinc Alloy-Coated by the Hot-Dip Process, General Requirements," ASTM A 792, *Annual Book of ASTM Standards,* Vol 01.06, ASTM, 1993
9. "Standard Specification for Steel Sheet, Long Terne (Lead-Tin Alloy) Coated by the Hot-Dip Process," ASTM A 308, *Annual Book of ASTM Standards,* Vol 01.06, ASTM, 1993
10. "Annual Statistical Report," American Iron and Steel Institute, 1992
11. A.J. Stavros, Continuous Hot-Dip Coatings, *Corrosion,* Vol 13, *ASM Handbook* (formerly 9th ed. *Metals Handbook*), ASM International, 1987, p 432-436
12. H.E. Townsend, L. Allegra, R.J. Dutton, and S.A. Kriner, Hot-Dip Coated Sheet Steels--A Review, *Materials Performance,* April 1986, p 36-46
13. H.E. Townsend, Coated Steel Sheet for Corrosion Resistant Automobiles, *Materials Performance,* Oct 1991, p 60-65
14. V. Jagannathan, Emerging Technologies in the Hot-Dip Coating of Automotive Sheet Steel, *Journal of Metals,* Aug 1993, p 48-51
15. H.E. Townsend and L. Allegra, Precoated Sheet Steel for Automotive Applications, *Automotive Corrosion by Deicing Salts,* R. Baboian, Ed., National Association of Corrosion Engineers, 1981, p 337-351
16. H. Bablik, *Galvanizing (Hot-Dip),* Wiley, 1950

Continuous Hot Dip Sheet-Coating Processes

In continuous hot dip coating of steel sheet, coils of steel are welded end-to-end and are coated at speeds of up to about 200 m/min (650 ft/min). In general, continuous hot dip coating facilities are classified as either *hot* or *cold,* as described below.

Hot Lines. In hot processing, steel strip is cleaned and heated in a reducing gas atmosphere, typically a mixture of hydrogen and nitrogen, in order to prepare the surface for coating. Annealing of cold-rolled steel by heating above its recrystallization temperature of about 700 °C (1300 °F) is usually a part of this heating process. Combining the steps of cleaning, heat treating, and bringing the sheet to coating temperature into a continuous operation contributes to making the hot process economical. Hot processing at lower temperatures without recrystallization is also done to produce full-hard, coated, high-strength sheet. Lower temperatures are also used to coat hot-rolled sheet, or to coat cold-rolled sheet that has been previously annealed.

A state-of-the-art hot line capable of producing 450,000 metric tons per year and coating sheet up to 1830 mm (72 in.) wide is shown schematically in Fig. 2. Coils of steel sheet are first loaded onto reels at the entry end on the left. The leading end of each coil is resistance seam welded to the tail end of the preceding coil. This is made possible by the looping tower, which acts as a reservoir for sheet. Sheet previously stored in the looping tower is released downstream so that sheet at the entry point can be stationary long enough for a new coil to be loaded and welded without interrupting the continuity of the coating process.

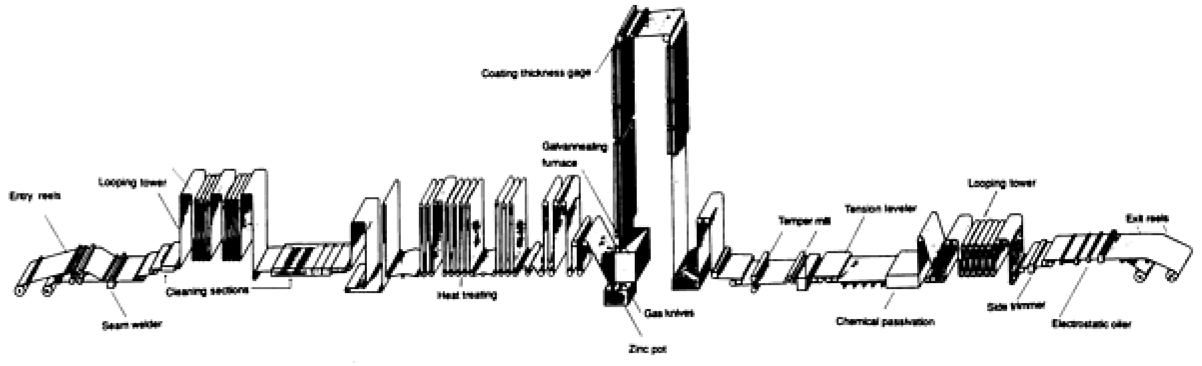

Fig. 2 Schematic diagram of a continuous galvanizing line. An example of a "hot" line with in-line annealing capability. See text for details.

After welding, the strip enters the first cleaning stage, an alkaline bath that removes oils, dirt, and residual iron fines from the rolling process. Upon exiting the looping tower, the strip surface is further cleaned by mechanical brushing and electrolytic alkaline cleaning. Older lines may rely solely on direct firing of gas burners on the strip surface in order to burn off residual oils.

Following cleaning, the sheet passes into a radiant tube furnace containing a mixture of hydrogen and nitrogen that reduces surface iron oxides. This atmosphere produces a very clean surface that can be easily wet by the coating metal. Heating of the steel also takes place in the furnace. Annealing of cold-rolled sheet is achieved by heating usually just above the temperature for subcritical recrystallization (about 720 °C, or 1330 °F). Following recrystallization, it is generally desirable to cool the sheet down to near the bath temperature (about 460 °C, or 860 °F in the case of zinc coatings) in order to avoid overheating of the metal bath. Most modern lines have jet coolers to convectively cool the strip before bath entry.

The steel strip next enters a pot containing a bath of the molten coating metal. Shown schematically in Fig. 3, the pot region is where the actual hot dip coating process takes place. The first coating pots were little more than steel tubs heated by gas flames. Modern pots are steel vessels lined with ceramic refractory and heated by electric induction. Any hardware in the bath, such as the rolls, bearings, and support members, is usually made of 316 stainless steel or a similar alloy in order to resist attack by the molten metal.

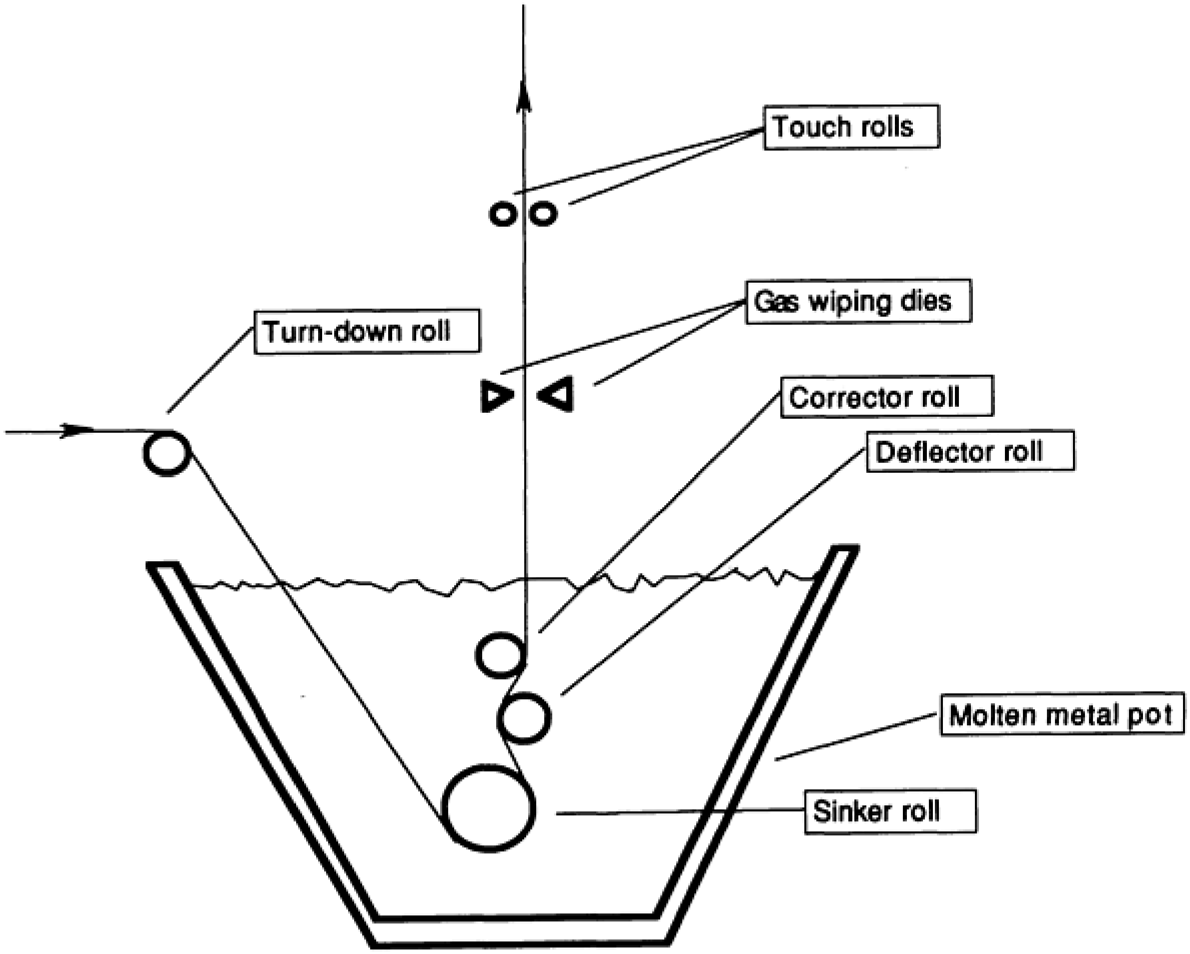

Fig. 3 Schematic of pot region in a typical continuous hot dip coating line

As the strip exits the pot, a film of molten coating adheres to the surface. The thickness of the molten film is controlled by passing the strip between gas wiping dies, which remove excess coating metal with a stream of gas. Coating thickness is determined by the geometry of the wipers, the velocity of the wiping gas, and the distance between the wiping dies and the sheet. The wiping gas may be steam, air, or nitrogen. On-line x-ray fluorescence or isotope gages continuously

monitor the actual coating thickness and enable rapid adjustments to be made. Figure 4 shows the region of a typical hot dip coating line where the coated strip exits the pot.

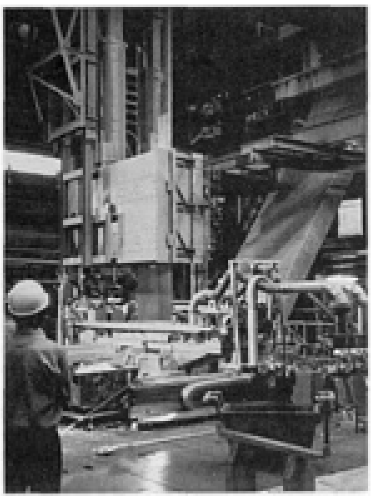

Fig. 4 Coated sheet exiting pot at a galvanizing line

In some coating facilities, the region above the pot and around the wipers is enclosed. The enclosed region is purged with the nitrogen wiping gas in order to reduce oxidation of the bath by air. This helps to reduce the incidence of surface defects and give a more uniform coating. In order to prevent fuming and copious clouds of zinc dust, it is also necessary to inject steam into the enclosure to form an oxide barrier on the surface of the molten metal.

Uniformity of coating thickness along and across the sheet surface is an important factor affecting the quality and performance of hot-dip-coated sheet. For this reason, it is critical to avoid fluctuations in the distance between sheet and wiping die that may result from poor sheet shape or vibrations. Shape-related difficulties are minimized by use of an adjustable deflector roll (see Fig. 3) that is submerged in the bath and pressed against the strip to reduce crossbow (i.e., excessive curvature in the plane of the sheet). The stationary corrector roll serves to keep the strip in alignment with the wiping dies. Variations in sheet-to-die distance resulting from sheet vibrations are minimized by use of the touch rolls located above the wipers. These reduce the amplitude of sheet vibration at the wiping dies by decreasing the unsupported length of sheet above the pot.

After coating, forced-air cooling is used to reduce sheet temperature. This prevents coating damage due to contact with the turnaround roll at the top of the upleg run. The sheet may be subjected to one or more post-treatments before being rewound into coil form, or sheared into cut lengths, at the exit end of the line.

Cold Lines. In cold processing, steel strip is cleaned, pickled, and fluxed in-line with no heating beyond that required to dry an aqueous flux solution on the sheet surface prior to entering the molten metal bath. Cold lines are also sometimes referred to as *flux* or *Cook-Norteman* lines. Because cold lines have limited heat-treating capability, incoming cold-rolled steel sheet requiring heat treatment will have been previously box annealed, or annealed on a separate continuous heat-treating line.

A typical cold line is shown schematically in Fig. 5. As with the hot line described above, this line is capable of producing 450,000 metric tons per year and coating sheet up to 1830 mm (72 in.) wide.

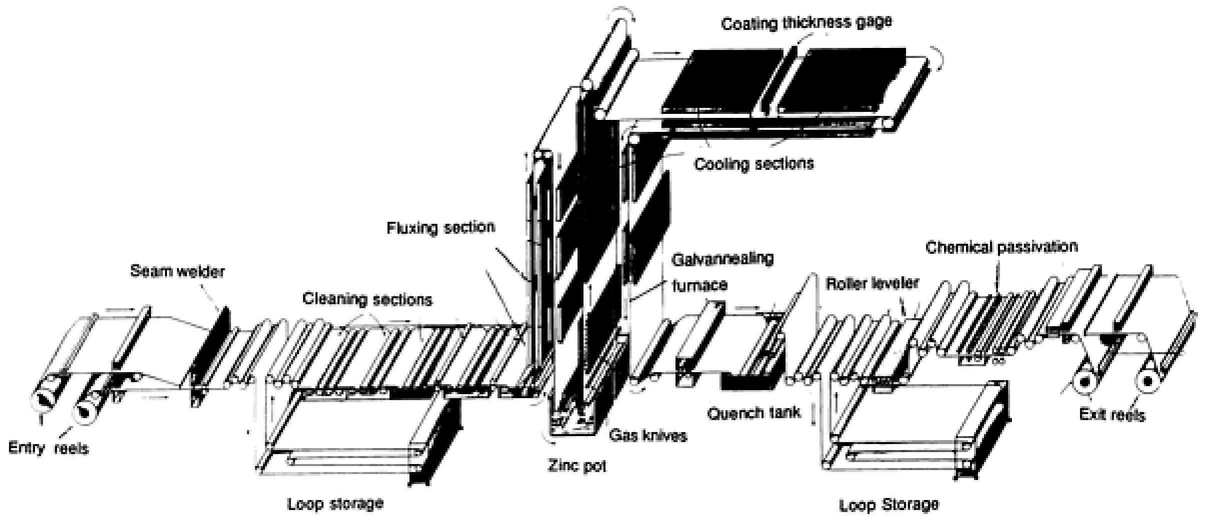

Fig. 5 Schematic diagram of a continuous galvanizing line. An example of a "cold" line without in-line annealing capability. See text for details.

Preparation of the sheet surface for coating includes alkaline and electrolytic cleaning, pickling in hydrochloric acid, and coating with flux, an aqueous solution of ammonium chloride and zinc chloride. After hot-air drying of the flux solution on the sheet surface, the strip enters the molten metal bath. Exhaust systems are essential to capture the fumes evolved when the fluxed sheet is submerged in the bath.

Because the sheet enters the bath at a relatively low temperature, considerable heat is transferred to the sheet by the bath. Consequently, cold lines generally have pots with a greater heating capacity in order to achieve the same throughput as an equivalent hot line. Downstream from the zinc pot, there is virtually no difference between hot and cold lines.

Post-Treatments. After the coating has been applied, several options are available for post-treatment of the strip. One possibility is galvannealing to produce zinc-iron alloy coatings, as discussed in the section "Zinc-Iron Alloy Coatings" in this article. Another is spangle minimizing, as described in the section "Zinc Coatings" in this article. Additional processing steps may be used to improve mechanical behavior, shape, corrosion resistance, and other properties as follows:

- Tension leveling or roller leveling to improve flatness
- Skin passing to make the surface smoother and to minimize yield-point behavior
- Overaging heat treatment to improve mechanical properties
- Slitting to narrower widths, shearing to produce cut lengths of sheet, and side trimming to remove nonuniform edges
- Chromate passivating to provide temporary protection against corrosion during shipment and storage. Passivation is done by spray or dip application of an acid chromate solution, removing excess solution by use of squeegee rolls, and drying the residue in hot air. Given the increasing environmental concerns about chromium, particularly in the hexavalent form, it is generally felt that other types of chemical passivation will eventually replace chromate.
- Oiling to provide lubricity during forming
- Oiling to provide temporary corrosion protection during shipment and storage. Inhibited oil is used in addition to chromate passivation to provide extra protection, or without chromate for applications in which chromate is inappropriate, such as those involving painting or contact with foodstuffs.
- Phosphating to improve formability
- Flash electroplating with iron to improve weldability

Some of these post-treatments are shown schematically in Fig. 2 and 5. Many could be done offline as separate operations, but in general they can be done more economically online as part of the continuous process, provided the necessary equipment is built into the line initially. Except in rare instances where unused space was deliberately left in a line, retrofit of the equipment for post-treating is problematic.

Zinc Coatings

Hot-dip-zinc-coated steel sheet, also called *galvanized*, is by far the most widely used coated sheet product. About 86% of the hot-dip-coated sheet produced in the United States (see Fig. 1) is zinc coated.

As evident in Table 1, hot dip zinc coatings for sheet are available in a broad range of coating thicknesses. For general-purpose galvanized sheet, 19 μm (0.75 mil) per side is the usual thickness. This corresponds to a two-side coating mass of 275 g/m^2 (0.9 oz/ft^2). Heavier coatings are used in applications requiring maximum corrosion resistance, such as highway drainage culverts. In the automotive industry, where formability and weldability are key considerations, lighter coatings such as 90 g/m^2 (0.3 oz/ft^2) are more typical.

Microstructure. The surface and cross section of a galvanized coating are shown in Fig. 6. Most of the coating is nearly pure zinc. Near to the steel-coating interface are prismatic particles of ζ-phase, a zinc-iron intermetallic compound containing about 6% Fe (see Fig. 7).

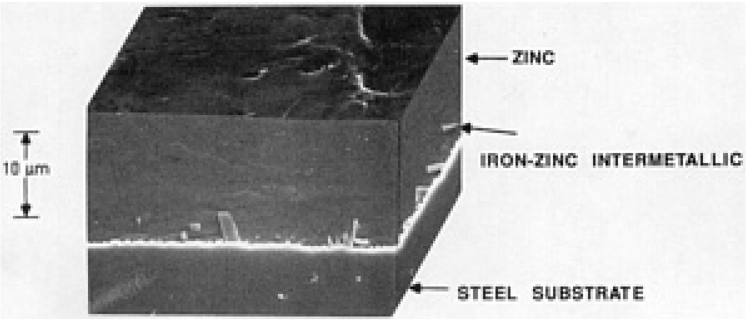

Fig. 6 Galvanized coating microstructure. Scanning electron microscope cross section

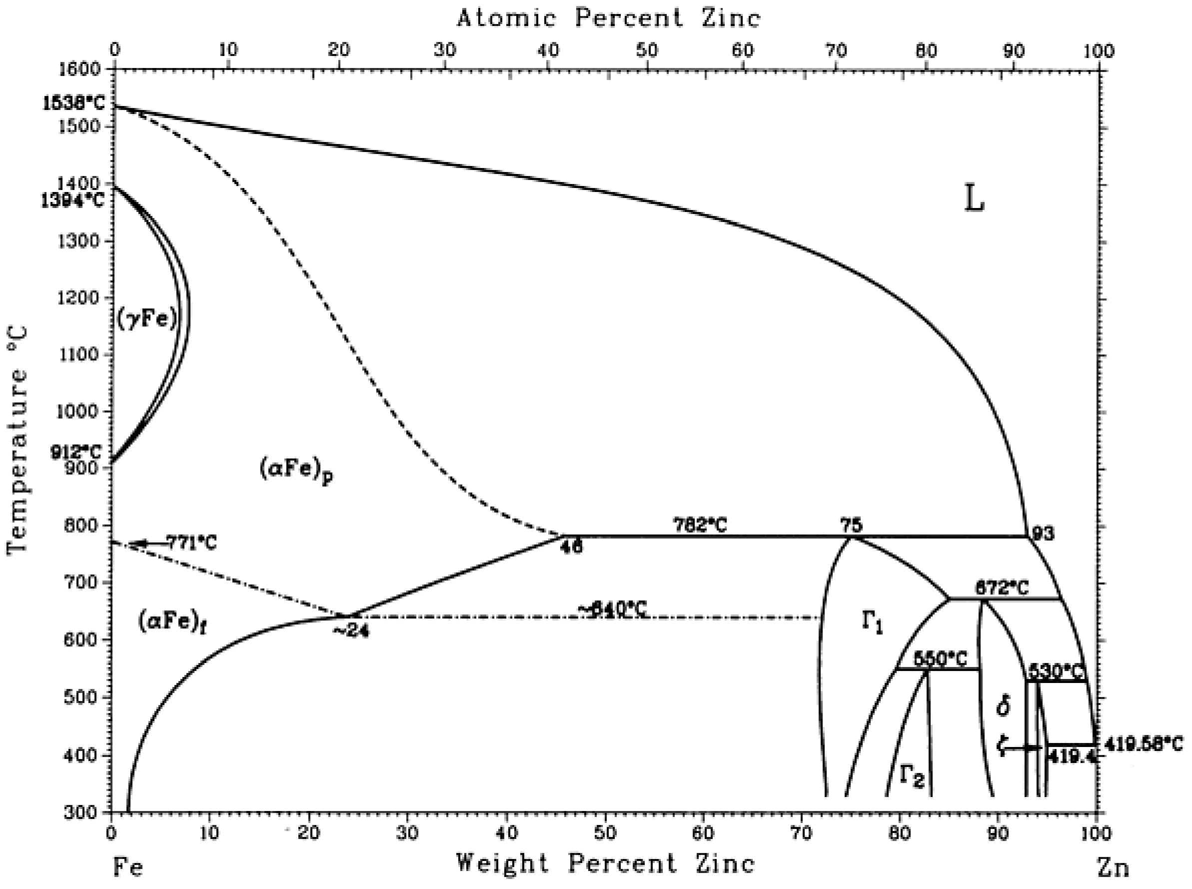

Fig. 7 Iron-zinc equilibrium phase diagram. Source: Ref 22

Alloy Additions. Aluminum, typically in the range of 0.1 to 0.2%, is added to the zinc bath in order to prevent formation of a thick, continuous layer of zinc-iron intermetallic that could lead to poor coating adhesion during forming. Aluminum reacts preferentially with the steel to form a thin layer of an iron-aluminum intermetallic that acts as a barrier and delays the growth of the zinc-iron intermetallic layer.

Lead was originally present in galvanized coatings as an impurity from the smelting process. The presence of lead causes the formation of spangles, the familiar dendritic surface pattern visible on galvanized ductwork and garbage cans. Historically, users relied on the spangled appearance to distinguish hot dip galvanized from less corrosion-resistant thin electroplated sheet. In order to maintain this distinction, it became common practice to add lead (typically about 0.1%) to keep the spangles, even after refining methods for producing lead-free zinc were developed. With increasing environmental concerns, however, the use of lead is declining. Antimony is now increasingly often used to produce spangled coatings without the environmental drawbacks of lead.

Spangles are also prone to spangle cracking, a phenomenon in which cracking occurs along certain crystallographic planes during forming of the coated sheet. For painted end uses, such as automobiles and metal buildings, a smoother, nonspangled surface is desirable for appearance purposes. When this is the case, lead or the other spangle-promoting elements can be omitted from the bath. When it is desirable to produce both spangled and nonspangled galvanized on the same line without having to change the composition of the zinc bath, an alternate approach is to spray the surface of the molten coating with steam, water, or fine zinc powder just after wiping. The spray increases the number of sites for spangle nucleation, which minimizes the spangle size so that the coating surface is smoother. Further increases in surface smoothness are achieved by a light temper roll of the coated product.

Corrosion Resistance. Zinc coatings protect steel in three ways:

- Initially, a continuous film of zinc at the surface of steel serves as a barrier to separate the steel from the environment.

- At voids in the coating, such as scratches and cut edges, the zinc behaves as a sacrificial anode to provide galvanic protection.
- After anodic dissolution of the zinc metal, zinc hydroxide can precipitate at the cathodic areas of exposed steel, thus forming a secondary barrier.

In order for a coating metal to serve as an effective corrosion barrier, it should corrode at a slower rate than the steel substrate. As shown in Table 5, the corrosion rate of zinc varies greatly, depending on the location of the exposure (Ref 17). Time of wetness and chloride and sulfate level are among the environmental factors that affect the corrosion rate of zinc. Nevertheless, zinc is generally one to two orders of magnitude more corrosion resistant than steel in a wide range of outdoor environments.

Table 5 Corrosion of zinc and steel at 45 locations (10 × 15 cm test specimens)

Location	2-year exposure, grams lost	
	Zinc	Steel
Norman Wells, N.W.T., Canada	0.07	0.73
Phoenix, AZ	0.13	2.23
Saskatoon, Sask., Canada	0.13	2.77
Esquimalt, Vancouver Island, Canada	0.21	6.50
Fort Amidor Pier, Panama, Canal Zone (C.Z.)	0.28	7.10
Melbourne, Australia	0.34	12.70
Ottawa, Ontario, Canada	0.49	9.60
Miraflores, Panama, C.Z.	0.50	20.9
Cape Kennedy, 0.8 km (0.5 mile) from ocean	0.50	42.0
State College, PA	0.51	11.17
Morenci, MI	0.53	7.03
Middletown, OH	0.54	14.00
Potter County, PA	0.55	10.00

Bethlehem, PA	0.57	18.3
Detroit, MI	0.58	7.03
Manila, Philippine Islands	0.66	26.2
Point Reyes, CA	0.67	244.0
Trail, B.C., Canada	0.70	16.90
Durham, NH	0.70	13.30
Halifax (York Redoubt), N.S.	0.70	12.97
South Bend, PA	0.78	16.20
East Chicago, IN	0.79	41.1
Brazos River, TX	0.81	45.4
Monroeville, PA	0.84	23.8
Daytona Beach, FL	0.88	144.0
Kure Beach, NC, 240 m (800 ft) lot	0.89	71.0
Columbus, OH	0.95	16.00
Montreal, Quebec, Canada	1.05	11.44
London (Battersea), Eng.	1.07	23.0
Pittsburgh, PA	1.14	14.90
Waterbury, CT	1.12	11.00
Limon Bay, Panama, C.Z.	1.17	30.3
Cleveland, OH	1.21	19.0
Dungeness, Eng.	1.60	238.0

Newark, NJ	1.63	24.7
Cape Kennedy, 55 m (60 yd) from ocean, 9 m (30 ft) elevation	1.77	80.2
Cape Kennedy, 55 m (60 yd) from ocean, ground level	1.83	215.0
Cape Kennedy, 55 m (60 yd) from ocean, 18 m (60 ft) elevation	1.94	64.0
Bayonne, NJ	2.11	37.7
Pilsey Island, Eng.	2.50	50.0
Kure Beach, NC, 25 m (80 ft) lot	2.80	260.0
London (Stratford), Eng.	3.06	54.3
Halifax (Federal Building), N.S.	3.27	55.3
Widness, Eng.	4.48	174.0
Galeta Point Beach, Panama, C.Z.	6.80	336.0

Source: Ref 17

The corrosion loss of a hot dip zinc coating is generally considered to be linear. Because of this, the life of a zinc coating is proportional to its thickness. In the industrial environment of Bethlehem, PA (see Fig. 8), the corrosion loss is approximately linear with time at an average rate of about 2 μm/year (Ref 18). Near-linear behavior is also observed in marine and rural environments.

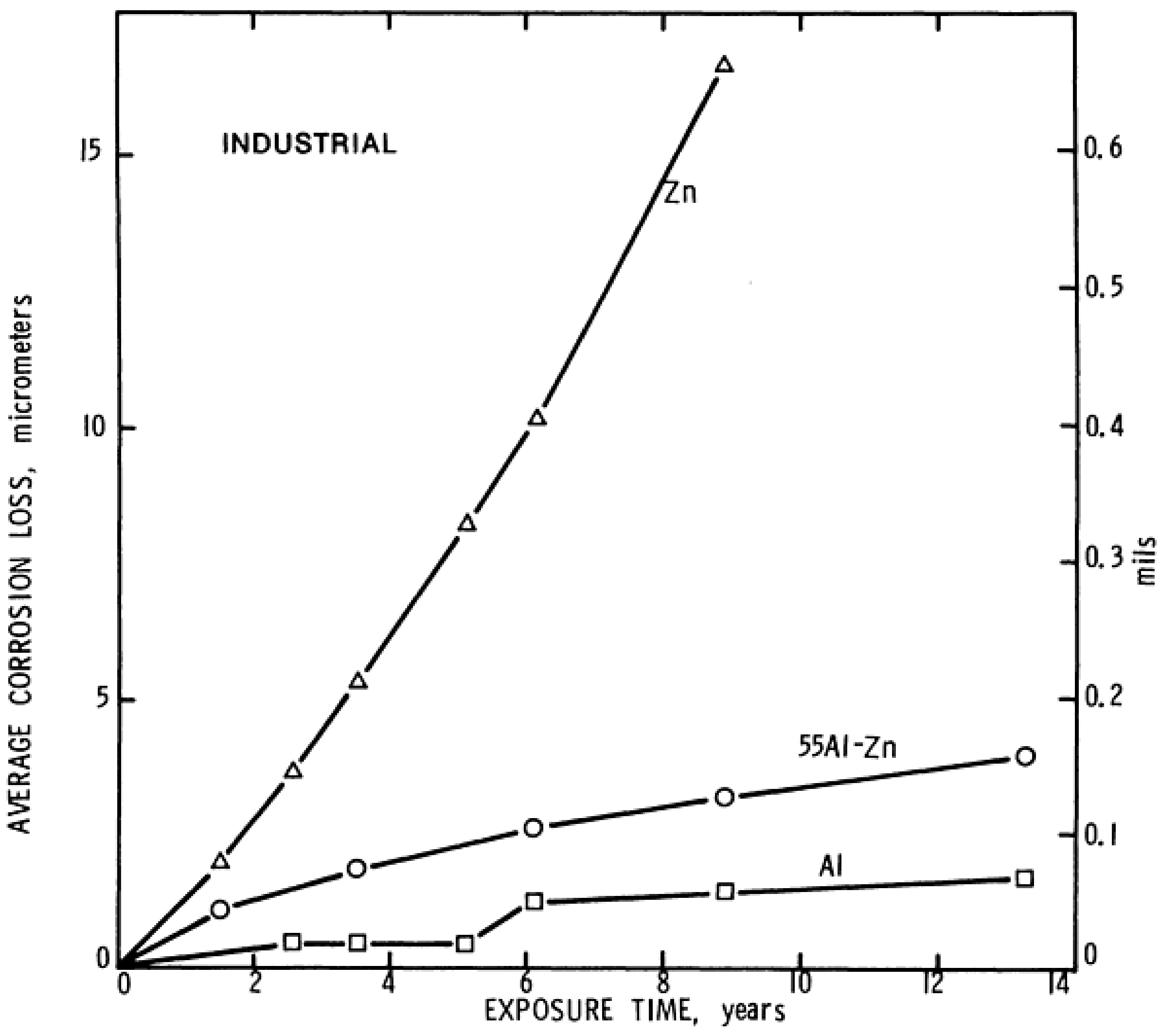

Fig. 8 Corrosion losses of hot dip coatings in the industrial environment of Bethlehem, PA. Source: Ref 18

The sacrificial properties of zinc coatings derive from the position of zinc relative to steel in the galvanic series. The corrosion potential of zinc is usually about 0.4 V less noble than steel in most environments at normal ambient temperatures. Thus, zinc will sacrifice itself to provide galvanic protection to steel exposed at voids in the coating. The effective distance of the sacrificial protection increases with the conductivity of the environment, but it is generally limited to a few millimeters in most atmospheres.

Other Properties. Zinc coatings provide some protection to steel against high-temperature oxidation. However, their usefulness for this purpose is limited to a maximum temperature of about 260 °C (500 °F) because of the tendency of zinc at higher temperatures and long exposure times to diffuse into the grain boundaries of the steel and cause embrittlement.

Zinc coatings may impair the formability of steel sheet under certain conditions. For example, in stretch-forming operations, the increased frictional coefficient of the zinc coating against the punch tends to concentrate the strain within a smaller area and thus result in less total stretch before fracture. Galling and coating pickoff can also occur in severe forming operations. The buildup of particulate material on die surfaces may cause impressions and poor appearance on the surface of formed parts.

The life of spot welding electrodes is reduced by zinc coatings, as shown in Table 6. This reduction occurs as a result of alloying of the copper electrode with zinc, which leads to higher local resistance, greater heating, and increased pitting and erosion of the electrode contact surface. Lower tip life reduces productivity and increases manufacturing costs because of more frequent interruptions to the welding operation to redress tips.

Table 6 Effects of hot dip coatings on tip life during spot welding of steel sheet

Type of coating	Coating mass, g/m^2	Electrode tip life, number of spots
None	. . .	>10,000
Zinc	197	2,500
Zinc-iron	110	6,000
Zn-55Al	150	700
Aluminum type 1	120	500

Source: Ref 15, 19

Galvanized sheet is used in both bare and painted conditions. In order for paint to have good adhesion to a hot-dip-zinc-coated surface, it is important that the surface is properly pretreated. Zinc phosphate or complex oxide pretreatments are the usual pretreatments for coil-line prepainted sheet. For galvanized components that are painted after fabrication, such as automobile body components, zinc phosphate or zinc phosphates modified with nickel or manganese are commonly used.

In the automotive industry, resistance to electrophoretic paint (e-coat) cratering is an important property. After phosphating, most automobile bodies produced today are primed with cathodic e-coat. In the e-coating process, the phosphated automobile body is immersed in an aqueous bath containing suspended, positively charged paint particles. A negative potential of several hundred volts is applied to the part, and the positively charged paint particles are attracted to the metal surface. Here the paint particles contact hydroxyl ions produced by the cathodic breakdown of water and coalesce to form a paint film. At higher voltages, the dielectric properties of the deposited paint film may be exceeded, with the result that sparking occurs. The heat generated by the sparks causes localized film disruption and premature curing of the paint. After overall curing of the paint, the sparked areas form pinpoint-size craters that are detrimental to the appearance of the painted surface.

Resistance to e-coat cratering can be expressed in terms of a threshold voltage below which cratering does not occur. As shown in Table 7, zinc-coated surfaces have a lower cratering threshold voltage than bare steel and hence are more prone to cratering (Ref 20). Although cratering can be avoided by reducing the voltage applied during e-coating to a level below the threshold, this may result in less productivity due to lower rates of coating deposition and slower line speeds.

Table 7 Effects of hot dip coatings on threshold voltages for cratering of cathodic electrophoretic primer

Type of surface	Cratering threshold, V
Uncoated bare steel	>400
Zinc	275
Zinc-iron	225
Zn-55Al	375

Aluminum	>400

Additional information about galvanized coatings is available in the article "Batch Hot Dip Galvanized Coatings" in this Volume.

References cited in this section

15. H.E. Townsend and L. Allegra, Precoated Sheet Steel for Automotive Applications, *Automotive Corrosion by Deicing Salts,* R. Baboian, Ed., National Association of Corrosion Engineers, 1981, p 337-351
17. D.C.H. Nevinson, Corrosion of Zinc, *Corrosion,* Vol 13, *ASM Handbook* (formerly 9th ed. *Metals Handbook*), ASM International, 1987, p 758
18. H.E. Townsend and J.C. Zoccola, *Materials Performance,* Vol 10, 1979, p 13-20
19. P. Howe and S.C. Kelley, "A Comparison of the Resistance Spot Weldability of Bare, Hot-Dipped, Galvannealed, and Electrogalvanized DQSK Sheet Steels," Paper 880280, Society of Automotive Engineers, 1988
20. R.G. Hart and H.E. Townsend, "Mechanism of Cathodic Electrocoat Primer Cratering," Paper 831818, *Proceedings of the Second Automotive Corrosion and Prevention Conference, P-136,* Society of Automotive Engineers, 1983
22. H. Baker, Ed., *Alloy Phase Diagrams,* Vol 3, *ASM Handbook,* ASM International, 1992, p 2·56, 2·206

Zinc-Iron Alloy Coatings

Also known as *galvanneal,* zinc-iron alloy coatings produced by the thermal diffusion and alloying of a galvanized coating with a steel substrate were developed during the 1970s, primarily for painted applications. Today, galvanneal is used increasingly often by the automobile industry because of its improved paintability and spot weldability (see Table 6) relative to a pure hot dip zinc coating of equal thickness. The iron content of the alloyed coating is usually in the range of 9 to 12%. For automotive body panels, the typical coating thickness for galvanneal is 7 μm (0.275 mil) with a coating mass of 50 g/m^2 (0.16 oz/ft^2).

In galvannealing, galvanized sheet is heated in-line just after coating and wiping in order to allow interdiffusion of iron from the substrate with zinc from the coating to form an iron-zinc alloy coating. Both gas-fired and induction furnaces are used for galvannealing. Heating to temperatures in the range of 500 to 550 °C (930 to 1020 °F) for about 10 s is sufficient to produce a 50 g/m^2 (0.16 oz/ft^2) coating with an iron content of about 10%.

Actual alloying time is influenced by coating thickness and the compositions of both zinc bath and steel substrate (Ref 21). More time is required to alloy a thicker coating. Alloying time also increases with increasing aluminum content of the bath, but it decreases for ultra-low-carbon, titanium- or titanium-niobium-stabilized steels as compared to ordinary low-carbon grades.

The galvannealing process is usually controlled by the "cook and look" method, in which the operator sets the initial galvannealing furnace conditions based on prior experience for the particular combination of steel thickness, line speed, bath composition, coating thickness, and steel composition. The operator then looks at the surface of the sheet as it exits the galvanneal furnace and adjusts the heat input to the furnace temperature until the sheet surface changes from the bright and shiny appearance of a pure zinc coating to the dull gray of an alloyed coating, except at the very edges of the strip where the coatings tend to be slightly thicker and take longer to alloy. Once this condition is attained, edge heaters can be employed in order to complete the alloying of the strip edges. The operator is also assisted in controlling the galvannealing process by information on the iron content of the coating provided by on-line x-ray fluorescence gages. Ideally, it would be desirable to have a fully automated galvanneal process based on actual measurement and control of strip temperature. However, this has been an elusive goal because of the difficulties inherent in temperature measurement by use of radiation pyrometry when surface emissivity changes as alloying proceeds.

The corrosion resistance of galvanneal is similar to that of a pure zinc coating. However, because of the iron in the coating, the galvanic potential is not as great as that of pure zinc. Also, the corrosion products are reddish brown. As a result, protection against rust stain at edges and scratches is not as good as with pure zinc.

Compared to ordinary galvanized metal, galvanneal is generally easier to paint without the use of special pretreatments. This is believed to result at least in part from the microscopically rougher surfaces of galvanneal (as seen when Fig. 6 is compared to Fig. 9 and 10). However, galvanneal coatings are more prone to cratering during e-coating, as shown in Table 7.

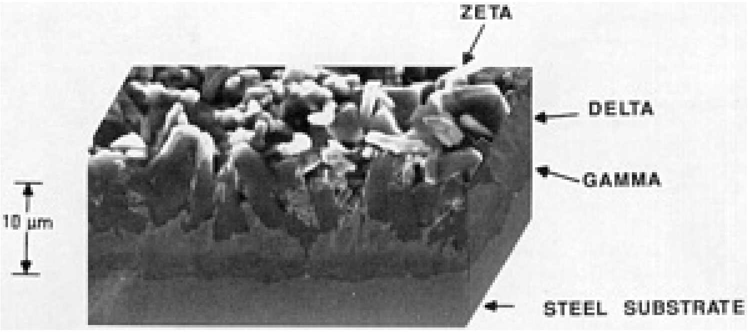

Fig. 9 Galvanneal coating microstructure composed of zeta, delta, and gamma phases. Scanning electron microscope cross section

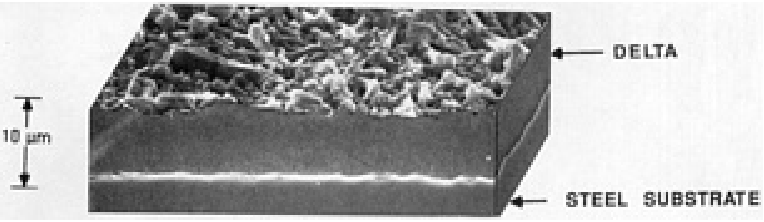

Fig. 10 Galvanneal coating microstructure composed of mostly delta phase. Scanning electron microscope cross section

Microstructure. As shown on the iron-zinc phase diagram, Fig. 7, a number of intermetallic compounds are possible in a galvanneal coating. In Fig. 9, a galvanneal coating composed of several phases is shown. The ζ-phase at the outer surface has a monoclinic crystal structure and contains about 6% Fe. It is believed that the ζ-phase has a relatively high friction coefficient and is thus undesirable for some forming and stamping operations. The intermediate δ-layer has a hexagonal close-packed structure and contains iron in the range of 8 to 12%. Next to the steel is a layer labeled simply Γ. In a galvanneal coating containing a mixture of these phases, it is difficult to distinguish between Γ_1 and Γ_2, both of which are cubic phases with iron contents in the range of roughly 16 to 28%. Thus, the Γ-layer shown in Fig. 9 could be Γ_1, Γ_2, or a mixture of the two.

The cubic Γ-phases have a large number of atoms per unit cell and limited ductility. Their presence is more likely with thicker coatings and higher iron contents. They also lead to powdering of the coating during forming. Powdering is undesirable because it results in a loss of coating and can lead to the buildup of coating debris on die surfaces, which in turn causes print-through and poor appearance on the surfaces of formed parts.

Because of the problems noted above with the zeta and gamma phases, galvanneal process conditions are ideally aimed at producing coatings composed of mostly δ-phase (see Fig. 10). However, as the thickness of the coating increases above about 9 μm, it becomes more difficult to make an all-δ coating.

Reference cited in this section

21. V. Jagannathan, The Influence of Coating Characteristics on Powdering and Corrosion Resistance of Galvanneal Coated Steel Sheet, *Proceedings of the Second International Conference on Zinc and Zinc Alloy Coated Steel Sheet,* Verlag Stahleisen, 1992, p 127-131

Aluminum Coating, Type 2

Two kinds of aluminum coating are produced. Type 2 is a thicker coating (typically 30 to 50 μm) that is applied by dipping in an unalloyed aluminum bath. This product is used for outdoor construction applications such as roofing, culverts, and silos that require resistance to atmospheric corrosion and have limited formability requirements.

As shown in Fig. 11, the microstructure of a Type 2 coating consists of an aluminum overlay and a thick iron-aluminum intermetallic layer. The formability and adhesion of the coating are limited by the poor ductility of this intermetallic layer.

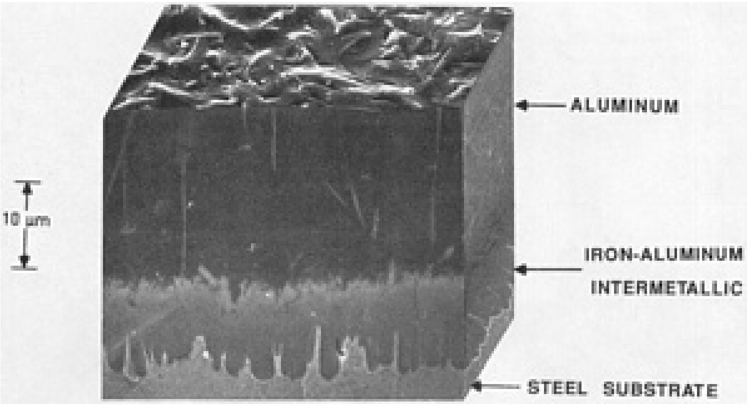

Fig. 11 Type 2 aluminum coating microstructure. Scanning electron microscope cross section

The outdoor durability of the Type 2 aluminum coating is excellent in most atmospheres because of the good barrier properties of the thick coating and its relatively low corrosion rate, as given in Fig. 8. However, except in severe salt environments, the aluminum coating does not provide sacrificial protection to steel. As a result, Type 2 tends to show rusting at cut edges and rust staining of adjacent surfaces in rural and industrial environments. In marine environments, the aluminum coating is susceptible to crevice corrosion.

Aluminum Coating, Type 1 (Aluminum-Silicon Alloy)

Type 1 aluminum coating is a thinner, aluminum-silicon alloy coating intended primarily for applications requiring formability and resistance to high temperatures, such as automobile exhaust components. Type 1 aluminum coatings are also applied to improve appearance. For most uses, the usual thickness of a Type 1 coating (Class 40) is about 20 to 25 μm (0.8 to 1 mil). When maximum formability is a critical requirement, a thinner 12 μm (Class 25) coating is specified.

Silicon is present in a Type 1 coating in the range of 5 to 11% in order to prevent formation of a thick iron-aluminum intermetallic layer, which would impair coating adherence and formability. Instead, a thinner iron-aluminum-silicon alloy layer is formed (Fig. 12).

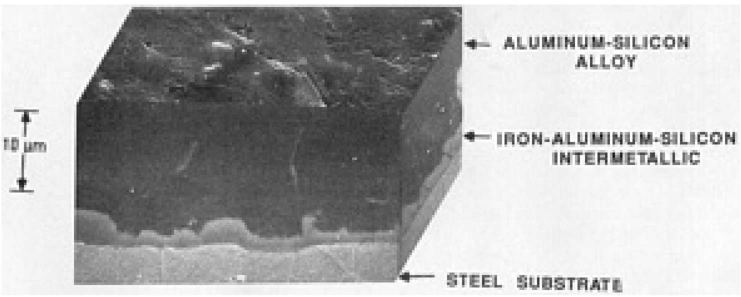

Fig. 12 Type 1 aluminum coating microstructure. Scanning electron microscope cross section

Aluminum has a more detrimental effect than zinc on the spot weldability of steel sheet. Accordingly, aluminum Type 1 and Zn-55Al alloy coatings show the lowest tip lives among the hot-dip-coated products listed in Table 6.

Zn-5Al Alloy Coatings

According to the aluminum-zinc equilibrium phase diagram (Fig. 13), a low-melting eutectic alloy occurs at 5% Al. Steel sheet coated with alloy coatings near to this composition (i.e., 4 and 7% Al) are more corrosion resistant than an equal-thickness galvanized coating when tested in accelerated laboratory tests or in severe marine atmospheres. However, the same alloy coatings perform no better than pure zinc in moderate marine, industrial, and rural environments, as shown in Table 8.

Table 8 Lifetimes of hot dip zinc and zinc-alloy coatings

Environment	Years to first rust			
	Zn	Zn-4Al	Zn-7Al	Zn-55Al
Severe marine				
25 m from ocean, Kure Beach, NC	4	9	9	15
Moderate marine				
250 m from ocean, Kure Beach, NC	16	15	14	>25
Rural				
Saylorsburg, PA	14	14	14	>25
Industrial				
Bethlehem, PA	10	10	9	>25

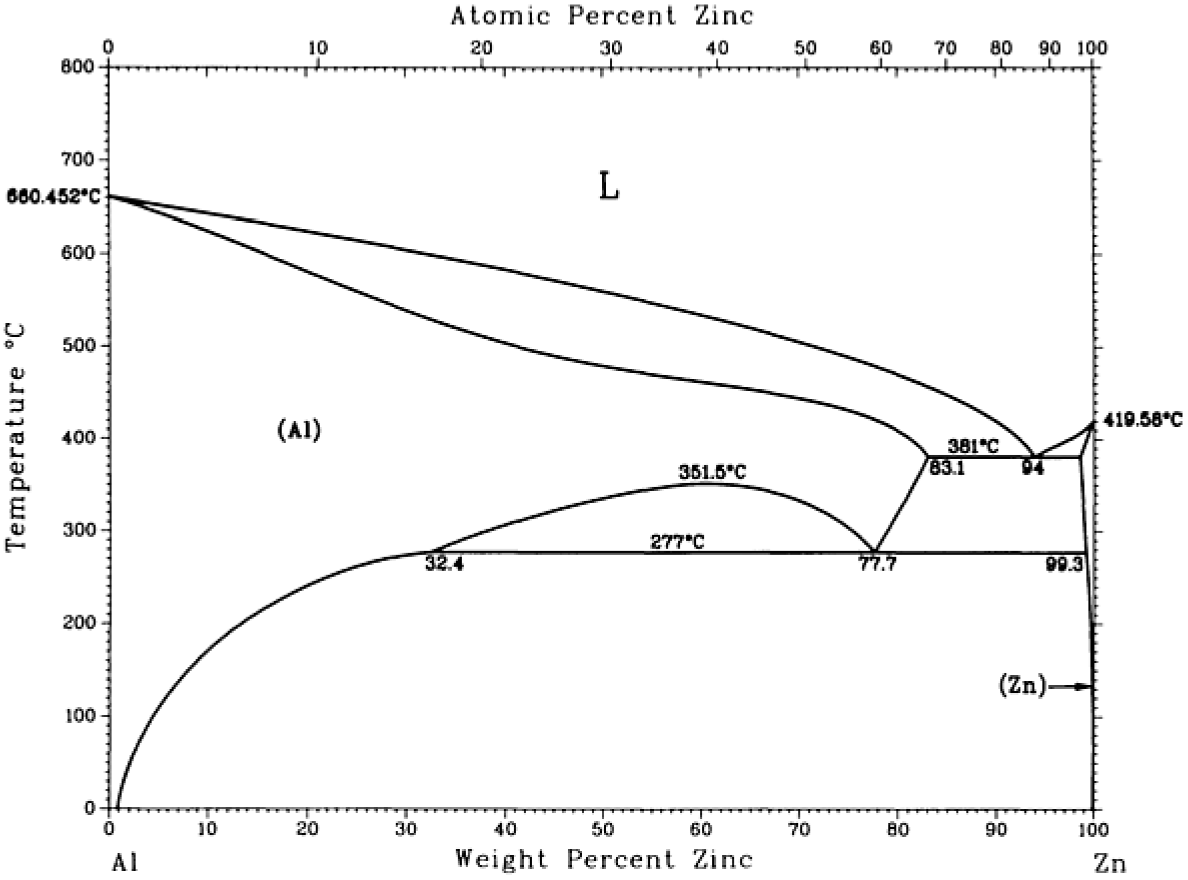

Fig. 13 Aluminum-zinc equilibrium phase diagram. Source: Ref 22

Commercially produced Zn-5Al alloy coatings have small additions of other elements. Galfan contains about 0.1% of mischmetal rare earths (cerium and lanthanum), which are added to increase the wettability of the bath and reduce the incidence of bare spots in the coating (Ref 25). Superzinc contains 0.1% Mg, which is added to counteract the adverse effects of lead and tin impurities on intergranular corrosion and paint adhesion (Ref 26).

The eutectic coatings generally have no added lead and no spangle. As a result, they are free of spangle cracking, and the coatings have better resistance to cracking during forming than does ordinary spangled galvanized.

The microstructure of a typical Zn-5Al alloy coating is characterized by a matrix of 5% Al eutectic and scattered regions of primary zinc (Fig. 14). No intermetallic layer is visible on steel sheet coated with the eutectic alloy because bath temperature is lower, and aluminum content is higher, than with ordinary galvanized.

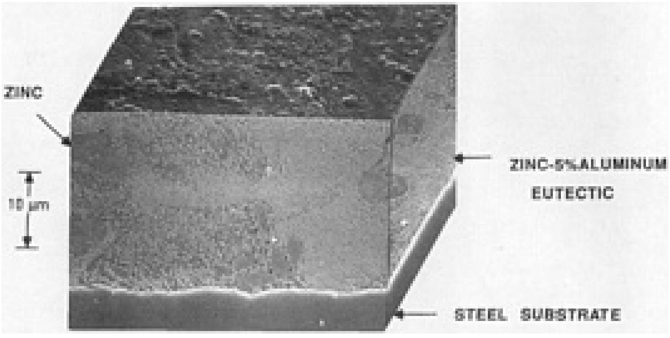

Fig. 14 Zn-5Al coating microstructure. Scanning electron microscope cross section

References cited in this section

22. H. Baker, Ed., *Alloy Phase Diagrams,* Vol 3, *ASM Handbook,* ASM International, 1992, p 2·56, 2·206
23. J.J. Friel and H.E. Townsend, Corrosion Resistance of Zinc and Zinc-Aluminum Alloy Coatings, *Sheet Metal Industries,* Vol 60 (No. 9), 1983, p 506-507
24. H.E. Townsend, Twenty-Five-Year Corrosion Tests of 55% Al-Zn Alloy Coated Steel Sheet, *Materials Performance,* Vol 32 (No. 4), 1993, p 68-71
25. J. Pelerin, B. Bramaud, J.F. Nouville, D. Coutsouradis, D.C. Herrschaft, and S.F. Radtke, Galfan: A New Zinc-Aluminum Coating, *Proceedings of the 13th International Galvanizing Conference,* Zinc Development Association, London, 1982, p 48/1-49/9
26. T. Kano and S. Higuchi, "Development and Properties of Zinc-Aluminum Alloy Coated Steel Sheet with High Corrosion Resistance (Superzinc)," Nippon Steel Technical Report 25, Nippon Steel Corp., April 1986, p 29-37

Zn-55Al Alloy Coatings

The purpose of Zn-55Al alloy coatings is to combine the excellent long-term atmospheric corrosion resistance of aluminum with the sacrificial characteristics of galvanized in a single coating (Ref 23, 24). Long-term studies showed that the 55% Al alloy was the optimum composition of the aluminum-zinc system. Steel sheet coated with this alloy was first produced commercially in 1972 in the United States under the trademark Galvalume. Coating thicknesses are usually in the range of 20 to 25 μm (0.8 to 1 mil).

About 80 vol% of the complex microstructure of the Zn-55Al alloy coating (Fig. 15) is composed of cored, aluminum-rich dendrites, representing the first solid to form during cooling. As predicted by the phase diagram (Ref 22) (Fig. 13), the final liquid to freeze in the interdendritic regions is enriched in zinc. A thin (1 to 2 μm) iron-aluminum-zinc intermetallic layer is evident at the steel surface.

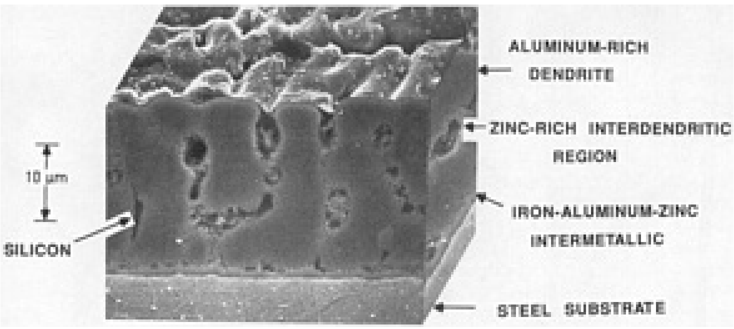

Fig. 15 Zn-55Al coating microstructure. Scanning electron microscope cross section

About 1.5% Si is added to the Zn-55Al bath for the purpose of minimizing alloy-layer growth during dipping. It is present in the form of scattered, needlelike particles, mostly in the interdendritic region. Some of the silicon is also concentrated in a thin layer at the overlay/alloy-layer interface, where it functions as a barrier to alloy-layer growth during the coating process.

Atmospheric corrosion resistance of the Zn-55Al alloy coating is generally at least two to four times that of an equal thickness of galvanized coating, as evident in Fig. 8 and Table 8. Most of the corrosion of the alloy coating takes place in the zinc-rich interdendritic regions. This enables the coating to exhibit the sacrificial characteristics of a galvanized coating. As the zinc-rich interdendritic regions of the coating corrode, zinc corrosion products are trapped in the

interdendritic interstices and act as a barrier that slows further corrosion. As a result, the corrosion rate of the alloy coating decreases with time, as shown in Fig. 8.

Although the effective distance of the galvanic action provided by a Zn-55Al coating is roughly half that of galvanized, it is generally adequate to protect the cut edges of steel sheet with a thickness of one millimeter or less in most environments. Moreover, because of the greater durability of the 55% aluminum-zinc coating, it provides galvanic protection for a longer duration.

As shown in Fig. 8, the corrosion rate of the 55% Al alloy is greater than that of an aluminum coating. However, unlike an aluminum coating, the 55% Al alloy is able to prevent rust staining at cut edges and scratches, as well as resist crevice corrosion in marine environments.

As shown in Table 6, the spot welding tip life of the 55% Al coated sheet is less than that of galvanized. This reduction is attributed to the adverse effect of aluminum.

References cited in this section

22. H. Baker, Ed., *Alloy Phase Diagrams,* Vol 3, *ASM Handbook,* ASM International, 1992, p 2·56, 2·206
23. J.J. Friel and H.E. Townsend, Corrosion Resistance of Zinc and Zinc-Aluminum Alloy Coatings, *Sheet Metal Industries,* Vol 60 (No. 9), 1983, p 506-507
24. H.E. Townsend, Twenty-Five-Year Corrosion Tests of 55% Al-Zn Alloy Coated Steel Sheet, *Materials Performance,* Vol 32 (No. 4), 1993, p 68-71

Lead-Tin Alloy Coatings

Lead-tin alloy coatings are widely known as *terne* coatings, from the French word that describes their characteristically dull surface appearance. Generally, 3 to 15% Sn is added to the hot dip bath in order to facilitate wetting of the steel substrate. The solid solubility of tin in lead is very small, and it appears as patches in the lead overlay matrix (Fig. 16).

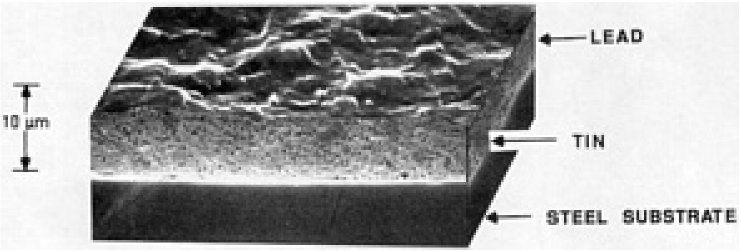

Fig. 16 Terne coating microstructure. Scanning electron microscope cross section

Terne-coated steel sheet has a long history of use in automotive fuel tanks and tubing because of its excellent weldability, solderability, and formability. Moreover, the low corrosion rate of terne allows it to function primarily as a barrier coating without the evolution of voluminous corrosion products that might otherwise clog fuel and hydraulic systems. Nickel terne is produced by applying the usual terne coating to steel sheet that has first been electroplated with a thin (1 g/m^2) nickel layer in order to improve the barrier properties.

Owing to concerns about the effects of lead in the environment, the future of terne is uncertain. Work is now under way to find suitable replacement materials. Zinc-alloy coatings (possibly hot dip zinc-iron or electroplated zinc-nickel) with an organic topcoat are among the most likely candidates.

Continuous Electrodeposited Coatings for Steel Strip

Stavros G. Fountoulakis, Bethlehem Steel Corporation

Introduction

CONTINUOUS ELECTRODEPOSITION involves electroplating a pure metal or alloy coating onto an endless steel strip. In practice, this is achieved by unwinding a coil of strip; welding it to the tail end of the preceding coil; passing it through the sequence of surface preparation, electroplating, and surface post-treatment; rewinding it; and then again cutting it from the preceding coil. The facilities used for this process are commonly called *continuous plating lines* and can handle strip of up to about 2080 mm (82 in.) in width. Strip is arbitrarily defined as having a rectangular cross section with a maximum thickness of 5 mm (0.2 in.) and width greater than 25 mm (1 in.) (Ref 1).

The greatest percentage of the steel processed in continuous steel strip plating lines is electrodeposited with one of five metallic coatings: zinc, tin, chromium, and alloys of zinc with either nickel or iron. Several other metallic coatings, such as copper, nickel, brass (Cu-Zn), and terne (Pb-Sn), are also applied by continuous steel strip plating but on a relatively smaller scale and production volume. Continuous strip plating of precious metals for electronics applications is also a related process. However, this too differs markedly from steel strip plating in both facility design and scale.

In 1991, the total capacity of continuous steel strip plating lines worldwide exceeded 34 million tons. It is very likely that more tonnage of steel and also more surface area is coated by this process than in all other batch-type plating processes combined (Tables 1, 2).

Table 1 Worldwide capacity for electrolytic tin- and chromium-coated steel for canstock by region, 1991

Region	Total capacity, tons/yr	ETLs	Number of continuous plating lines		
			ECPLs	Dual	Total
Western Europe	6,900,000	27	2	10	39
North America	6,665,000	16	6	7	29
Japan	3,288,000	13	9	. . .	22
Latin America	1,997,000	14	1	3	18
S.E Asia	1,220,000	9	. . .	1	10
Eastern Europe	1,510,000	5	1	. . .	4
South Korea	680,000	1	. . .	4	5
South Africa	550,000	1	1	1	3
Australia	500,000	2	. . .	. . .	2
Taiwan	250,000	3	. . .	. . .	3
China	160,000	2	. . .	. . .	2

Total	**22,720,000**	**90**	**19**	**25**	**134**

Source: Ref 4

(a) ETLs, electrotinning lines; ECPLs, electrolytic chromium plating lines,

Table 2 Worldwide capacity for electrolytic zinc and alloy (Zn-Ni, Zn-Fe) coated steel strip for primarily automotive body panels, 1991

The list does not include some medium and small strip plating lines that plate narrow steel strip for appliances, furniture, and other nonautomotive applications.

Region	**Total capacity, tons/yr**	**Number of plating lines**		
		Zn only	**Zn and Zn alloy**	**Total**
North America	3,500,000[(a)]	4	5	9
Japan	4,320,000[(b)]	1	10	11
Europe	2,480,000[(c)]	8	6	14
Korea	700,000	. . .	2	2
Taiwan	200,000	. . .	1	1
Latin America	250,000	1	1	1
Total	**11,450,000**	**13**	**25**	**38**

(a) See Table 4.

(b) See Table 6.

(c) See Table 5.

This article begins by describing some of the applications of continuous electroplated steel, to explain why there is a need for such a high production volume. For each category of applications, the type of coating needed and the key attributes of the coating are noted. The bulk of the article describes electrodeposition technology, including plating line components and process classification.

Acknowledgements

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References

1. L.W. Austin and J.L. Lindsay, "Continuous Steel Strip Electroplating," slide course, American Electroplaters and Surface Finishers Society, 1989
4. E. Mayo, World Tin Mill Production, *The Canmaker,* Dec 1992
7. G.W. Bush, Development in the Continuous Galvanizing of Steel, *Journal of Metals,* Aug 1989
8. B. Meuthen, Aspects of Zinc and Zinc Alloy-Coated Sheet Steel in Western Europe--with a Special View of the German Scene, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan, p 91-100
9. S.G. Denner, An Overview of the Manufacture and Application of Zinc and Zinc Alloy Coated Sheet Steel in North America, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan, p 101-110
10. T. Hada, Present and Future Trends of Coated Steel for Automotive Use, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan, p 111-119

Applications

There are many applications for continuously electrodeposited steel strip (Table 3). Most of these fall within four of the largest markets in today's economy: food containers and other general packaging, automobiles, appliances, and furniture. The first two markets account for most of the total volume of production.

Table 3 Typical applications for continuous electrodeposited coatings for steel strip

Coating	Applications
Zinc	Auto body outer panels and some structural components
Zn-Ni (10-14 wt% Ni) alloy	Auto body outer and inner panels and some structural components
Zn-Fe (10-20 wt% Fe) alloy with or without a flash of Zn-Fe (>80% Fe)	Auto body outer panels and some inner panels
Zn-Ni with thin, weldable organic coating	Auto body outer and inner panels
Zn or Zn-Ni with various post-treatments (chromate, phosphate, organic)	Doors, housings, appliances
Tin (matte)	Two-piece drawn and ironed cans, automotive oil and air filters, baking trays
Tin (reflowed)	Three-piece welded cans with and without enameling, battery cases, lighting fixtures,

Chromium plus chromium oxide	Draw-redraw cans, can ends, crowns, signs, housings, parts in appliances, etc.

Packaging and containers include the main sector, food and beverage cans (Fig. 1), as well as general-purpose containers ranging from photographic film canisters to paint and solvent cans. The steel for these containers is electrodeposited with either tin or chromium, depending on the end use and the surface lubricity requirements of the manufacturing process (Ref 2, 3, 4, 5).

Fig. 1 Examples of containers made from continuous electrodeposited strip steel

Electrolytic tin-plated strip, commonly called *tinplate*, is used for applications requiring severe forming, with the tin coating serving as a lubricant. The tin coating also protects steel against corrosion and protects certain foods from discoloration. It can also prevent food oxidation, because tin is a strong reducing agent in certain environments (Ref 6).

Electrolytic chromium-coated steel, more commonly called *tin-free steel*, was developed in the late 1960s as a lower-cost alternative to tinplate. The extremely thin coating, composed of layers of metallic and nonmetallic chromium, is both a barrier coating against corrosion and an adherence enhancer for subsequent lacquering. However, it supplies no lubricity in forming operations or for food preservation. It is used mainly for draw-redraw containers and can ends, both of which are usually manufactured after a lacquer coating is applied.

Automobiles. Continuously electrodeposited steel strip is used in the manufacturing of automobiles (Ref 7, 8, 9, 10), almost exclusively for body panels but also for components such as oil filter shells and fuel tanks. Body panels are primarily made from zinc-plated strip, referred to as *electrogalvanized sheet*, but also from steel sheet plated with zinc alloys (Zn-Ni or Zn-Fe).

From 1986 to 1991, in the United States as well as throughout Europe and Asia, there was a tremendous increase in electroplating capacity and in the production of electrogalvanized sheet (Tables 4, 5, 6). This occurred because of the need to make outer body panels more resistant to corrosion in hot, humid, and marine environments and in regions where there is frequent use of deicing salt. Electrogalvanized steel was selected by most automakers for its superior surface quality vis-à-vis that of the hot-dipped galvanized products available at the time. The zinc coating generally follows the texture of steel and has no significant effect on surface roughness or paint appearance. Zinc was also chosen because of its galvanic or sacrificial protection of steel in areas where paint, which simply provides barrier protection for the steel, is scratched or otherwise damaged.

Table 4 Major U.S. electrogalvanizing lines and their capabilities

Plating line location	Nominal capacity[(a)], tons/y	Plating cells		Total amperage kA	Coatings	Start-up
		No.	Type			
Middletown, OH	250,000	16	Gravitel	736	Zn	1986
	280,000	21	Gravitel	1,056	Zn, Zn-Ni	1991
Dearborn, MI	700,000	42	CAROSEL	2,352	Zn, Zn-Fe	1986
Cleveland, OH	400,000	20	Vertical	1,320	Zn	1986
Columbus, OH	300,000	15	Vertical	990	Zn, Zn-Ni, Zn-Ni + organic	1991
Ecorse, MI	400,000	20	Vertical	1,000	Zn	1985
Gary, IN	400,000	18	CAROSEL	900	Zn	1977
Walbridge, OH	400,000	20	Gravitel	1,000	Zn, Zn-Ni, Zn-Ni + organic	1986
New Carlisle, IN	400,000	24	Gravitel	1,200	Zn, Zn-Ni	1991
Total	**3,530,000**					

Source: Updated from Ref 7

(a) Nominal capacity figures represent rough estimates made by the author from miscellaneous data.

Table 5 Major European electrogalvanizing lines started since 1980

Plating line location	Nominal capacity, tons/yr	Plating cells		Total amperage, kA	Coatings	Width		Start-up
		No.	Type			mm	in.	
Linz, Austria	200,000	12	Gravitel	360	Zn, Zn-Ni	1600	63	1985
Ste. Agathe, France	300,000	16	CAROSEL	928	Zn, Zn-Ni	1830	72	1983
Beautor, France	220,000	8	Radial	400	Zn, Zn-Ni	1520	60	1976
Mardyck, France	200,000	12	CAROSEL	600	Zn	1900	75	1991

Dormund, Germany	150,000	5	Vertical	300	Zn	1950	77	1986
Bochum, Germany	150,000	10	Horizontal	360	Zn	1600	63	1987
Neuwied, Germany	150,000	15	Vertical	320	Zn-Ni	1570	62	1985
Salzgitter, Germany	300,000	13	Gravitel	650	Zn	1850	73	1987
Duisburg, Germany	200,000	11	Horizontal	450	Zn	1900	75	1987
Torino, Italy	200,000	16	Radial	512	Zn	1600	63	1987
Genoa, Italy	80,000	10	Radial	320	Zn	1850	73	1991
Potenza, Italy	30,000	6	Horizontal	60	Zn	1800	71	1988
Varzi, Italy	50,000	4	Radial	100	Zn	1400	55	1986
Luxemburg	60,000	8	Vertical	150	Zn	1550	61	1983
Sagundo, Spain	60,000	4	Horizontal	160	Zn	1700	67	1986
Shotton Works, Deside, Wales	200,000	8	Vertical	528	Zn, Zn-Ni	1600	63	1972/1989
Genk, Belgium	300,000	10	Vertical	600	Zn, Zn-Ni	1080	43	1992

Source: Ref 8

Table 6 Major Asian electrogalvanizing lines started since 1976

Plating line location	**Nominal capacity, tons/yr**	**Plating cells**		**Total amperage, kA**	**Coatings**	**Width**		**Start-up**
		No.	**Type**			**mm**	**in.**	
Mizushima, Japan	360,000	19	Radial	662	Zn, Zn alloy	1830	72	1987
	300,000	. . .	Horizontal	. . .	Zn, Zn-Ni	1830	72	1991
Chiba, Japan	300,000	7	Radial	310	Zn, Zn-Ni	1700	67	1982
Fukuyama, Japan	360,000	11	Horizontal	550	Zn, Zn-Fe	1880	74	1983

	300,000	12	Horizontal	500	Zn, Zn-Ni	1830	72	1987
	240,000	7	Horizontal	350	Zn	1830	72	1992
Nagoya, Japan	360,000	17	Horizontal	640	Zn, Zn-Fe	1830	72	1983
Kimitsu, Japan	300,000	6	Horizontal	320	Zn, Zn-Ni, Zn-Ni + organic	2080	82	1985
Kashima, Japan	360,000	14	Vertical	672	Zn, Zn-Ni	1600	63	1984
	180,000	8	Vertical	384	Zn, Zn-Ni, Zn-Ni + organic	1600	63	1988
Wakayama, Japan	260,000	10	Horizontal	196	Zn, Zn alloy	1880	74	1968/1986
Kakogawa, Japan	360,000	10	Horizontal	400	Zn, Zn alloy	1600	63	1986
	300,000	. . .	Horizontal	. . .	Zn, Zn-Ni	1830	72	1991
Sakai, Japan	200,000	12	Horizontal	. . .	Zn-Ni	1600	63	1986
Hanshin, Japan	140,000	3	Horizontal	120	Zn, Zn alloy	1830	72	1986
Kwangyang, Korea	400,000	20	Radial	1008	Zn, Zn-Fe	1860	73	1990
Pohang, Korea	300,000	12	Radial	448	Zn, Zn-Ni	1650	64	1986
Kaohsiang, Taiwan	200,000	6	Radial	336	Zn, Zn-Ni	1676	66	1992

Source: Ref 10

Furniture and appliances markets make use of zinc and zinc alloy continuously plated steel strip. Metal office furniture, for example, may be manufactured using electrogalvanized sheet, normally with only a "flash" (about 1 to 2 μm) of zinc coating. Appliances such as toasters, dishwashers, washing machines, dryers, and so on may also be manufactured in part from further treated and painted electrogalvanized steel for extra corrosion protection.

References cited in this section

2. P.K. Frame, "The Year 2001--Will There Be Enough Tin?," *Proceedings of the Fifth International Tinplate Conference*, International Tin Research Institute, 1992
3. T.P. Murphy, Some Economic and Environmental Aspects of the Corrosion Behaviour of Tin and Its Alloys, *Progress in the Understanding and Prevention of Corrosion,* Vol 1, The Institute of Materials, 1993, p 696-711
4. E. Mayo, World Tin Mill Production, *The Canmaker,* Dec 1992

5. "Tin Mill Products," The Iron and Steel Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers, 1992
6. E.E. Hoare, E.S. Hedges, and B.T.K. Barry, *The Technology of Tinplate,* St. Martin's Press, 1965
7. G.W. Bush, Development in the Continuous Galvanizing of Steel, *Journal of Metals,* Aug 1989
8. B. Meuthen, Aspects of Zinc and Zinc Alloy-Coated Sheet Steel in Western Europe--with a Special View of the German Scene, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan, p 91-100
9. S.G. Denner, An Overview of the Manufacture and Application of Zinc and Zinc Alloy Coated Sheet Steel in North America, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan, p 101-110
10. T. Hada, Present and Future Trends of Coated Steel for Automotive Use, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan, p 111-119

Key Coating Properties and Characteristics

Described below are the key properties and characteristics of the major coatings that are applied by continuous strip electrodeposition. These include zinc-base coatings, which are applied primarily on automotive sheet steel, and electrolytic coatings, which are applied on the tin mill products used in the container industry.

Pure Zinc (Electrogalvanized) Coatings. Electrogalvanized sheet has a pure zinc coating. It is currently the most widely used coated sheet in the United States for exposed body panels of automobiles because of its generally uniform coating thickness and excellent surface characteristics. Coating thicknesses range from 4 to 14 μm (30 to 100 g/m^2) per side, although the most common coating masses are 8 and 10 μm (60 and 70 g/m^2). For nonautomotive applications such as doors, furniture, and appliances, a thickness of as low as 1.5 μm (10 g/m^2) can be used.

Typically, the electrodeposited zinc coating microstructure (Fig. 2) is a single-phase pure zinc, featureless, in unetched cross section (Ref 11). On the other hand, the coating surface is characterized by crystallographic facets of the hexagonal zinc crystals. Surface morphology, coating texture, and grain size may vary, depending on the chemistry of the plating solution employed as well as the specific deposition conditions of current density, temperature, and level of trace contaminants or additives (Ref 12). The zinc coating does not significantly alter the surface roughness of the steel sheet, and thus it does not affect appearance after painting. In addition, zinc galvanically protects the steel if a corrosive environment penetrates the paint layer.

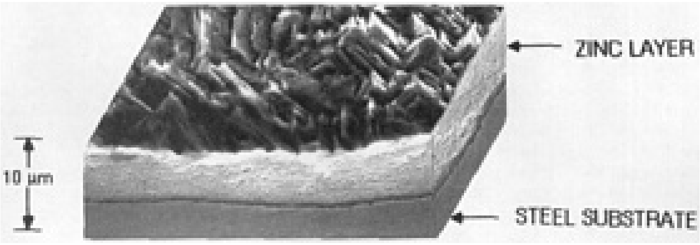


Fig. 2 Surface morphology and microstructure of electrogalvanized sheet. Scanning electron microscope section. Source: Ref 11

Zinc-nickel alloy coatings generally contain 10 to 14 wt% Ni. Coating thicknesses are typically 3 to 6 μm (20 to 40 g/m^2). Zn-Ni coated sheet steel is used for both exposed and unexposed automobile body panels. Although Zn-Ni electrodeposited strip has been available in the United States since the 1950s in narrow widths for automotive trim and nonautomotive applications, its production and use on wide sheet for body panels started in Japan in 1983-1984 (Ref 13). Currently, it is the most widely used electroplated automotive sheet steel in Japan, second only to Zn-Fe hot-dip coated sheet for auto bodies.

Zn-Ni coated automotive sheet is coated either with Zn-Ni only (Ref 14) or with Zn-Ni plus a thin organic coating. The latter product was initially developed in Japan (Ref 15) and is now available in the United States and Europe. The organic coating system normally consists of a proprietary chromate chemical pretreatment of the order of 20 to 100 mg/m^2 of chromium and a thin (about 1 μm) organic topcoat (epoxy or urethane-based) containing silicates. The organic coating was originally applied on one side of the sheet, protecting unexposed surfaces against inside-out perforation corrosion.

However, a two-side organic/Zn-Ni composite system, with chromate and organic layers applied on both sides of the sheet, is also now available and is used by at least one automaker.

In cross section, Zn-Ni coating microstructure is typically fine-grained, single-phase (gamma), Zn-Ni intermetallic. The surface is generally nodular and lacks the sharp crystallographic facets of electroplated zinc (Fig. 3). Reactivity of the Zn-Ni coating in wet salt environments, typically simulated by the salt spray test, is about three times lower than that of pure zinc. Its superior performance in salt spray and fog tests prompted its use as a thinner and more cost-effective alternative to pure zinc.

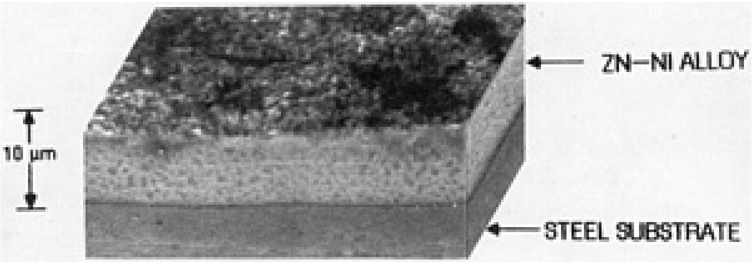


Fig. 3 Surface morphology and microstructure of zinc-nickel alloy coated sheet. Scanning electron microscope section. Source: Ref 11

Zinc-Iron Alloy Coatings. The electroplated Zn-Fe coating was developed mainly for automotive steel sheet for exposed panels, where the characteristics of the Zn-Fe hot-dip coating are desired but the uniformity and surface appearance of an electroplated coating are also required. However, recent advances in hot-dip coating technology have improved the quality of the hot-dip Zn-Fe coating or so-called *Galvanneal coating.* This has contributed to a decline in the production and use of the electroplated Zn-Fe coating, along with the fact that the Zn-Fe process is very difficult to operate at high speeds and volumes when insoluble anodes and sulfate-based electrolyte are used. The electrolyte, which should contain mainly ferrous iron, is easily oxidized to ferric iron, by both air and electrochemical oxidation at insoluble anodes. Therefore, such electroplating facilities must have added equipment or peripheral chemical processing plants for reducing or removing ferric iron and maintaining electrolyte stability. However, there are also chloride-based Zn-Fe processes used in the United States, Japan, and Korea that use soluble anodes to produce a uniform alloy composition over a fairly broad range of plating parameters, without the operational problems of the sulfate-based Zn-Fe electrolyte and insoluble anode process.

The electrodeposited Zn-Fe coating (Ref 16) normally contains 10 to 20 wt% Fe and is used in thicknesses up to 7 μm (50 g/m^2) per side. The coating microstructure for Zn-Fe may show fine layers corresponding to the number of plating cells in the line (Fig. 4). The surface morphology appears as nodular but becomes smoother with increasing iron content. At certain automakers, when this type of coating is used for exposed automotive panels, the Zn-Fe sheet is further electroplated with a second but much thinner top layer of iron-rich Zn-Fe coating, 3 to 5 g/m^2 of Zn-Fe containing at least 80 wt% Fe (Ref 17). The iron-rich top layer was developed to improve the paintability and formability of the primary zinc-rich alloy coating.

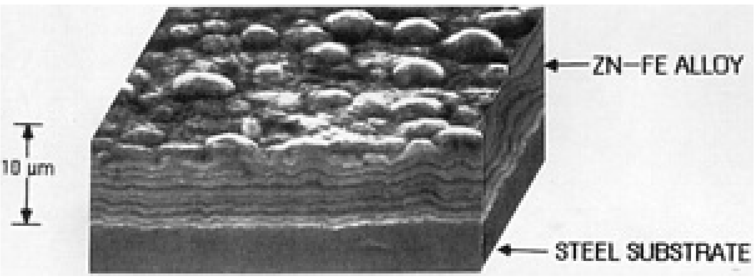


Fig. 4 Surface morphology and microstructure of zinc-iron alloy coated sheet. Scanning electron microscope section. Source: Ref 11

Electrolytic Tin Coatings. The continuous electrodeposition of tin on wide strip was introduced in 1940 (Ref 6), and wartime conditions stimulated its development. The electrodeposition process offers three main advantages over the hot-dip process: (a) higher-speed continuous strip processing; (b) better control and uniformity of coating thickness, allowing the use of thinner tin coatings; and (c) ability to plate different coating thicknesses on each surface of the strip, producing differential tinplate that can more cost-effectively meet the different corrosion resistance requirements of the inside and outside of containers.

Tin coatings are of the order of 0.4 μm thick, although they are usually expressed in terms of coating mass. Present values range from about 0.5 to 11 g/m^2 on each surface. In the United States, tin coatings have numbers (Table 7) that designate the total weight of tin (i.e., the weight of the tin on the two sides per base box, a measure of surface area equal to 31,360 in.^{2}, originally defined as 112 sheets, 14 by 20 in.). Presently there is a tendency, for economical and technological reasons, to apply lower-tin coatings, most commonly No. 20 or 25 (2.2 or 2.8 g/m^2).

Table 7 Electrolytic tin coating weight and mass designations

Designation No.	Nominal tin coating weight each surface, lb/base box[a]	Minimum average coating weight each surface test value, lb/base box[a][b]
Coating weights per ASTM A 624		
10	0.05/0.05	0.04/0.04
20	0.10/0.10	0.08/0.08
25	0.125/0.125	0.11/0.11
35	0.175/0.175	0.16/0.16
50	0.25/0.25	0.23/0.23
75	0.375/0.375	0.35/0.35
100	0.50/0.50	0.45/0.45
D50/25[c]	0.25/0.125	0.23/0.11
D75/25[c]	0.375/0.125	0.35/0.11
D100/25[c]	0.50/0.125	0.45/0.11
D100/50[c]	0.50/0.25	0.45/0.23
D135/25[c]	0.675/0.125	0.62/0.11

Nominal tin coating mass each surface, g/m²	Minimum average coating mass each surface test value, g/m²[(d)]
Coating masses per ASTM A 624M	
1.1/1.1	0.9/0.9
2.2/2.2	1.8/1.8
2.8/2.8	2.5/2.5
3.9/3.9	3.6/3.6
5.6/5.6	5.2/5.2
8.4/8.4	7.8/7.8
11.2/11.2	10.1/10.1
D5.6/2.8[(c)]	5.2/2.5
D8.4/2.8[(c)]	7.8/2.5
D11.2/2.8[(c)]	10.1/2.5
D11.2/5.6[(c)]	10.1/5.2
D15.2/2.8[(c)]	14.0/2.5

Note: Listed above are the commonly produced coating weights and masses. Upon agreement between the producer and the purchaser, other combinations of coatings may be specified and the appropriate minimum average test values will apply.

Source: Ref 5

(a) Base box is a measure of surface area equal to 31,360 in.^{2}.

(b) The minimum value shall be not less than 80% of the minimum average tin coating weight.

(c) The letter D on differentially coated tin plate indicates the coated surface to be marked. For example, the examples indicate that the heavy-coated side is marked.

(d) The minimum spot value shall be not less than 80% of the minimum average tin coating mass.

Electrolytic tinplate is produced in two primary finishes. The first type is the so-called *matte-finish tinplate*, which is used simply with the as-deposited tin coating with its nonreflective microcrystalline surface morphology (Fig. 5). Matte-finish tinplate is used primarily for drawn and ironed two-piece containers for beverages and, more recently, for foods, with the body of the container being a single piece and the end being the second piece. The second and more common type is bright tinplate, which results when strip is heated above the melting point of tin and is quenched with water to form a bright, reflective surface. The high reflectivity and smoothness of this type of tinplate facilitates lithography, and it provides a good appearance for the end product, which is usually three-piece containers. Several variations of decorative effects and surface finishes can be obtained by varying the surface of the work rolls in the final temper-rolling or cold-rolling pass.

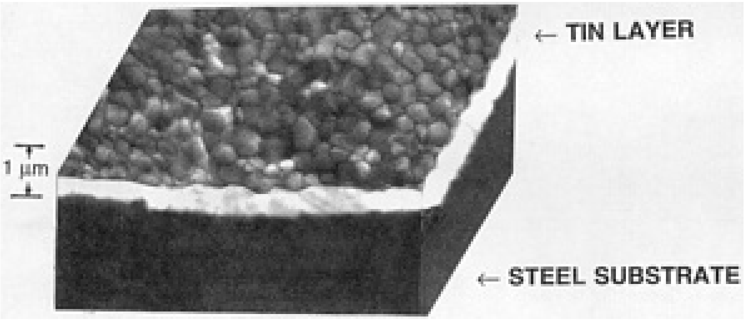


Fig. 5 Surface morphology and microstructure of tinplate. Scanning electron microscope section

Chromium Coatings. The chromium coating that is most widely applied to steel strip by continuous electrodeposition is an extremely thin coating consisting of layers of both metallic chromium and hydrated trivalent chromium oxides. The coating is specified by the coating weight range of the metallic chromium, 30 to 140 mg/m^2 Cr, and by the amount of chromium present as the oxide, 8 to 27 mg/m^2 (Ref 5). Electrolytic chromium-coated steel is further coated with a lubricating film and is used principally for can ends, closures as well as drawn bodies. However, it requires the application of an organic coating or plastic film to minimize abrasion, corrosion, and external rusting.

References cited in this section

5. "Tin Mill Products," The Iron and Steel Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers, 1992
6. E.E. Hoare, E.S. Hedges, and B.T.K. Barry, *The Technology of Tinplate,* St. Martin's Press, 1965
11. H.E. Townsend, Coated Steel Sheets for Corrosion-Resistant Automobiles, *Materials Performance,* Oct 1991, p 60-65
12. T.R. Roberts, F.H. Guzzetta, and R.Y. Lin, The Effect of Processing Temperature on the Microroughness of Electroplated Zinc Coatings on Steel, *Proceedings of the Fifth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1987
13. S.A. Watson, "Zinc-Nickel Alloy Electroplated Steel Coil and Other Precoated Coil for Use by the Automotive Industry: A Review of Literature Published 1983 to 1987," Nickel Development Institute, 1988
14. R.N. Steinbicker and S.G. Fountoulakis, Production of Zinc-Nickel Electroplated Coatings, *Iron and Steel Engineer,* July 1989, p 28-31
15. T. Watanabe, Y. Shindou, T. Shiota, and S. Nomura, Development of Organic Composite Coated Steel Sheet with Bake Hardenability and High Corrosion Resistance, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan

16. T. Adaniya, T. Hara, et al., "Corrosion Resistance of Zn-Fe Alloy Electroplated Steel," Metals/Materials Technology Series 8512-022, American Society for Metals, 1985
17. M. Toda, H. Kojima, et al., "Development of Two-Layered Zn-Fe Alloy Electroplated Steel Sheet," Paper 840212, Society of Automotive Engineers, 1984

Components of Continuous Steel Strip Plating Lines

Figures 6, 7, 8, and 9 show schematic diagrams of continuous steel electroplating lines for tin, chromium, and zinc coatings. Figure 9 may be consulted in the following discussion of the general features of these lines. The line in Fig. 9 is also designed for painting over the metallic coated strip, which for economic reasons may become the trend, particularly for zinc and zinc alloy coating lines whose lower speeds can allow roll coating of the organic films.

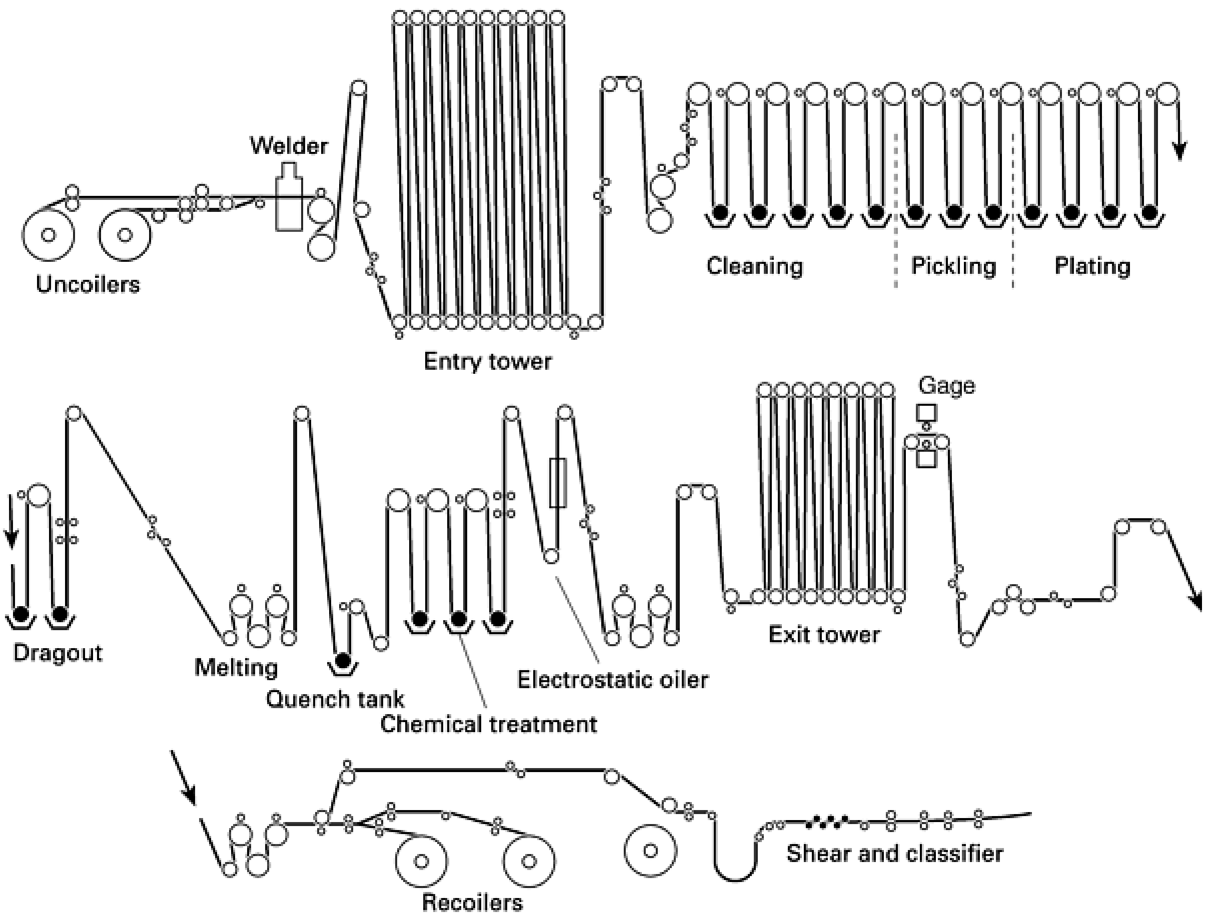


Fig. 6 Schematic diagram of a typical electrotinning line, using vertical plating cells. Source: Ref 1

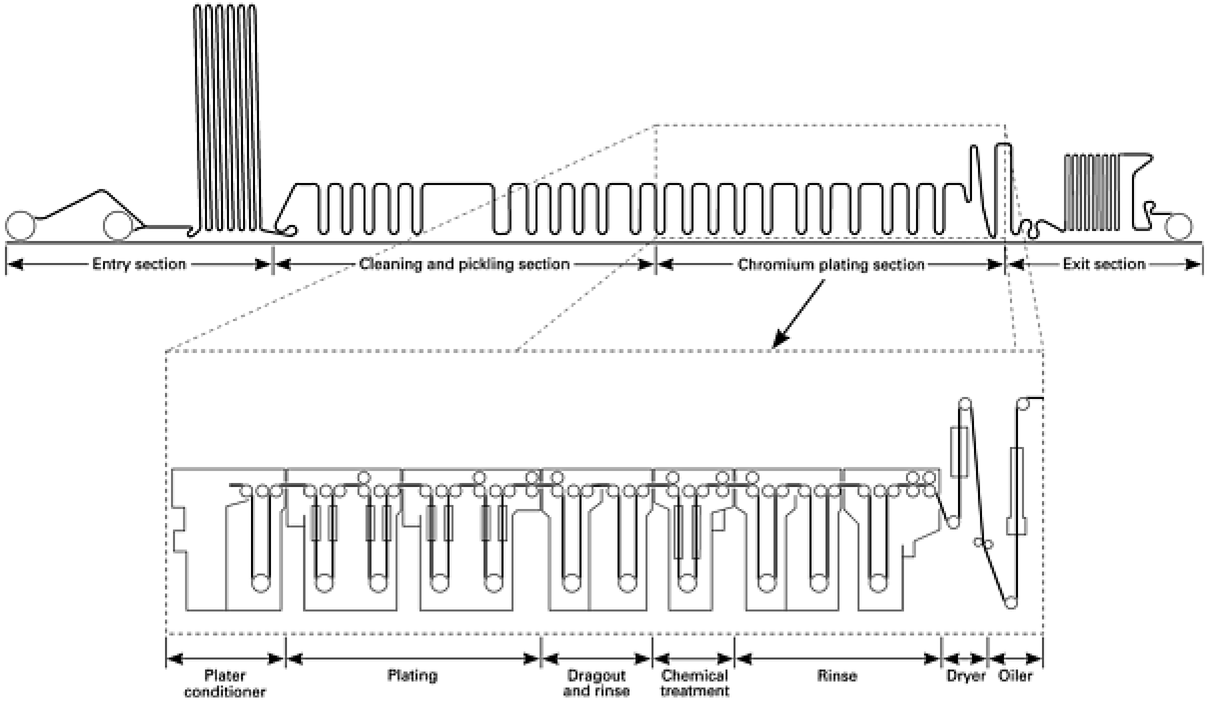


Fig. 7 Schematic diagram of a typical two-step chromium plating line, also called a tin-free steel line. Source: Ref 1

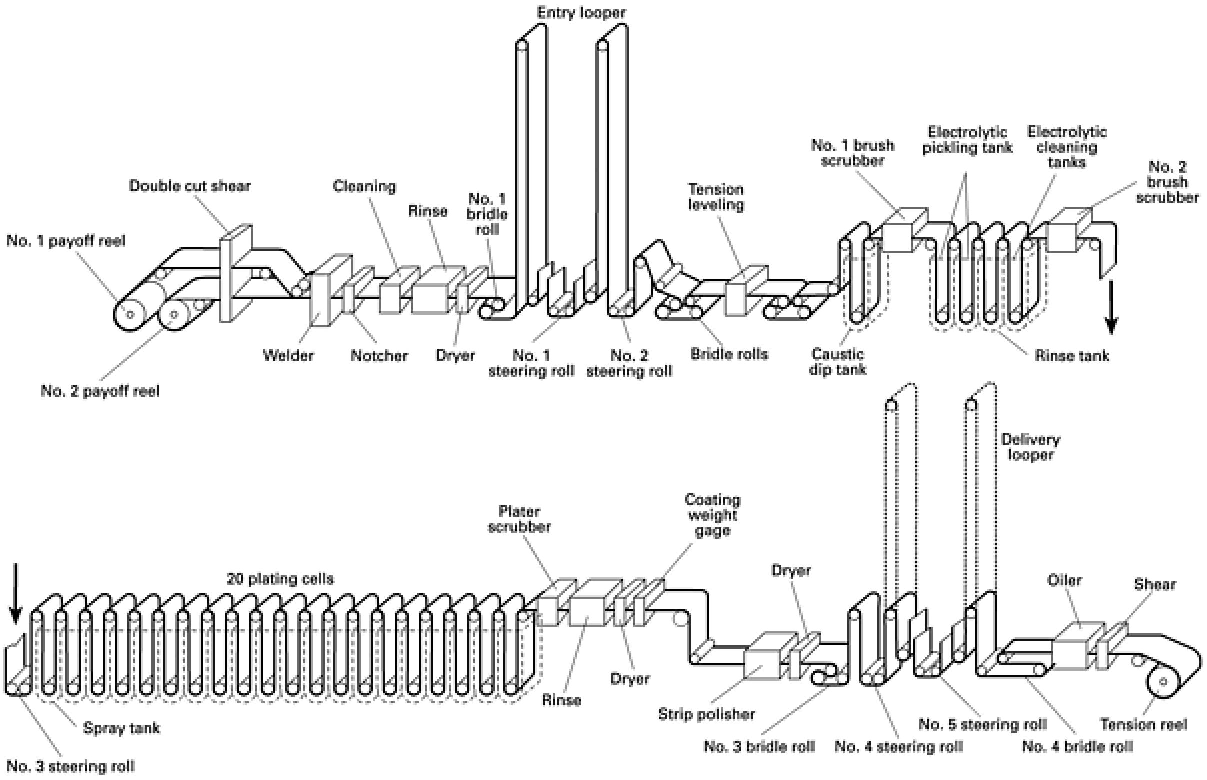


Fig. 8 Schematic diagram of a typical electrogalvanizing line with vertical plating cells. Source: Ref 1

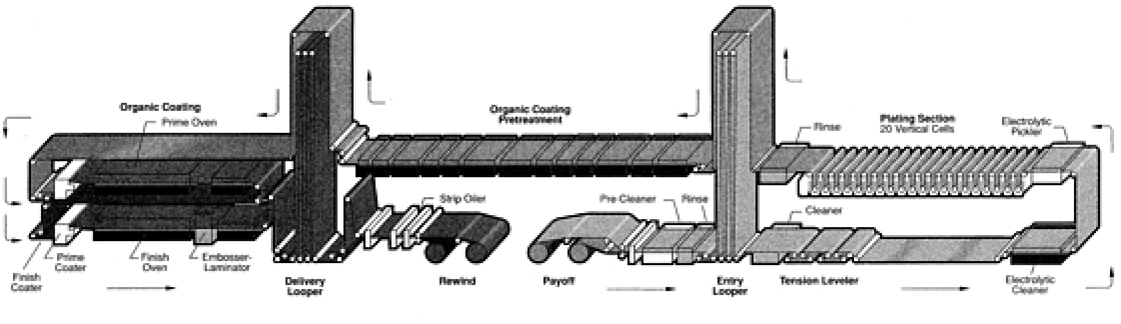


Fig. 9 Schematic diagram of an 1830 mm (72 in.) combination electrogalvanizing and coil coating line. Source: Ref 18

A typical continuous plating line has five main sections: payoff, pretreatment, plating, post-treatment, and delivery. The functions and key pieces of equipment of each of these sections are described below.

The payoff section feeds the strip into the line. It may consist of payoff reels, a shear, a strip welder, an edge-notcher, a burr masher, a degreasing section, and an accumulator tower. Coils of cold-rolled, fully annealed steel are loaded onto the entry reels and are fed into the continuous line. The head end of a new coil is welded to the tail end of the previous coil. The edges of the weld are notched or cut out to eliminate loose flaps when two different widths are welded together, and any steel edge burr is mashed. The strip passes through a precleaning and rinse station where the bulk of the rolling and protective oils are removed, then moves into the entry strip accumulator or looper. The looper, which can be either vertical or horizontal, accumulates extra strip ahead of the plating section and provides it to that section when the entry end is stopped to load a new coil.

The pretreatment section is where residual oil, surface carbon, and any light surface oxide are removed prior to plating. It normally consists of one or more alkaline cleaning and electrocleaning stations, brushing or scrubbing stations, pickling or electropickling stations, and rinsing stations. Many modern, high-speed lines have a tension leveler within the pretreatment section to flatten the strip. This guarantees the uniform anode-to-strip spacing needed to produce a highly uniform coating. The leveler location is such that strip coming into the unit is fairly clean, but additional cleaning follows the leveling process.

The plating section, the heart of the process, always consists of multiple plating cells located in a row (Fig. 10). At the beginning of the plating section, there is frequently a conditioning or preplating cell. A conditioning cell may simply contain the process electrolyte, to wet the strip surface prior to the application of current, but a preplating cell may also contain a slightly different or completely different electrolyte to deposit a thin initial layer. This layer can be used either to enhance the adherence of the main coating (e.g., in the case of alloys of zinc with nickel or iron) or to control a postplating process (e.g., a thin nickel layer may be deposited to limit tin-iron alloy growth during reflowing or subsequent processing of tinplate).

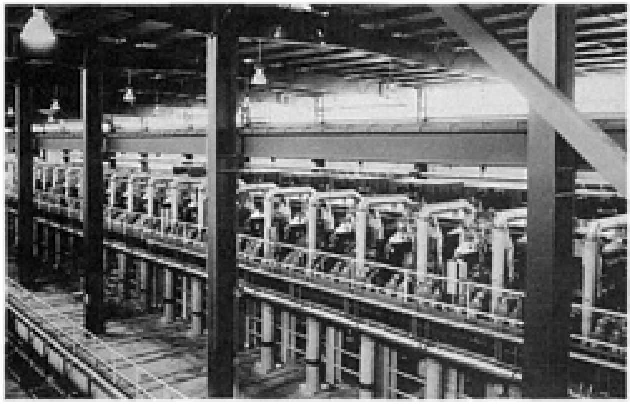


Fig. 10 Twenty vertical plating cells in a continuous plating line that applies zinc and zinc-nickel alloy coatings on sheet steel, primarily for the automotive market

The full thickness of the main coating is built up gradually as the strip moves from cell to cell. Associated with the cells are electrolyte distribution tanks, pumps, filters and heat exchangers, and electrolyte chemical replenishment reactors and systems. Upon exiting the last cell, the coated sheet is immediately rinsed and dried to prevent streaking or staining of the coated surface. Following the dryer, there is normally a coating thickness gage (x-ray fluorescence) that continuously monitors and records the edge-to-edge distribution of the coating on both sides of the strip.

The post-treatment section is present on most, although not all, strip plating lines. There are three basic types of post-treatments:

- *Surface-stabilizing post-treatments*: Examples are the etching solutions used to clean and stabilize the uncoated side of one-side electrogalvanized sheet (Ref 19, 20, 21)
- *Property-enhancing post-treatments* chemically convert the surface to accept further coatings, such as paint. In addition, post-treatments can impart certain surface properties, such as lower friction or change in ohmic surface resistance (which are important properties for forming and welding) or changes in surface brightness or appearance. Examples are the chromium-containing chemical conversion coatings that slow down surface oxide growth on tin (Ref 5, 6), zinc coatings that serve as pretreatments for the adhesion of paints for zinc and Zn-Ni (Ref 15), and enamels for tinplate (Ref 6).
- *Proprietary rinses, phosphates, and dry film lubricants* may be used to aid in the final manufacturing of parts (Ref 22).

Melting and reflowing of the tin coatings can also be characterized as a post-treatment. It is almost always followed by a chromate conversion or electrolytic post-treatment.

The delivery section starts with a delivery accumulator, which allows the processing sections to continue running while the delivery reels are stopped to remove coils. Several additional stations and pieces of equipment are included in the delivery section, such as for edge trimming, inspecting, marking, oiling, and sampling the final strip before it is coiled again onto the rewind reels (Fig. 11).

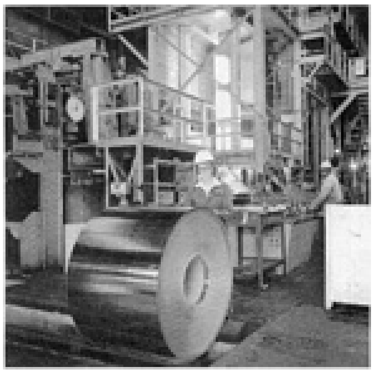


Fig. 11 Delivery section of a continuous tinning line

References cited in this section

1. L.W. Austin and J.L. Lindsay, "Continuous Steel Strip Electroplating," slide course, American Electroplaters and Surface Finishers Society, 1989
5. "Tin Mill Products," The Iron and Steel Society of the American Institute of Mining, Metallurgical, and

Petroleum Engineers, 1992

6. E.E. Hoare, E.S. Hedges, and B.T.K. Barry, *The Technology of Tinplate,* St. Martin's Press, 1965
15. T. Watanabe, Y. Shindou, T. Shiota, and S. Nomura, Development of Organic Composite Coated Steel Sheet with Bake Hardenability and High Corrosion Resistance, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan
18. W.A. Carter, R.L. Price, and R.N. Steinbicker, Electrogalvanizing at Walbridge Coatings, *Proceedings of the Fifth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1987
19. S.G. Fountoulakis, R.N. Steinbicker, and D.E. Hruskoci, Chemical Post-Treatment Process for One-Side Electrogalvanized Steel Strip, U.S. Patent 4,708,779, 1987
20. H. Bersch, K.-H. Kilian, and H.U. Weigel, "Method for Electroplating a Steel Strip with a Coating Metal, in Particular Zinc or Zinc-Containing Alloy," U.S. Patent 4,855,021, 1989
21. G.E. Jones, The Application of Tin Coatings in the Manufacture of Tinplate, *The Production of Wide Steel Strip,* Special Report 67151, Iron and Steel Institute, 1960
22. K.S. Raghavan, J.G. Speer, and T.J. Garrett, "Sheet Steel Surface Treatments for Enhanced Formability," Paper 94095, Society of Automotive Engineers, 1994

Classification of Continuous Electrodeposition Processes

Strip plating processes are generally classified by three process characteristics (Table 8): anode type, electrolyte chemistry, and plating cell geometry.

Table 8 Classification of continuous processes for the main electrodeposited coatings for steel strip, and key features of each category

Coating	Cell geometry	Anode	Bath chemistry
Zinc, Zn-Ni, Zn-Fe	Vertical	Insoluble (Pb alloys, Ir/IrOx coated Ti)	Zinc sulfate (plus nickel or ferrous sulfate), sodium and/or magnesium sulfate for conductivity, pH ≈2
		Soluble (Zn, plus Fe or Ni)	Zinc (plus nickel or ferrous) sulfate, and alkali sulfate conductive salts, pH ≈4
	Gravitel	Insoluble (Ir/IrOx coated Ti)	Zinc sulfate, pH ≈2
	Radial	Soluble	Zinc chloride, pH ≈4
		Insoluble (Pb alloys, Ir/IrOx coated Ti)	Zinc sulfate, pH ≈2
	Horizontal	Soluble	Zinc sulfate or chloride, pH ≈3-5
		Insoluble	Zinc sulfate, pH ≈2
Tin	Vertical	Soluble	Tin phenolsulfonate, pH ≈1

	Horizontal	Soluble	Tin fluoride and chloride (Halogen process), pH ≈ 3
	Radial	Insoluble	Methanesulfonate, pH ≈ 1
Chromium	Vertical, horizontal	Insoluble (Pb-Ag)	Chromic acid, catalyzed with sulfate and fluorosilicate ions

Anode type is either soluble or insoluble. Soluble anodes are consumable, dissolving anodically to replenish the metal or metals, which eventually deposit onto the steel strip as the coating. Insoluble anodes generally oxidize water and have oxygen evolution as the anodic reaction within each plating cell. More information about anode selection is given in the following paragraphs.

Electrolyte chemistry is generally characterized by the primary anionic species, such as sulfate or chloride. The key factor is obviously the capability of the particular chemistry to produce a high-quality, smooth, and compact coating. However, there are many other factors, including availability and cost of the starting metal salts; the ability of the resulting electrolyte to sustain electrodeposition at high current density, so as to maintain high line speed and productivity; and compatibility with the anode material.

Zinc and zinc alloy electrodeposition of steel strip, done at up to 213 m/min (700 ft/min), takes place from either a sulfate- or chloride-based electrolyte, although a mixed chemistry is used in some of the smaller and older plating lines. These electrolytes are aqueous solutions of zinc ions and ions of the alloying nickel or iron metal with sulfate or chloride ions, acidified with sulfuric or hydrochloric acid, respectively. Alkali or ammonium salts may also be used to increase the conductivity of these solutions.

As shown in Table 8, chloride electrolytes are used exclusively with soluble anodes, because insoluble anodes would oxidize the chloride into chlorine gas, which cannot be handled economically because of it corrosivity and hazardous nature. The most significant advantage of the chloride process is that the conductivity of the bath is many times higher than that of the sulfate bath, and so less electric power is consumed to deposit the same amount of coating as in the sulfate process. On the other hand, one must invest in corrosion-resistant materials for construction of equipment and have extra equipment or labor to replenish the consumable anodes. In addition, the chloride process may require some type of organic additive as a grain-refining agent in order to produce coatings with improved galling resistance. The world's largest steel electroplating line, in Dearborn, MI, uses this chemistry for depositing zinc and/or Zn-Fe coatings on over 700,000 tons of sheet steel per year (Ref 23, 24).

The most widely used zinc and zinc alloy steel plating process is the sulfate type. The main attribute of sulfate electrolytes is that they are compatible with insoluble anodes. Selecting the anode type, therefore, is truly the first step in deciding on the plating process to use. Sulfate-based processes are also simple in chemistry, as shown in Table 8. The main advantages of sulfate electrolytes are that they deposit finer-grain coatings without organic additives and operate over a wide range of current densities, temperatures, and acidity.

Tin electrodeposition of steel strip is normally done at 549 m/min (1800 ft/min) or higher line speeds. The two most widely used processes today are the Ferrostan and Halogen processes (Ref 25). Only one major tinplate producer, in Andernach, Germany, operates a third process, based on a fluoroborate electrolyte, and the original 1940s alkaline stannate electrolyte (Ref 6) is now employed in only one or two of the older remaining lines. A new process based on a solution of tin in methanosulfonic acid has been invented and evaluated (Ref 26), and it was recently put into commercial use in at least two electrolytic tin lines.

The electrolyte for the Ferrostan process is a solution of stannous tin in phenolsulfonic acid, with various addition agents to mitigate oxidation of stannous tin, promote the deposition of a compact and smooth coating, and improve wetting characteristics. This process was invented in 1942 (Ref 27), but it has since undergone some changes, primarily in terms of the addition agents used. The original additive package, dihydroxydiphenylsulfone and monobutylphenylphenol sodium monosulfonate (Ref 28) has been replaced with ethoxylated alpha-naphthol sulfonic acid. Ferrostan lines always employ vertical cells and generally employ soluble tin anodes.

The Halogen process, also known as the horizontal acid process, was developed in 1943 (Ref 29). It employs an aqueous solution of stannous and alkali (e.g., sodium) fluorides and chlorides. The basic composition has been modified over the years by various companies to suit their needs (Ref 30). To obtain smooth, compact deposits having the right wetting characteristics, addition agents are also required. Naphtholsulphonic acids or polyalkylene oxides are normally used, although others have also been found to be effective over the years.

Chromium and chromium oxide electrodeposition of steel strip employs two processes, both of which use similar electrolytes. In fact, the electrolyte is simply an aqueous solution of chromic acid (CrO_3), catalyzed with very small amounts of sulfate ions and fluorosilicate ions (Ref 31, 32). The two processes differ only in the number of steps used in depositing the metallic and nonmetallic components of the coating. The older process (Ref 31) uses two steps with two banks of plating cells or passes. In the first series of passes, the metallic chromium is normally deposited at higher current density and from a more concentrated chromic acid solution, and then the chromium oxides are deposited in the last plating passes, using low current density and dilute chromic acid solution as the electrolyte. The more recent process employs an electrolyte of intermediate chromic acid concentration, but still high current density, to deposit a mixture of metallic and nonmetallic chromium in one step (Ref 32). The two-step process is normally operated with vertical plating cells, whereas the single-step process uses vertical cells for conventional current density operation and horizontal cells for high-current-density operation. Both processes use insoluble lead alloy anodes.

Plating Cell Geometry. There are many different plating cells, with varying sophistication in coating capability, productivity, automation, specialized components, and so on. However, these can be classified into three main groups based on cell geometry: vertical, horizontal, and radial. Both the vertical and horizontal cells have been used for many decades in the production of tinplate for the container industry. In the 1970s, when the automotive industry started to downgage and thus required increased corrosion resistance, particularly for inside-out rust-through, radial cell geometry was developed to produce electrogalvanized sheet plated on only one side for use as the inner surfaces of auto body panels. Today, most electrogalvanized sheet is coated on two sides, but with the use of edge shielding, vertical and horizontal cells can also produce good-quality one-side plated product.

All three cell types can be used with either soluble or insoluble anodes. Each type must provide adequate current transfer to the steel strip and good electrolyte flow in the anode-to-strip gap. Both of these factors increase the speed of electrodeposition and thus the material throughput of the cell. Over the years, there have been many innovations in the basic cell designs, and the key innovations are discussed below within the description of each basic design.

Vertical Cell Design. Figure 12 shows four major variations of vertical cell design. The simple flooded cell is used with soluble anodes and phenolsulfonic acid electrolyte for tin plating, or with lead alloy anodes for the deposition of chromium and chromium oxide from chromic acid solutions. However, for electrogalvanizing, which is done at about a third of the speed used for tin and chromium, the vertical cell is normally modified to become a forced-flow or counter-current-flow cell in order to operate at higher current densities (Ref 33). The forced flow is provided by pumping electrolyte through nozzles, as shown in Fig. 12(a). Generally, these electrogalvanizing cells are used with insoluble anodes, lead alloy or noble-metal-coated titanium. However, they have also been used with soluble (zinc) anodes, with the anodes in the form of solid bars suspended from busbars (Fig. 12b) or pellets contained in a special anode basket (Fig. 12c).

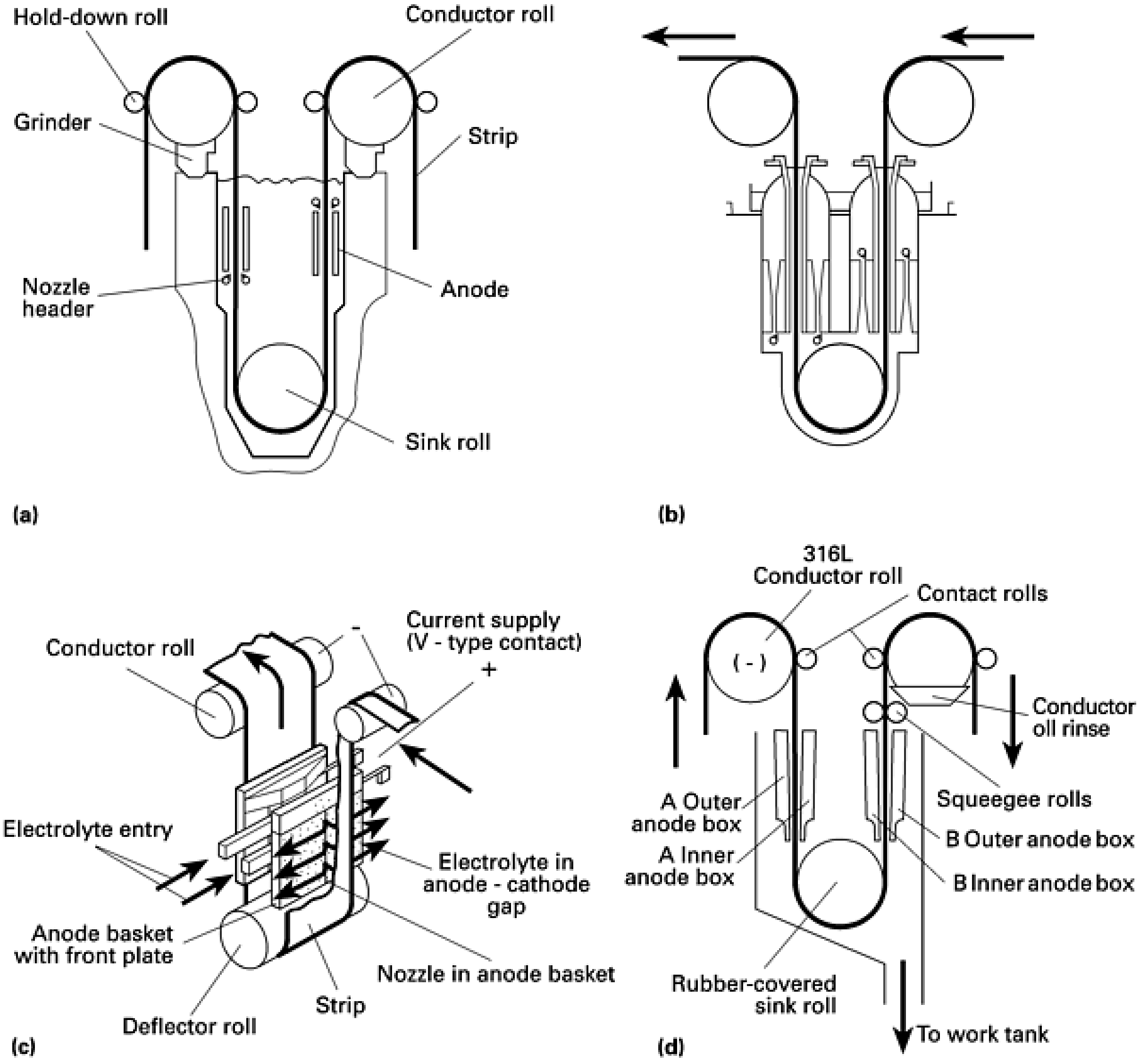


Fig. 12 Four major variations of vertical plating cell design. (a) Flooded and counter-current-flow plating cell with insoluble anodes. Source: Ref 33. (b) Flooded and counter-current-flow cell with soluble anode bars. Source: Ref 34. (c) Flooded cell with anode baskets containing metal granules. Source: Ref 35. (d) Gravitel plating cell with insoluble anodes. Source: Ref 36

A new type of insoluble anode vertical cell called Gravitel (Fig. 12d) was commercialized in 1985 (Ref 36). In this cell design, only the anode-to-strip gap is filled with electrolyte, and although the cell is housed in a similar tank, that tank is not filled with solution but simply contains the splashing of the solution, sending it down under the cell and into a large recirculation tank. Solution is pumped inside each hollow anode box, overflows the top of the box through a special V-shaped weir, falls into the gap between the anode and the strip, fills the gap, falls out the bottom of the gap, and returns by gravity to the recirculation tank. Because gravity increases the speed of the electrolyte along the height of the cell, the gap is tapered, being wider at the top (9 mm) and narrower at the bottom (7 mm). To plate both sides, opposing pairs of anode boxes are operated simultaneously. To plate one side of the strip, the anode boxes facing the unplated side are moved away, and electrolyte flow and plating current are maintained only on the side being plated.

Radial Cell Design. Figure 13 shows four major variations of radial cell design. The first radial cell (Ref 23, 24) evolved into the CAROSEL (Consumable-Anode Radial One-Side ELectroplating) technology. The distinguishing characteristics of this cell are a single but very-large-diameter conductor roll (about 2.4 m, or 8 ft, in diameter) in the center of the cell and large cylindrical consumable anode sections under this roll. Like all radial cells, this cell plates only one of the surfaces of the steel strip. However, by arranging multiple cells within a line into two tiers or elevations, and by inverting the strip as it goes from one tier to the next, the second surface can also be plated.

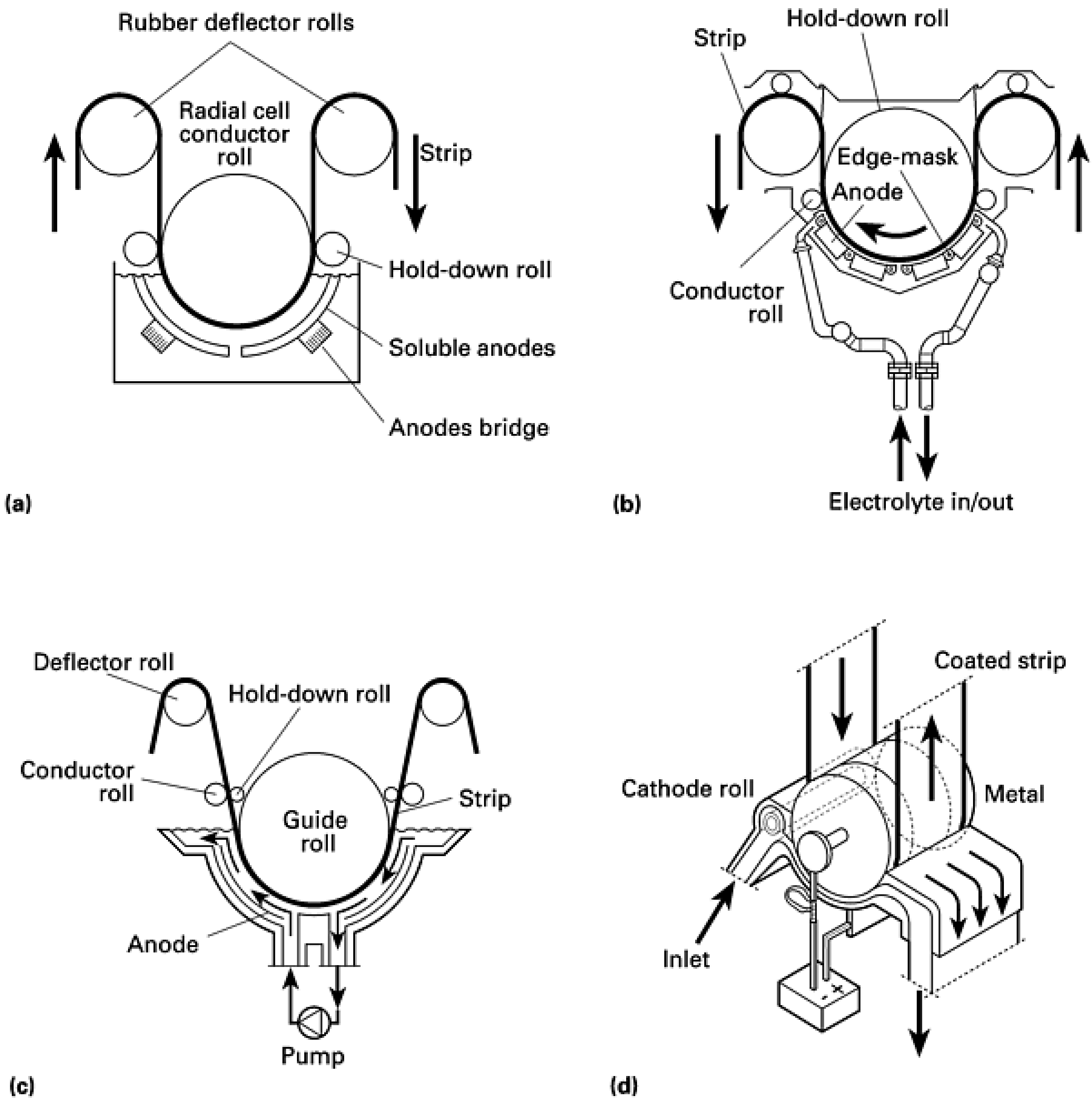


Fig. 13 Four major variations of radial plating cell design. (a) CAROSEL radial cell with soluble anodes (Ref 23), a large 8 ft diameter conductor roll, and the more recent addition of hold-down rolls. Source: Ref 24. (b) Soluble-anode radial cell with modifications made in the way new anodes are inserted into the cell. Source: Ref 37. (c) A radial cell with insoluble anodes and small-diameter conductor rolls in either side of the guide roll. Source: Ref 38. (d) Radial Jet Cell developed primarily for tin plating, not yet in commercial use. Source: Ref 39

Horizontal cell design was first employed for the Halogen tin process (Fig. 14a), which plates one surface of the strip at a time. However, horizontal cells with top and bottom anodes (initially soluble anodes) were later developed for electrogalvanizing (Fig. 14b). Then, in the 1980s, high-current-density (high-productivity) horizontal cells with insoluble anodes were introduced (Fig. 14c, d) to meet the high productivity requirements for electrogalvanized sheet production.

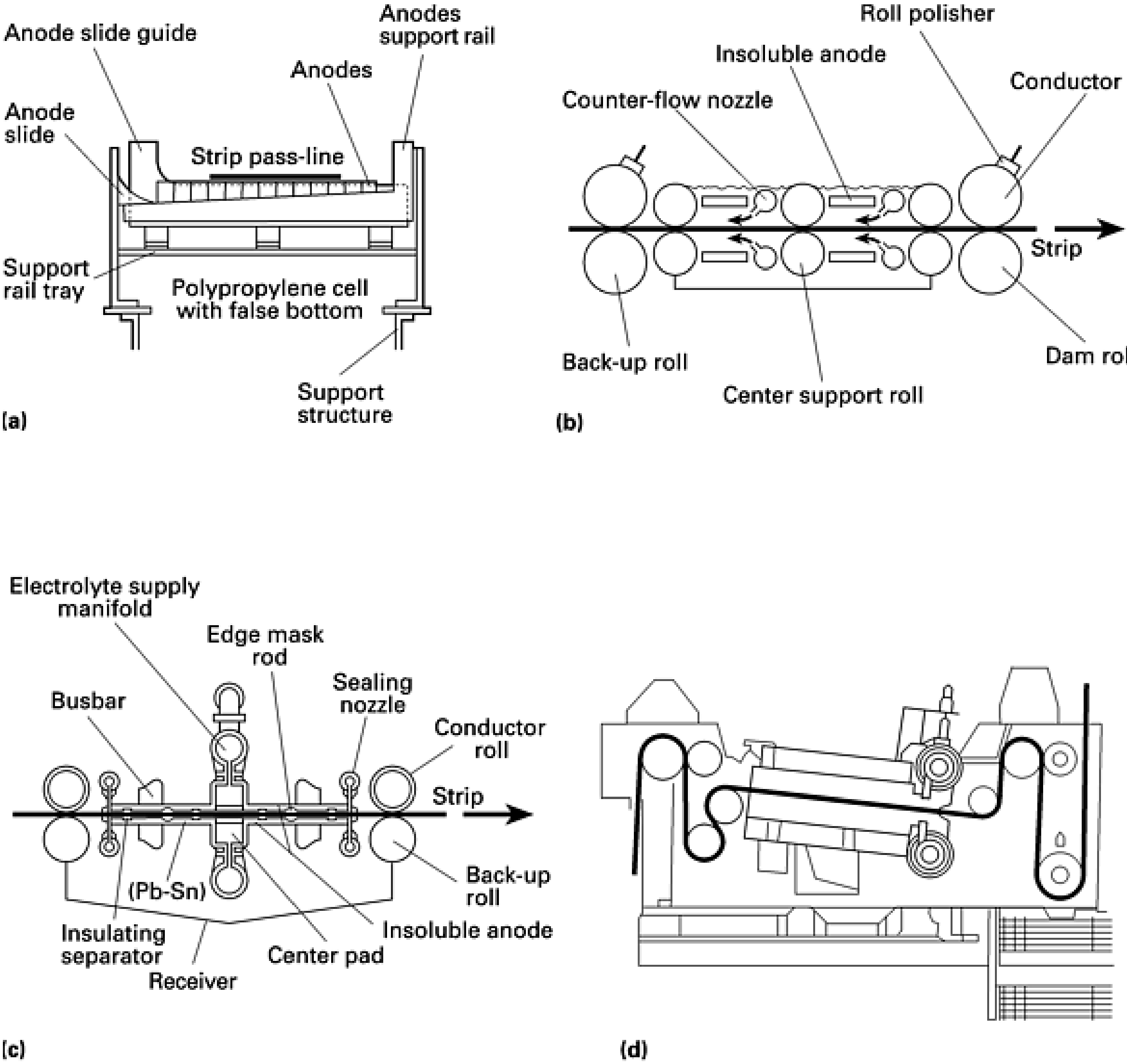


Fig. 14 Four examples of horizontal plating cells for continuous steel strip plating. (a) Front view of horizontal plating cell with soluble anodes, used in the Halogen tinning process. Source: Ref 30. (b) Conventional horizontal cell with insoluble anodes. Source: Ref 40. (c) LCC-H, a liquid-cushioned horizontal cell. Source: Ref 41. (d) Horizontal cell for high-current-density tin-free steel plating. Source: Ref 42

References cited in this section

6. E.E. Hoare, E.S. Hedges, and B.T.K. Barry, *The Technology of Tinplate,* St. Martin's Press, 1965
23. R.F. Higgs and W.R. Johnson, Coated Sheet Steel from Double Eagle Steel Coating Company, *Proceedings of the Fifth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1987
24. W.R. Johnson, C.J. Wu, T.A. Modrowski, and J.O. Stoddart, Improved Current Transfer and Productivity on the U.S. Steel CAROSEL Process through the Use of Hold Down Rolls, *Proceedings of Galvatech 1992* (Amsterdam, The Netherlands), Verlag Stahleisen, Dusseldorf, Germany
25. "Electrotinning of Continuous Steel Strip," slide course, American Electroplaters and Surface Finishers Society, 1992
26. G. Federman et al., U.S. Patents 4,871,429 and 4,880,507
27. T.W. Lippert, Food in Cans, *Iron Age,* Vol 149, 1942, p 29
28. E.F. Harris and Carnegie-Illinois Steel Co., Electrodeposition of Tin, U.S. Patent 2,450,794, 1948

29. A.H. DuRose, "Some Contributions from U.S. Supply Houses to Plating Science and Technology," *Plating,* Aug 1970
30. R.N. Steinbicker, Some Effects of Plating Bath Variables on the Quality Performance of a Halogen Tinning Line, *Proceedings of the Seventh Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1993
31. "Tin Free Steel (TFS) Product and Plating Process," slide course, American Electroplaters and Surface Finishers Society, 1992
32. G.A. Claytor, R.F. Higgs, et al., Chromium Plating by High Current Density, *Proceedings of the Fourth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1984
33. H. N. Hahn, D. R. Vernon, and K. Watanabe, The New L-S Electrogalvanizing Line, *Proceedings of the Fifth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1987
34. B. Meuthen, J.H. Meyer, and D. Wolfhard, A New Lease on Life for Electrolytic Zinc-Coated Sheet Steel: The German Scene, *Proceedings of the Fifth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1987
35. K.H. Kilian, K. Taffner, F. Weber, and H.-U. Weigel, Zinc-Nickel Coated Sheet Steel, *Proceedings of the Fifth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1987
36. W. Karner and G. Maresch, Electrogalvanizing of Strip Steel by the Gravitel Process, *Iron and Steel Engineer,* Nov 1989
37. A. Komoda, A. Kibata, et al., Development of Kawasaki Steel's Cassette Loading Cell for Electrogalvanizing, *Proceedings of Galvatech 1989,* The Iron and Steel Institute of Japan, p 170-177
38. R. Ulivieri, High Speed Electrodeposition of Mono- and Multi-layer Electrogalvanized Steel Strip, *Proceedings of the Fifth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1987
39. G.C. van Haastrecht and B.K. Paramanathan, Economic Aspects of Reactor Design for Strip Plating Cells, *Proceedings of the Seventh Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1993, p 163-174
40. T. Nonaka, H. Oishi, et al., High Performance Continuous Strip Plating Process with Insoluble Anode, *Proceedings of the Fifth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1987
41. K. Sakia, M. Kamada, et al., Development of the Liquid Cushion Electroplating Cell,*Proceedings of the Fourth Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1984
42. M. Develay, C. Kharouf, et al., Latest Developments in the Area of High V-Current Density Tin-Free Steel Process, *Proceedings of the Seventh Continuous Steel Strip Plating Symposium,* American Electroplaters and Surface Finishers Society, 1993, p 163-174

Batch Hot Dip Galvanized Coatings

Revised by Donald Wetzel, American Galvanizers Association

Introduction

HOT DIP GALVANIZING is a process in which an adherent, protective coating of zinc and zinc/iron compounds is developed on the surfaces of iron and steel products by immersing them in a bath of molten zinc. The protective coating usually consists of several layers (Fig. 1). Those closest to the basis metal are composed of iron-zinc compounds; these, in turn, may be covered by an outer layer consisting almost entirely of zinc.

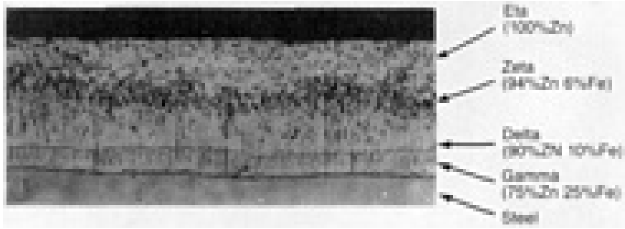


Fig. 1 Photomicrograph of typical hot dip galvanized coating. The molten zinc is interlocked into the steel by the alloy reaction, which forms zinc-iron layers and creates a metallurgical bond. See Table 3 for properties of alloy layers. 250×

The complex structure of layers that comprise a galvanized coating varies greatly in chemical composition and physical and mechanical properties, being affected by chemical activity, diffusion, and subsequent cooling. Small differences in coating composition, bath temperature, time of immersion, and rate of cooling or subsequent reheating can result in significant changes in the appearance and properties of the coating.

Hot dip galvanized coatings are produced on a variety of steel mill products, using fully mechanized, mass production methods. This article, however, is concerned primarily with the hot dip galvanizing of fabricated articles in manual or semiautomatic batch operations. For information about continuous coatings, see the article "Continuous Hot Dip Coatings" in this Volume.

ASTM and other standards related to galvanized coatings are given in Table 1.

Table 1 Standards relating to hot dip galvanized materials

ASTM	
A 123	Standard Specification for Zinc (Hot Dip Galvanized) Coatings on Iron and Steel Products
A 143	Standard Practice for Safeguarding Against Embrittlement of Hot Dip Galvanized Structural Steel Products and Procedure for Detecting Embrittlement
A 153	Standard Specification for Zinc Coating (Hot Dip) on Iron and Steel Hardware
A 384	Standard Recommended Practice for Safeguarding Against Warpage and Distortion During Hot Dip Galvanizing of Steel Assemblies
A 385	Standard Practice for Providing High Quality Zinc Coatings (Hot Dip)
A 767	Standard Specifications for Zinc Coated (Galvanized) Steel Bars for Concrete Reinforcement
A 780	Standard Practice for Repair of Damaged Hot Dip Galvanized Coatings
E 376	Standard Practice for Measuring Coating Thickness by Magnetic-Field or Eddy Current (Electromagnetic) Test Methods
AASHTO	

M111	Standard Specification for Zinc (Hot Dip Galvanized) Coatings on Iron and Steel Products
M232	Standard Specification for Zinc Coating (Hot Dip) on Iron and Steel Hardware
CSA	
G164-M	Hot Dip Galvanizing of Irregularly Shaped Articles

Source: Ref 1

Reference

1. *Galvanizing for Corrosion Protection: A Specifier's Guide to Bridge and Highway Applications,* American Galvanizers Association, 1992

Applications

Galvanized coatings are applied to iron and steel primarily to provide protection against corrosion of the base metal. Some major applications of hot dip galvanized coatings include:

- Structural steel for power generating plants, petrochemical facilities, heat exchangers, cooling coils, and electrical transmission towers and poles
- Bridge structural members, culverts, corrugated steel pipe, and arches
- Reinforcing steel for cooling towers, architectural precast concrete, and bridge decks exposed to chlorides
- Pole line hardware and railroad electrification structures
- Highway guard rails, high-rise lighting standards, and sign bridge structures
- Marine pilings and rails
- Grates, ladders, and safety cages
- Architectural applications of structural steel, lintels, beams, columns, and related building materials
- Galvanized and painted structural steel for aesthetic, color-coded or extended-life applications, including communication towers, pipe and sign bridges, railings, fencing, and agricultural equipment
- Wastewater treatment facilities, composting buildings, catwalks, gratings, railings, support steel, and related nonimmersion applications

Hot dip galvanized tower and high-strength bolts are produced and used in large quantities for service conditions where long-term integrity of bolted joints is required. In short, wherever steel is exposed to atmospheric, soil, or water corrosion, hot dip galvanized zinc coatings are a standard, effective, and economical method of protection.

The usefulness of hot dip galvanized coatings depends on:

- The relatively slow rate of corrosion of zinc as compared with that of iron (Table 2)
- The electrolytic protection provided to the basis steel when the coating is damaged
- The durability and wear resistance of the zinc coating and the intermetallic iron-zinc alloy layers (Table 3)
- The relative ease and low cost of painting the zinc coating either initially or later, when it is necessary to further extend the life of the structure; such painting is usually done after 25 to 40 years of maintenance-free service in rural and light industrial atmospheres

Table 2 Comparative rankings of 37 locations based on steel and zinc losses

Note the relatively slow rate of corrosion for zinc as compared to steel.

Ranking of location by least amount of material lost		Location	Material lost after 2-year exposure, g		Steel:zinc loss ratio
Zinc	**Steel**		**Zinc**	**Steel**	
1	1	Norman Wells, N.W.T., Canada	0.07	0.73	10.3
2	2	Phoenix, Ariz.	0.13	2.23	17.0
3	3	Saskatoon, Sask., Canada	0.13	2.77	21.0
4	4	Esquimalt, Vancouver Island, Canada	0.21	6.50	31.0
5	6	Fort Amidor Pier, Panama, C.Z.	0.28	7.10	25.2
6	8	Ottawa, Ontario, Canada	0.49	9.60	19.5
7	22	Miraflores, Panama, C.Z.	0.50	20.90	41.8
8	28	Cape Kennedy, $\frac{1}{2}$ mile from ocean	0.50	42.00	84.0
9	11	State College, Pa.	0.51	11.17	22.0
10	7	Morenci, Mich.	0.53	7.03	18.0
11	15	Middletown, Ohio	0.54	14.00	26.0
12	9	Potter County, Pa.	0.55	10.00	18.3
13	20	Bethlehem, Pa.	0.57	18.30	32.4
14	5	Detroit, Mich.	0.58	7.03	12.2
15	36	Point Reyes, Calif.	0.67	244.00	364.0
16	19	Trail, B.C., Canada	0.70	16.90	24.2
17	14	Durham, N.H.	0.70	13.30	19.0

18	13	Halifax (York Redoubt) N.S., Canada	0.70	12.97	18.5
19	18	South Bend, Pa.	0.78	16.20	20.8
20	27	East Chicago, Ind.	0.79	41.10	52.1
21	29	Brazos River, Texas	0.81	45.40	56.0
22	23	Monroeville, Pa.	0.84	23.80	28.4
23	34	Dayton Beach, Fla.	0.88	144.00	164.0
24	32	Kure Beach, N.C. (800 ft lot)	0.89	71.00	80.0
25	17	Columbus, Ohio	0.95	16.00	16.8
26	12	Montreal, Quebec, Canada	1.05	11.44	10.9
27	16	Pittsburgh, Pa.	1.14	14.90	13.1
28	10	Waterbury, Conn.	1.12	11.00	9.8
29	25	Limon Bay, Panama, C.Z.	1.17	30.30	25.9
30	21	Cleveland, Ohio	1.21	19.00	15.7
31	24	Newark, N.J.	1.63	24.70	15.1
32	33	Cape Kennedy (180 ft from ocean, 30 ft elevation)	1.77	80.20	45.5
33	35	Cape Kennedy (180 ft from ocean, ground level)	1.83	215.00	117.0
34	31	Cape Kennedy (180 ft from ocean, 60 ft elevation)	1.94	64.00	33.0
35	26	Bayonne, N.J.	2.11	37.70	17.9
36	37	Kure Beach, N.C. (80 ft lot)	2.80	260.00	93.0
37	30	Halifax (Federal Building) N.S., Canada	3.27	55.30	17.0

Source: Ref 1

Table 3 Properties of alloy layers of a hot dip galvanizing coating

Layer[a]	Composition	Hardness, DPN	Iron, %	Melting Temperature	
				°C	°F
Eta	Zn	70	0	454	850
Zeta	$FeZn_{13}$	179	6	530	986
Delta	$FeZn_7$	244	7-12	530-670	986-1238
Gamma	Fe_8Zn_{10}	. . .	21-28	670-780	1238-1436

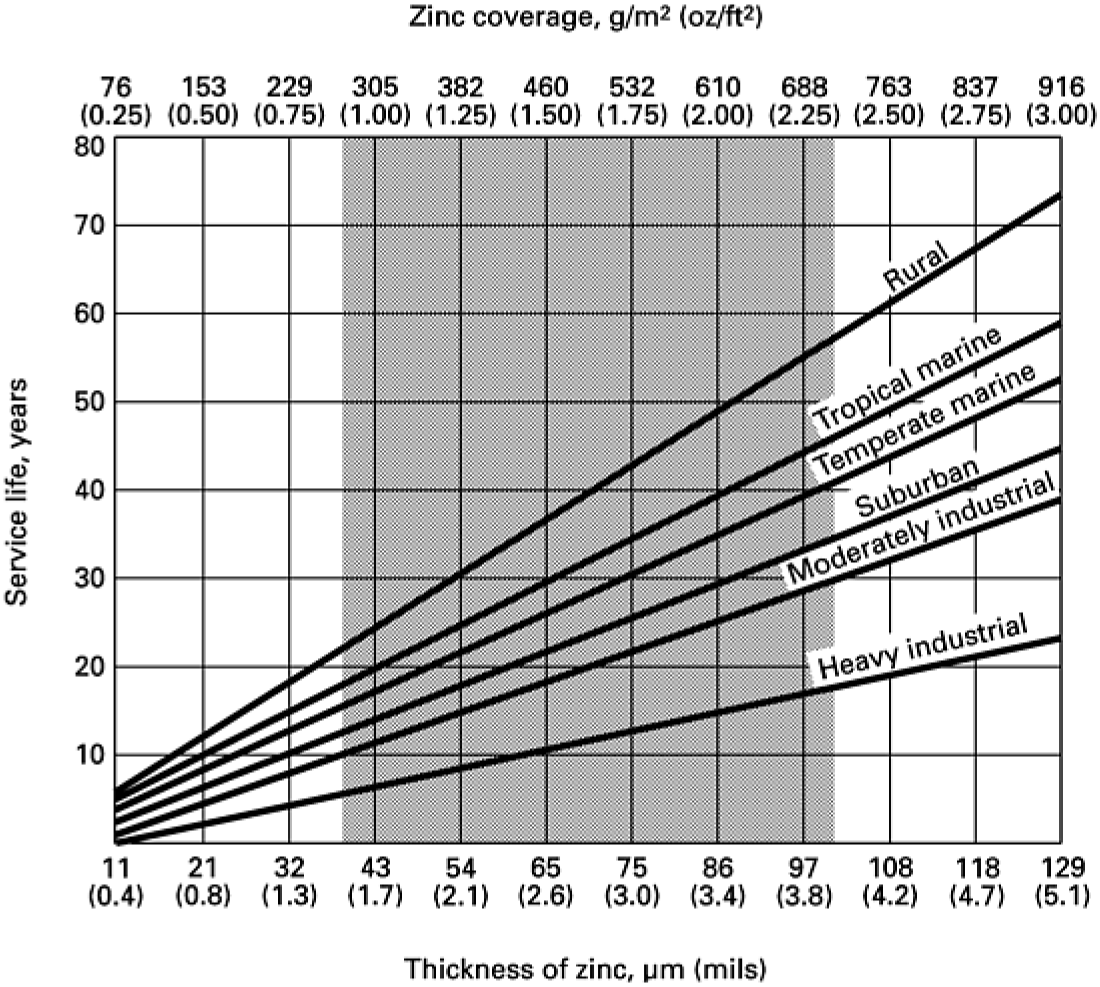
(a) See Fig. 1.

Hot dip galvanized zinc coatings have their longest life expectancy in rural areas where sulfur dioxide and other industrial pollutant concentrations are low (Fig. 2). These coatings also give satisfactory service in most marine environments (Table 4). Although the life expectancy of hot dip galvanized coatings in more severe industrial environments is not as long as for less aggressive environments, the coatings are still used extensively in those exposures, because in general, no more effective and economical method of protection is available. In cases involving particularly severe exposure conditions, coatings slightly heavier than the standard 710 g/m^2 (2.3 oz/ft^2) minimum in ASTM standard specifications A 123-89 or paint over galvanized coatings (known as duplex coatings) are often selected as the preferred protective system.

Table 4 Corrosion of zinc in different types of water

Water type	Attacking substances	Passivating substances	Corrosion products		Relative corrosion rate
			Solubility	Adhesion	
Hard water	O_2+CO_2	Ca+Mg	Very low	Very good	Very low
Sea water	O_2+CO_2+Cl	Mg+Ca	Low	Very good	Moderate
Soft water, with free air supply	O_2+CO_2	. . .	High	Good	High
Soft or distilled, with poor air supply	O_2	. . .	Very high	Very poor	Very high

Note: The different compositions of the corrosion products have not been included here because they are complex and depend on different compounds, salts, etc., that are present in all natural waters.



Atmosphere	Description
Heavy industrial atmospheres	These contain general industrial emissions such as sulfurous gases, corrosive mists, and fumes released from chemical plants and refineries. The most aggressive conditions are often found in places of intense industrial activity where the coating is frequently wetted by rain, snow, and other forms of condensation. In these areas, sulfur compounds can combine with atmospheric moisture to convert the normally adherent and insoluble zinc carbonates into zinc sulfite and zinc sulfate. These sulfur compounds are water soluble and adhere poorly to the zinc surface. They are removed by rain with relative ease, exposing a fresh zinc surface to additional corrosion. In general, zinc dissipates more when exposed to this type of environment than any other atmospheric environment. Still, the steel corrodes far more slowly in this type of environment when protected by zinc than when just bare steel is used.
Moderately industrial atmospheres	These environments are similar to those of heavy industrial atmospheric environments but, from the standpoint of corrosion, are not quite as aggressive. The amount of emissions in the air may be somewhat lower than that of heavy industrial environments, and/or the type of emissions may be less aggressive. Most city or urban area atmospheres are classified as moderately industrial.
Suburban atmospheres	These atmospheres are generally less corrosive than moderately industrial areas and, as the term suggests, are found in the largely residential, perimeter communities of urban or city areas.
Temperate marine	The length of service life of the galvanized coating in marine environments is influenced by proximity to the coastline and prevailing wind direction and intensity. In marine air, chlorides from sea spray can react with the

atmospheres	normally protective, initial corrosion products to form soluble zinc chlorides. When these chlorides are washed away, fresh zinc is exposed to corrosion. Nevertheless, temperate marine atmospheres are usually less corrosive than suburban atmospheres.
Tropical marine atmospheres	These environments are similar to temperate marine atmospheres except they are found in warmer climates. Possibly because many tropical areas are found relatively far removed from heavy industrial or even moderately industrial areas, tropical marine climates tend to be somewhat less corrosive than temperate marine climates.
Rural atmospheres	These are usually the least aggressive of the six atmospheric types. This is primarily due to the relatively low level of sulfur and other emissions found in such environments.

Fig. 2 Service life (time to 5% rusting of steel surface) versus thickness of zinc for selected atmospheres. Shaded area is thickness range based on minimum thicknesses for all grades, classes, etc., encompassed by ASTM A 123 and A 153. Source: Ref 2

When hot dip galvanized after-fabrication coatings are painted for protective or decorative reasons, a variety of surface preparation systems may be employed to prepare the galvanized surface for the top coat system. Table 5 shows the adhesion of paints to variously prepared galvanized surfaces. A wide range of proprietary top coat systems are available for use with materials hot dip galvanized after fabrication.

Table 5 Adhesion of air-drying paints applied to selected hot dip galvanized steel surfaces

Adhesion as determined by cross-hatch or V-cut test: E, excellent; G, good; F, fair; P, poor. See Table 9 for other characteristics of these paints.

Type of paint (vehicle base)	Adhesion on indicated surface			
	Freshly galvanized[a]	Weathered galvanized[b]	Cold or hot phosphated	Sweep-blasted and galvanized
1. Alkyd-tung oil-phenolic resin combinations[c]	F	G	E	E
2. DCO-alkyd-calcium plumbate[d]	E	E	E	E
3. Alkyd-acrylic combinations	G	G	E	E
4. Chlorinated rubber	F-G	F-G	G	E
5. Chlorinated rubber-acrylic combinations	G	G	E	E
6. Acrylate dispersions[e]	F-G	F-G	G	G
7. Acrylic-styrene dispersions[e]	G	G	G	E
8. Acrylic/diisocyanate (2 compositions)	G	F	G	E
9. Vinyl copolymers	F-G	F-G	G	G

10. PVC/acrylic combinations	G	G	E	E
11. PVC-dispersions[(e)]	F	F-G	G	F-G
12. Epoxy resin (2 compositions)[(f)]	G	G	G	E
13. Epoxy ester[(g)]	P	F	G	G
14. Epoxy/tar (2 compositions)	P	F	F	G
15. Polyurethane (2 compositions)[(h)]	P	F	F-G	G

Note: Variations in film properties may occur with variations in formulation.

Source: Ref 3

(a) Up to about 4 h after galvanizing.

(b) Weathered in an unpolluted or mildly polluted climate, for 1 to 3 months only.

(c) Precooked tung oil/alkylphenolic resin combinations, chilled with drying-oil-modified alkyd resins.

(d) Dehydrated castor oil (DCO)-modified alkyd resin, pigmented with calcium orthoplumbate (COP) as main pigment in the priming coat.

(e) Finely dispersed polymers in water.

(f) With polyamide hardener.

(g) Epoxy resin-dehydrated castor oil ester.

(h) With encapsulated diisocyanate hardener.

Galvanized steels perform well in contact with a wide variety of other materials (Table 6). Moisture conditions play an important role in the performance of galvanized steels in contact with other materials.

Table 6 Additional corrosion of zinc and galvanized steel resulting from contact with other metals

0, Either no additional corrosion, or at the most only very slight additional corrosion; usually tolerable in service. 1, Slight or moderate additional corrosion; may be tolerable in some circumstances. 2, Fairly severe additional corrosion; protective measures will usually be necessary. 3, Severe additional corrosion; contact should be avoided.

Metal in contact	**Environment**

	Atmospheric			Immersed	
	Rural	**Industrial/urban**	**Marine**	**Fresh water**	**Sea water**
Aluminum and aluminum alloys	0	0 to 1	0 to 1	1	1 to 2
Aluminum bronzes and silicon bronzes	0 to 1	1	1 to 2	1 to 2	2 to 3
Brasses, including high-tensile-strength brass (manganese bronze)	0 to 1	1	0 to 2	1 to 2	2 to 3
Cadmium	0	0	0	0	0
Cast irons	0 to 1	1	1 to 2	1 to 2	2 to 3
Cast iron (austenitic)	0 to 1	1	1 to 2	1 to 2	1 to 3
Chromium	0 to 1	1 to 2	1 to 2	1 to 2	2 to 3
Copper	0 to 1	1 to 2	1 to 2	1 to 2	2 to 3
Copper-nickels	0 to 1	0 to 1	1 to 2	1 to 2	2 to 3
Gold	(0 to 1)	(1 to 2)	(1 to 2)	(1 to 2)	(2 to 3)
Gun metals, phosphor bronzes, and tin bronzes	0 to 1	1	1 to 2	1 to 2	2 to 3
Lead	0	0 to 1	0 to 1	0 to 2	(0 to 2)
Magnesium and magnesium alloys	0	0	0	0	0
Nickel	0 to 1	1	1 to 2	1 to 2	2 to 3
Nickel-copper alloys	0 to 1	1	1 to 2	1 to 2	2 to 3
Nickel-chromium-iron alloys	(0 to 1)	(1)	(1 to 2)	(1 to 2)	(1 to 3)
Nickel-chromium-molybdenum alloys	(0 to 1)	(1)	(1 to 2)	(1 to 2)	(1 to 3)

Nickel silvers	0 to 1	1	1 to 2	1 to 2	1 to 3
Platinum	(0 to 1)	(1 to 2)	(1 to 2)	(1 to 2)	(2 to 3)
Rhodium	(0 to 1)	(1 to 2)	(1 to 2)	(1 to 2)	(2 to 3)
Silver	(0 to 1)	(1 to 2)	(1 to 2)	(1 to 2)	(2 to 3)
Solders, hard	0 to 1	1	1 to 2	1 to 2	2 to 3
Solders, soft	0	0	0	0	0
Stainless steel (austenitic and other grades containing approximately 18% Cr)	0 to 1	0 to 1	0 to 1	0 to 2	1 to 2
Stainless steel (martensitic grades containing approximately 13% Cr)	0 to 1	0 to 1	0 to 1	0 to 2	1 to 2
Steels (carbon and low-alloy)	0 to 1	1	1 to 2	1 to 2	1 to 2
Tin	0	0 to 1	1	1	1 to 2
Titanium and titanium alloys	(0 to 1)	(1)	(1 to 2)	(0 to 2)	(1 to 3)

Notes: Ratings in parentheses are based on very limited evidence and hence are less certain than other values shown. Values are in terms of additional corrosion, and the symbol 0 should not be taken to imply that the metals in contact need no protection under all conditions of exposure.

Source: Ref 2

Galvanized surfaces have a good tolerance to various chemicals within the range of 4 to 12.5 pH (Fig. 3). Some chemicals that have been successfully stored in galvanized containers are listed in Table 7.

Table 7 Selected chemicals that have been successfully stored in galvanized containers

Hydrocarbons
Benzene (benzole) Toluene (toluole) Xylene (xylole) Cyclohexene Petroleum ethers Heavy naphtha

Solvent naphtha

Alcohols

Methyl parafynol (methyl pentynol)
Morpholinoisopropanol
Glycerol (glycerin)

Halides

Carbon tetrachloride
Amyl bromide
Butyl bromide
Butyl chloride
Cyclohexyl bromide
Ethyl bromide
Propyl bromide
Propyl chloride
Trimethylene bromide (1, 3-dibromopropane)
Bromobenzene
Chlorobenzene
Aroclors and pyroclors (chlorobiphenyls)

Nitriles (cyanides)

Diphenylacetonitrile
p-chlorobenzglycyanide

Esters

Allyl butyrate
Allyl caproate
Allyl formate
Allyl propionate
Ethyl butyrate
Ethyl isobutyrate
Ethyl caproate
Ethyl caprylate
Ethyl propionate
Ethyl succinate
Amyl butyrate
Amyl isobutyrate
Amyl caproate
Amyl caprylate
Methyl butyrate
Methyl caproate

Methyl propionate
Methyl succinate
Benzyl butyrate
Benzyl isobutyrate
Benzyl propionate
Benzyl succinate
Octyl butyrate
Octyl caproate
Butyl butyrate
Butyl isobutyrate
Butyl caproate
Butyl propionate
Butyl succinate
Butyl titanate[a]
Propyl butyrate
Propyl isobutyrate
Propyl caproate
Propyl formate
Propyl propionate
Isobutyl butyrate
Isobutyl caproate
Isopropyl benzoate
Isopropyl caproate
Isopropyl formate
Isopropyl propionate
Cyclohexyl butyrate

Phenols

Phenol
Cresols (methylphenols)
Xylenols (dimethylphenols)
Biphenol (dihydroxybiphenyl)
2,4-dichlorophenol
p-chloro-o-cresol
Chloroxylenols

Amines and Amine salts

Pyridine
Pyrrolidine
Methylpiperazine
Dicarbethoxypiperazine
1-benzhydryl-4-methylpiperazine
2,4-diamino-5-(4-chlorphenyl-6-)ethylpyrimidine
Hydroxyethylmorpholine (hydroxyethyldiethylenimide oxide)
p-aminobenzenesulphonyl-guanidine
Butylamine oleate
Piperazine hydrochloride monohydrate
Carbethoxypiperazine hydrochloride (dry)

Amides
Formamide Dimethylformamide

Miscellaneous
Glucose (liquid) Benzilideneacetone p-chlorbenzophenone Sodium azobenzenesulphonate Melamine resin solutions Crude cascara extract Creosote

Source: Ref 2

(a) And other unspecified titanates.

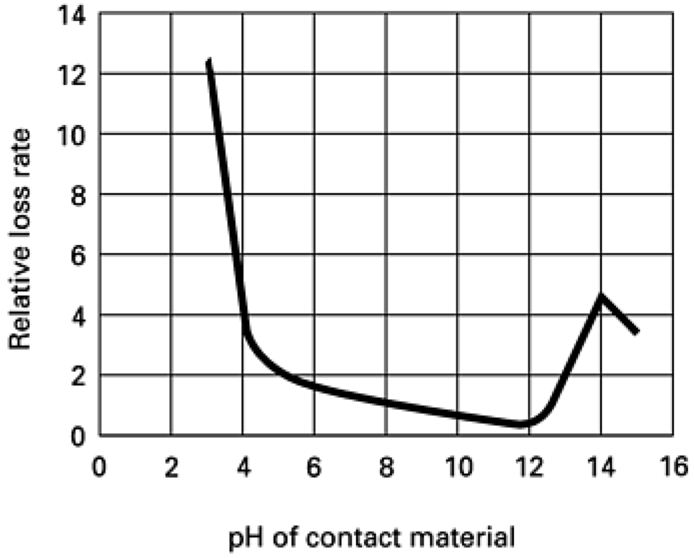


Fig. 3 Effect of pH on corrosion of zinc. Source: Ref 1

References cited in this section

1. *Galvanizing for Corrosion Protection: A Specifier's Guide to Bridge and Highway Applications,* American Galvanizers Association, 1992
2. *Hot Dip Galvanizing for Corrosion Protection of Steel Products,* American Galvanizers Association, 1989
3. Frank Porter, *Zinc Handbook: Properties, Processing, and Use in Design,* International Lead Zinc Research Organization, 1991

Metallurgical Characteristics of Galvanized Coatings

Iron and Steel Substrates. The chemical composition of irons and steels, and even the form in which certain elements such as carbon and silicon are present, determines the suitability of ferrous metals for hot dip galvanizing and may markedly influence the appearance and properties of the coating. Steels that contain less than 0.25% C, less than 0.05% P, less than 1.35% Mn, and less than 0.05% Si, individually or in combination, are generally suitable for galvanizing using conventional techniques. The results of a recent study suggest that a silicon level of 0.15% to 0.25% should also produce acceptable results. Another study suggests that optimum amounts of silicon and phosphorus can be defined by the formula %Si + 2.5(%P) = 0.09.

To avoid brittleness of the iron-zinc alloy layer in cast iron materials, substrate iron must be low in phosphorus and silicon; a preferred composition may contain about 0.01% P and about 0.15% Si.

Type of Zinc. Any grade of zinc in ASTM B 6-87(92) can be used in galvanizing. ASTM A 123-89 now stipulates that the zinc being used for galvanizing must contain 98% pure zinc. The remaining 2% may be such other elements as desired to produce an optimum coating. ASTM A 123 does not require prime western zinc, but some other galvanizing specifications do. Most galvanizers use either prime western (98.0% Zn) or high grade (99.90% Zn). Prime western has a lead alloy content of 0.5 to 1.4%, which is beneficial for hot dip galvanizing, and higher allowed levels of iron and other elements as impurities. When high grade zinc is used, lead is often added separately to the kettle. During galvanizing, there is a buildup of iron in the bath caused by dissolution of iron from the surface of steel work and the tank walls so that the equilibrium iron content of the bath is nearly equal regardless of the grade of zinc used. High purity special high grade (99.99% Zn) zinc coatings have the same metallurgical properties as those obtained with prime western zinc. High purity zinc has little metallurgical advantage for use on fabricated items.

Bath Alloying Elements. Cadmium and iron are usually present in zinc baths as contaminants, but are not intentionally added to the bath as alloying elements. An aluminum concentration up to 0.01% will improve drainage and increase the brightness of the galvanized coating. Small amounts of lead may be added to promote proper spangle and better drainage and to aid with drossing the bath. Other alloying elements have been tried with success. Nickel, vanadium, antimony, titanium, and rare earth metals are known to produce positive results under some circumstances.

An aluminum concentration less than 0.01% is generally maintained in the zinc bath when a preflux and/or a bath flux are used. The high chloride content of the fluxes reacts with the aluminum in the bath, producing a surface film of dross, oxide, and chloride on the bath surface.

Coating Thickness. In addition to base metal chemistry and surface profile, the thickness of coatings applied by hot dipping is primarily a function of:

- The duration of immersion, which controls the thickness of alloy layer (Fig. 4)
- The speed of withdrawal from the bath, which controls the amount of unalloyed zinc adhering (Fig. 5)
- The temperature of the bath, which affects both the alloy and the free zinc layers (Fig. 6)

Coating weight can be further affected by the amount of zinc removed by wiping, shaking, or centrifuging after the dipping process.

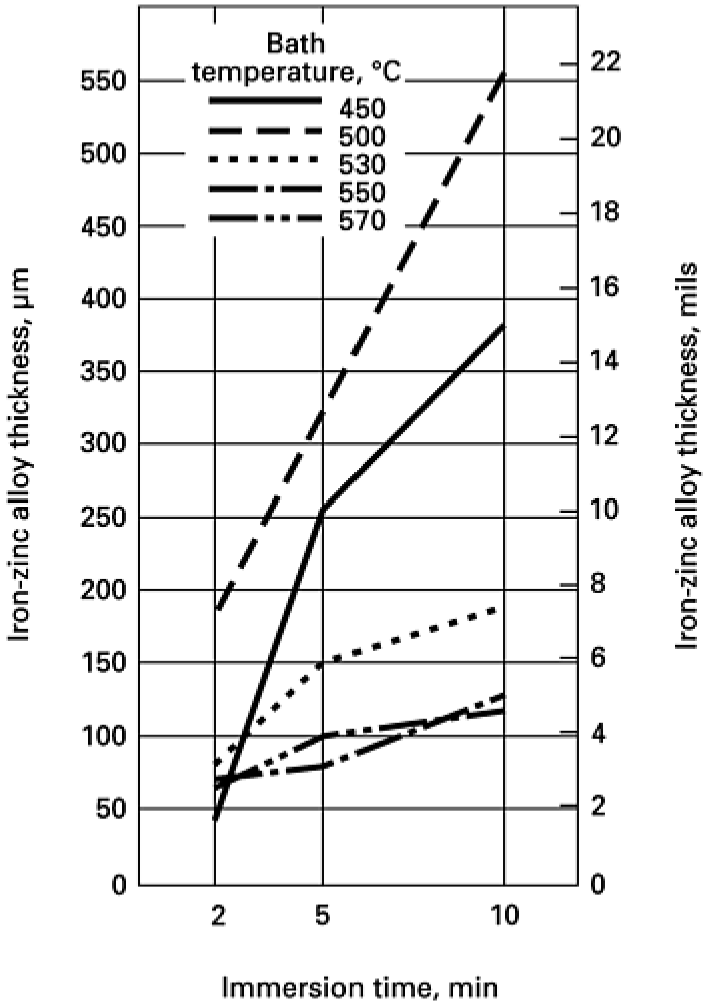


Fig. 4 Coating thickness versus immersion time for a typical silicon-killed steel galvanized at various temperatures. Source: Ref 4

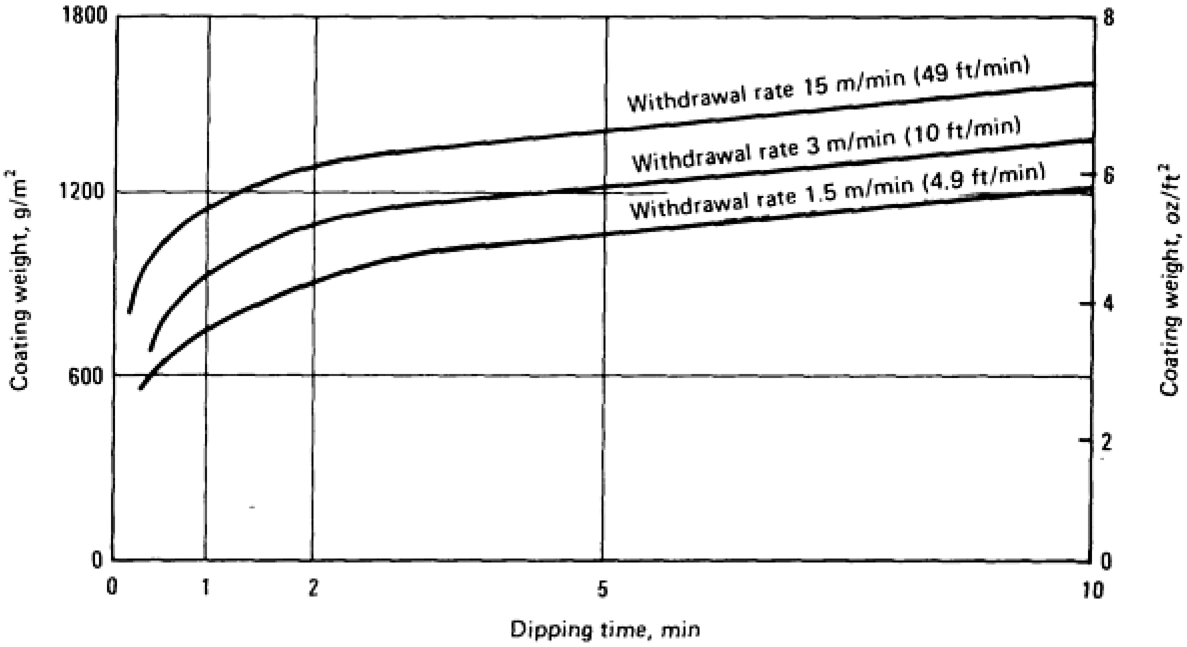


Fig. 5 Effect of withdrawal rate on weight of galvanized coatings. Bath temperature, 435 °C (815 °F)

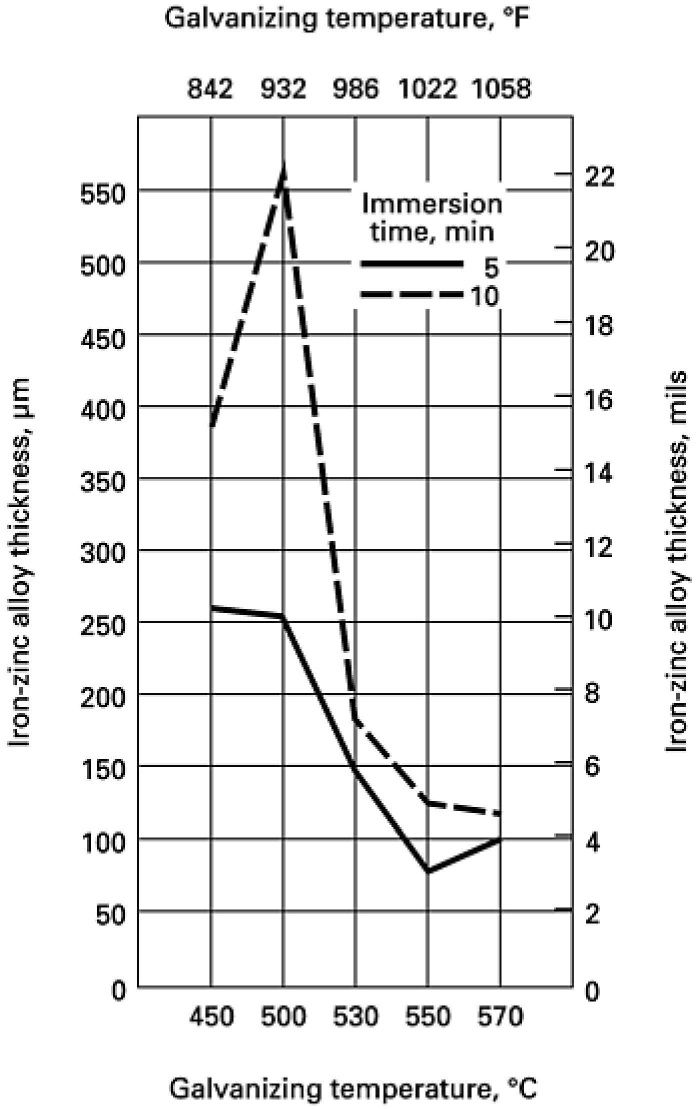


Fig. 6 Coating thickness versus galvanizing temperature for a typical silicon-killed steel at two different immersion times. Source: Ref 4

The protection against corrosion provided by zinc coatings is essentially determined by the thickness of the coating (Fig. 2). Many comprehensive studies have shown that all other factors, such as method of applying the zinc coating, purity of the zinc, and the extent to which it is alloyed with the iron, are minor in determining life, as compared with the thickness of the coating.

Zinc coatings applied by hot dipping after fabrication are measured in mils of zinc on the surface. However, the weight of galvanized coatings on sheet is stated in ounces per square foot (grams per square meter) of sheet. Since the sheet is coated on both sides, the coating weight per square foot (meter) of surface on each side is approximately one half the average weight of coating per square foot (grams per square meter) of sheet. ASTM A 123 and A 153 give coating weight requirements as a function of thickness and type of material to be coated.

Reference cited in this section

4. Richard Amistadi, *Very High Temperature Galvanizing,* St. Joe Minerals Corporation (now Zinc Corporation

of America), 1974

Effect of Galvanizing Process on Substrate Materials

Tensile Strength, Impact Toughness, and Formability. The tensile strength, yield strength, elongation at rupture, and reduction of area of hot rolled steels remain virtually unchanged after hot dip galvanizing. A study by BNF Technologies, Oxfordshire, England, indicates that, in welded structures, the weld stresses may be reduced by 50 to 60% as a result of hot dip galvanizing. Increased strength levels induced by cold working or heat treatment are generally reduced by hot dip galvanizing. The degree of strength reduction depends on such factors as the amount of working, the nature of heat treatment, and base steel chemistry. Impact toughness is slightly reduced, but not so much that the applicability of the steel is affected.

The formability of the steel is not affected. However, if the steel is sharply bent, the zinc coating may craze or crack on the tension side of the bend, depending on thickness of coating and bend radius.

Fatigue strength of various types of steels is affected differently as a result of the hot dip galvanizing process. Rimmed and aluminum-killed steels exhibit relatively little reduction of fatigue strength, whereas the fatigue strength of silicon-killed steels can be reduced considerably by hot dip galvanizing.

The reason for this difference in fatigue strength for silicon-killed steels is attributable to the different structure of the coating (Fig. 7). Under the influence of fatigue stresses, cracks may form in the iron-zinc layer and act as crack initiators in the steel surface.

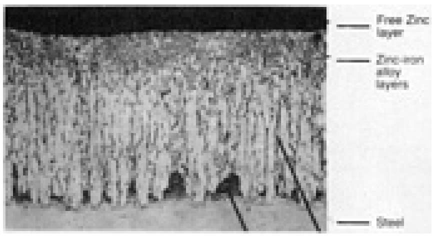


Fig. 7 Photomicrograph of a galvanized coating on a steel containing 0.40% Si. 250×

Fatigue strength is typically determined by laboratory tests where untreated new steels with mill scale are compared with hot dip galvanized material. If a steel structure is exposed outdoors in the untreated state, it is immediately attacked by rust. The corrosion pits that form result in a loss in fatigue strength. Thus, under in-service exposure conditions, the fatigue strength of ungalvanized steel declines rapidly as a result of the rust attack that occurs at the point of damage. For hot dip galvanized steels, however, the fatigue strength of the steel does not appreciably change during the exposure period as long as the zinc coating remains on the steel surface.

Hydrogen embrittlement does not result from the hot dip galvanizing of ordinary unalloyed and low-carbon mild steels. Any hydrogen absorbed during pickling is effectively eliminated on immersion in the zinc bath because of the relatively high temperature of about 460 °C (860 °F). Hardened steels can become brittle because of hydrogen diffusion into the steel. Such materials should always be tested for embrittlement after pickling before large lots are hot dip galvanized.

Intergranular cracking because of the penetration of zinc into the grain boundaries in steel can sometimes occur in connection with hot dip galvanizing, but only in cases where large stresses have been induced in the steel by welding or hardening. The risk of intergranular cracks and embrittlement failure because of zinc penetration is negligible in connection with hot dip galvanizing of ordinary low-carbon structural steels. However, hardened materials may be sensitive and should be tested for susceptibility to zinc penetration and cracking before hot dip galvanizing on large quantities of material is undertaken.

Cleaning Before Galvanizing

Iron and steel pieces to be hot dip galvanized after fabrication must be free of oil, grease, drawing lubricants, mill scale, and other surface contaminants before fluxing and immersion in molten zinc. Inadequate or improper surface preparation is the most frequent cause of defects and bare spots in galvanized coatings.

In batch hot dip galvanizing, the material to be galvanized is first degreased and then pickled in sulfuric or hydrochloric acid. Since any iron salts or particles left on the surface of the material form dross in the galvanizing kettle, each of the degreasing and pickling steps is followed by a water rinse.

Degreasing. Organic contaminants can be removed from the work by several methods. The most common of these in the after-fabrication hot dip galvanizing process is the use of heated alkaline cleaning baths. The alkaline cleaning process performs five basic functions.

- Dispersion by washing soil from the work
- Emulsification by breaking up the soil and suspending it in solution
- Film shrinkage by forming beads of oil to remove oil films
- Saponification by converting animal and vegetable oils to water-soluble soaps
- Aggregation by collecting soil particles away from the work where they can be more easily removed from the solution

The alkaline cleaning solutions should be heated to between 65 to 82 °C (150 to 180 °F).

Control of the strength of the heated alkaline solution is essential to an effective degreasing operation. These solutions lose strength because of chemical cleaning action effects and are diluted by make-up water added to replace dragout losses. Although experience can be a good indicator of cleaning solution activity, a better method is to test the alkaline solution periodically for strength and to make periodic additions to maintain the solution at the desired concentration. See the article "Alkaline Cleaning" in this Volume for additional information.

Acid Pickling. Aqueous solutions of sulfuric acid or hydrochloric acid are generally used to remove mill scale and rust from steel parts before galvanizing. These pickling solutions may either be sulfuric acid, 3 to 14 wt%, or hydrochloric acid, 5 to 15 wt%. To increase effectiveness, sulfuric acid solutions are always used hot at 60 to 79 °C (140 to 175 °F); hydrochloric acid solutions are usually used at about room temperature, 24 to 38 °C (75 to 100 °F), to avoid excessive fuming. To avoid overpickling, inhibitors are often used with both sulfuric and hydrochloric acid solutions.

Nitric acid pickling, although rarely used, may be employed for removing silicates from malleable and gray iron castings. Silicates are insoluble in hydrochloric or sulfuric acid.

Wetting and/or foaming agents may be added to the acid solutions to promote better drainage of acids and to minimize heat loss of hot solutions.

Abrasive Cleaning. Some assemblies are made up of both cast and wrought materials; these assemblies require additional surface preparation prior to fluxing and galvanizing. All assemblies of cast iron, cast steel, and malleable iron with wrought steel should be abrasively cleaned after assembly and before pickling. Many other parts may also be abrasively cleaned to minimize or eliminate pickling.

In general, cast materials require less pickling than hot-rolled steel products, unless scale is removed from steel by blast cleaning. Therefore, care must be exercised to avoid burning or damaging the castings in an assembly during the time required to pickle the hot rolled components.

General Batch Galvanizing Procedures

Wet and Dry Galvanizing. Two types of conventional batch galvanizing practices currently in use are the wet process and the dry process. Dry galvanizing was developed and refined in Europe. Recent surveys indicate that 40% of galvanizing operations in North America are wet and the remaining 60% dry. The dry process is generally considered to be less energy intensive than the wet process, but it is more sensitive to surface preparation deficiencies.

Wet galvanizing involves a kettle-top flux blanket; dry galvanizing uses a preflux, and no flux blanket on the kettle. Sulfuric or hydrochloric acid pickling can be used with either wet or dry galvanizing. The choice is primarily based on disposal and reprocessing costs for the acids.

In the dry galvanizing process, after the material is degreased and pickled, the workpieces are immersed in an aqueous flux solution, dried, and then immersed in the molten zinc bath. In the wet galvanizing process, the work is not usually prefluxed after cleaning and pickling but is placed in the molten zinc bath through a top flux blanket on the kettle. However, an aqueous preflux may be used in conjunction with a top flux on the zinc bath.

Workpieces are handled either mechanically, using overhead hoists, or with hand tools. Small items such as washers, fasteners, and nails are handled in baskets. The baskets are usually centrifuged as the work leaves the molten zinc bath to remove excess zinc and to distribute the coating evenly. In all cases, workpieces must be handled properly until the coating has completely solidified, which is accomplished by either quenching or air cooling.

Surface Conditioning Requirements. Although degreasing, pickling, water rinsing, and other cleaning procedures remove most of the surface contamination and scale from iron and steel, small amounts of impurities in the form of oxides, chlorides, sulfates, and sulfides are retained. Unless removed, these impurities will interfere with the iron-zinc reaction when the iron or steel part is immersed in molten zinc.

In the wet galvanizing process, a flux blanket on the surface of the molten zinc bath is used to remove these impurities and to keep that portion of the surface of the zinc bath through which the steel is immersed free from oxides. The flux blanket floats on the surface, and when workpieces are immersed in the bath, their surfaces are wetted by the molten flux. The flux must have sufficient chemical stability to maintain a chemically active foam at the galvanizing temperature and to perform its cleaning function at a high rate of speed.

Zinc ammonium chloride is generally used to provide a flux blanket on the molten zinc bath. There are several procedures for preparing the flux blanket. One generic method consists of mixing ammonium chloride (sal ammoniac) and zinc oxide to form the monoamine of zinc chloride. In the ensuing reaction, hydrogen and nitrogen are released, and the flux takes the form of a foam. Today, most commercial kettles are operated using premixed fluxes, which can be obtained from a variety of suppliers.

To be fully effective and to attain minimal fume galvanizing conditions, the flux should not contain an excess of ammonium chloride. To prevent abnormally rapid chemical breakdown of the flux, glycerin and other organic substances are added to the flux in small amounts of 1 to 2 vol%. These substances increase the foaming action, markedly reduce the loss of ammonia, and serve as insulators. Because the boiling point of a mixture of zinc chloride and ammonium chloride decreases as the ammonium chloride content increases (Fig. 8), no more than 2 to 3% ammonium chloride will remain in the molten salt solution at a kettle temperature of 455 °C (850 °F). However, to function effectively, a zinc chloride-ammonium chloride top flux must normally contain more than 5 to 10% dissolved ammonium chloride. To minimize fuming, it is necessary to reduce the top flux surface temperature, maintain an optimal level of dissolved ammonium chloride, and to disturb this equilibrium as little as possible.

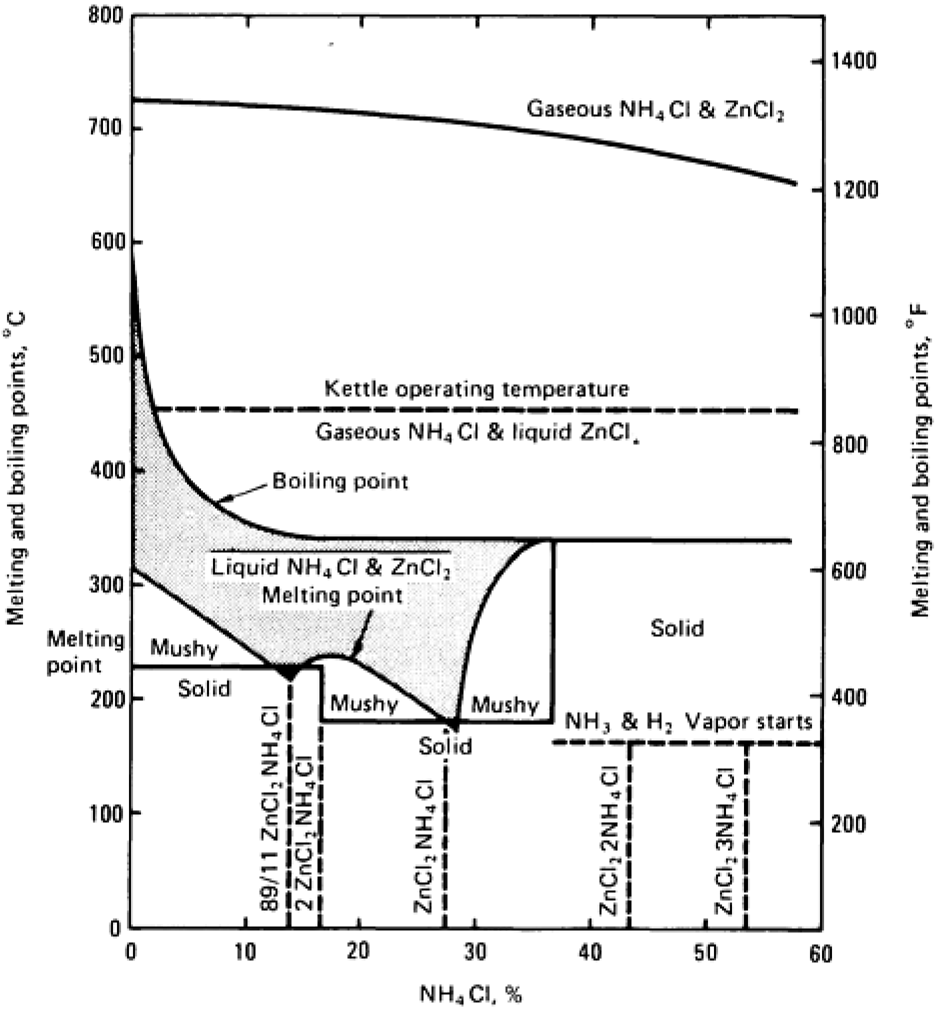


Fig. 8 Zinc chloride and ammonium chloride phase diagram

For dry galvanizing, it was once common practice to take the work directly from the hydrochloric acid pickle, dry it, and then put it in the molten zinc. However, the practice of going from the pickle tank to drying and then to the molten zinc produces more dross than the procedures of rinsing, prefluxing, and drying.

A preferred method, widely used today, is to pickle, rinse, flux in an aqueous zinc ammonium chloride, dry, and dip in the molten zinc bath. By using a preflux step, better control of the fluxing is possible, resulting in a more consistent finish. Also, the material may be held for about 1 h before dipping, which gives the galvanizer some flexibility in work flow on the galvanizing line.

Galvanizing Bath. The molten zinc bath is operated at temperatures usually in the range of 445 to 454 °C (830 to 850 °F). At 480 °C (900 °F) and above, the dissolution rate of iron and steel in zinc is extremely rapid, and the effects of these temperatures on both workpiece and galvanizing tank are generally harmful. Within the conventional galvanizing temperature range, an increase in temperature:

- Increases the fluidity of molten zinc
- Accelerates the formation of oxides on the bath surface
- Heats the part to a higher temperature, thus increasing the time required for the zinc to solidify when the part is withdrawn
- Reduces immersion time, thereby increasing the kettle utilization factor

Each of these considerations has a distinct effect and may be used to control the galvanizing process.

An increase in the fluidity of the bath improves drainage and is desirable provided the bath temperature does not exceed the normal operating range. An increase in bath temperature produces a much sharper temperature gradient from the surface to the center of the part, which depending on shape may result in an increase in distortion.

Unless the bath contains aluminum or unless its surface is well protected by a foam blanket of flux, an increase in bath temperature will accelerate the formation of an oxide film (or ash) on the surface of the bath. Some of this oxide film may cling to the workpiece when it is withdrawn from the bath, interfering with drainage and contributing to the formation of a coating with less desirable aesthetic properties. The effects of these oxides are most apparent on parts of thin cross section and large surface area.

Depending on the chemical composition of the iron or steel, the bath temperature may have significant metallurgical effects on the galvanized coating. The temperature at which the iron-zinc alloy layers are formed affects the relative amounts of each iron-zinc phase formed and the depth or total thickness of alloy layer (Fig. 4).

In the hot dip galvanizing of fabricated articles, the thickness of the coating is controlled by immersion time. Although timing is to some extent dependent on ease of handling and must be established by trial for each design of part being coated, the duration of immersion is usually in the range of 3 to 6 min. The speed of immersion influences the uniformity of the coating, particularly with long articles for which the difference in immersion time between the first and last areas to enter the bath may be considerable.

The reaction between clean low silicon steel and molten zinc proceeds rapidly for the first 1 or 2 min after the work has been immersed, producing an alloy layer that continues to grow at decreased rate the longer the article is left in the bath. However, for steels containing silicon in excess of 0.05%, the coating weight increases linearly with respect to the time of immersion producing, in general, heavier coatings (Fig. 9) Therefore, it is important to minimize immersion time for silicon-bearing steels to prevent excessive alloy growth and coating weight.

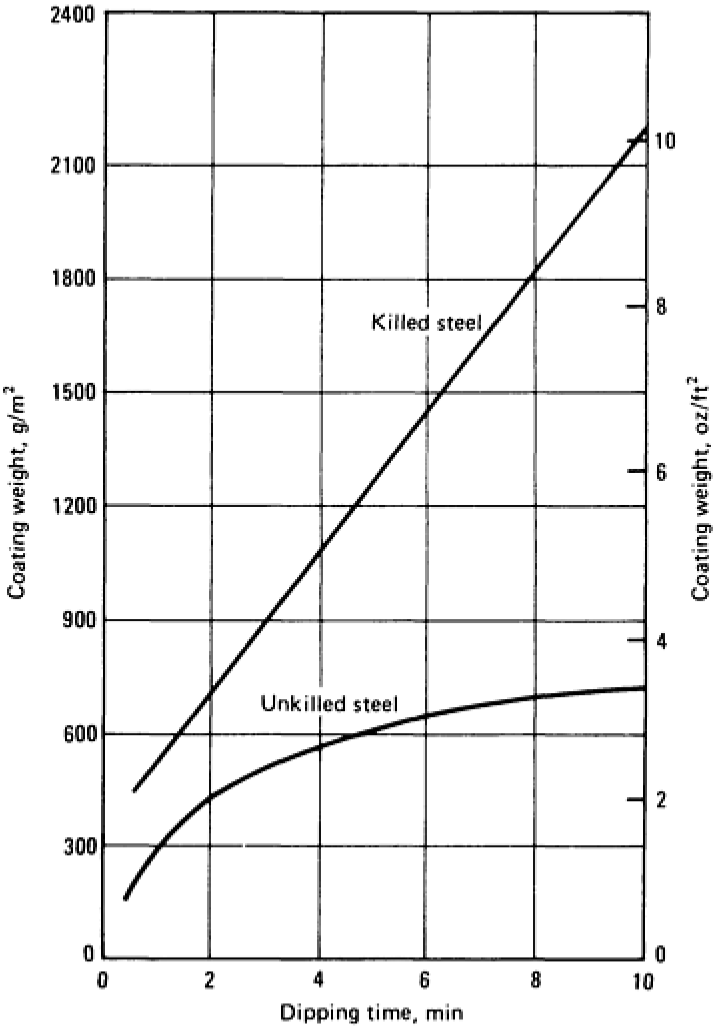


Fig. 9 Effect of immersion time on galvanized coating weight for killed and unkilled steels. Galvanizing temperature, 455 °C (850 °F). Killed steel: 0.35% C, 0.26% Si, 0.46% Mn. Unkilled steel: 0.13% C, trace Si, 0.40% Mn

To provide a uniform coating of minimum thickness, work that is not subsequently to be centrifuged is withdrawn from the bath slowly and at a controlled rate, thus permitting maximum drainage. Two-speed hoists are usually employed, permitting the work to be immersed rapidly and withdrawn slowly. The rate of withdrawal, which partially determines the thickness of the unalloyed zinc layer left on the work (Fig. 5), varies according to the type of process being operated. The optimum withdrawal rate for most articles is about 1.5 m/min (5 ft/min).

With long articles, for which the withdrawal occupies a large part of the total cycle time, higher speeds may be necessary to maintain a reasonable rate of production. If possible, however, it is better to overcome this difficulty by using special jigs and carriers for dipping and withdrawing the work in batches. Provided the work is not withdrawn faster than the rate at which the zinc drains freely from the surface, the unalloyed zinc layer of the coating is uniformly distributed. With faster rates of withdrawal, the surplus zinc carried clear of the bath runs down the surface until it solidifies, and the resultant coating may be lumpy and uneven.

When withdrawal from the bath at a slow controlled rate of speed is not feasible or economical, as it generally is not for small parts, the withdrawal rate may be greatly increased, and drainage is accomplished by spinning the parts in a basket. The excess zinc is drained from the parts by centrifugal force. Mechanically wiping the excess zinc from the parts with tools designed for this purpose is an alternative method of forced drainage.

Cooling. Because of retained heat, the iron-zinc reactions can continue to occur even after the surface layer of zinc has frozen. This type of post-immersion reaction may occur if cooling is hindered by the stacking of parts in close proximity

and by the heat capacity of the part. Some or all of the pure zinc layer may be converted to iron-zinc alloy, thus darkening the surface and altering its properties. Very slow cooling or holding of the material at temperatures over 190 °C (375 °F) may cause small voids in the coating due to interdiffusion between the coating and the base metal. The problem, known as the Kirkendall effect, may result in peeling failure of the coating.

To avoid delayed cooling, parts should be spaced adequately after immersion to permit the free circulation of air. Parts with large cross-sectional areas or parts fabricated of silicon-bearing steel may require forced cooling with air or water.

Galvanizing of Silicon-Killed Steels. The difficulties encountered in galvanizing silicon-bearing steels have been noted under the preceding discussions on conventional galvanizing practice. Many techniques have been studied in an effort to find a better way to control the iron-zinc reaction kinetics in the presence of silicon, none of which has proven to be fully acceptable over the silicon content ranges commonly being encountered. At temperatures not exceeding 460 °C (860 °F), aluminum additions of 0.02 to 0.04% to the bath may be of advantage for steels containing up to 0.05% Si. The most common method has been to use conventional techniques at a temperature not exceeding 440 °C (825 °F) coupled with a short immersion time. For light structural shapes, this is possible without any additional measures. Heavy structural shapes require preheating to reduce the immersion time to an acceptable level.

However, three technologies developed during the 1970s permit better control to be maintained in the galvanizing at reactive temperatures of silicon-bearing steels. One is a patented process using the zinc alloy Polygalva for galvanizing. The second is by galvanizing at high temperatures, 550 °C (1020 °F), instead of the temperatures used for the conventional process, 450 °C (840 °F). The third uses small amounts of nickel in the bath. All three methods are used to some extent in Europe. Polygalva is not available in North America, but the other two methods have seen limited use. Several North American galvanizers use the nickel addition method, and at least one uses the high-temperature method.

Polygalva Process. Polygalva is essentially a zinc alloy containing controlled amounts of aluminum, magnesium, tin, and lead. The aluminum is used to retard the formation of the intermetallic layer, and the other elements help to ensure continuity of the galvanized coating. As with the conventional process, thorough surface preparation prior to galvanizing is essential for good results and must include the following steps unless otherwise indicated:

- Degrease in an alkaline bath heated to 80 to 90 °C (176 to 194 °F)
- Rinse in running water
- Pickle in 50% hydrochloric acid with inhibitor
- Rinse in running water
- Pickle in 70% hydrochloric acid without inhibitor (in most situations this step is optional)

Routine maintenance of pretreatment facilities is important.

Also, a weekly zinc bath chemical analysis is required to ensure that the alloy composition is being maintained within the working range. During galvanizing operations, two master alloys are added to the bath to compensate for losses of aluminum and magnesium. By doing this, proper alloy balance is reportedly readily maintained.

As shown in Fig. 10, Polygalva is most effective in galvanizing steels with silicon in the range of 0.05 to 0.20%. Comparative micrographs of a steel with 0.08% silicon galvanized using conventional and Polygalva techniques are shown in Fig. 11. Above 0.20% Si, the Polygalva alloy reportedly loses at least part of its effectiveness.

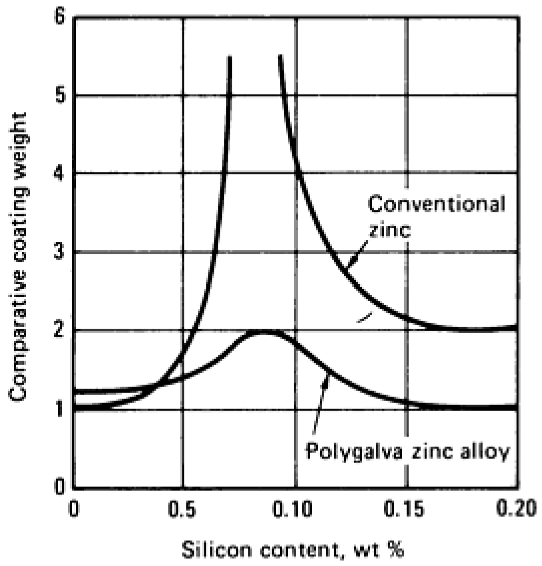


Fig. 10 Comparison of coating weight as a function of silicon content for conventional and Polygalva galvanizing processes

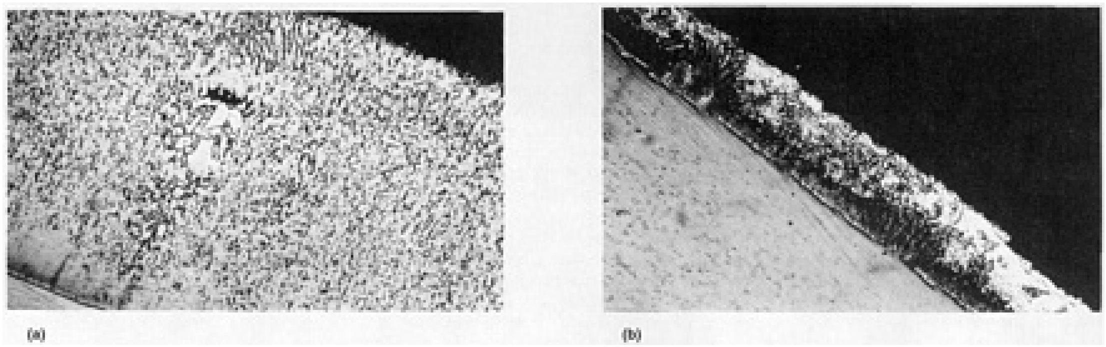


Fig. 11 Micrographs of a silicon-bearing steel (0.08% Si) galvanized (a) in a conventional bath and (b) in a Polygalva bath

High-Temperature Galvanizing. It has been found that when galvanizing is performed at a temperature of approximately 550 to 560 °C (1020 to 1040 °F), a coating weight to immersion time relationship is obtained for silicon-bearing steels which is much less sensitive than at conventional galvanizing temperatures (Fig. 6). The effect of immersion time at elevated galvanizing temperatures is shown in Fig. 12; the coating weight increases at a rate less than linear with time. Doubling the time of immersion from 4 to 8 min increases the coating weight by about 30%.

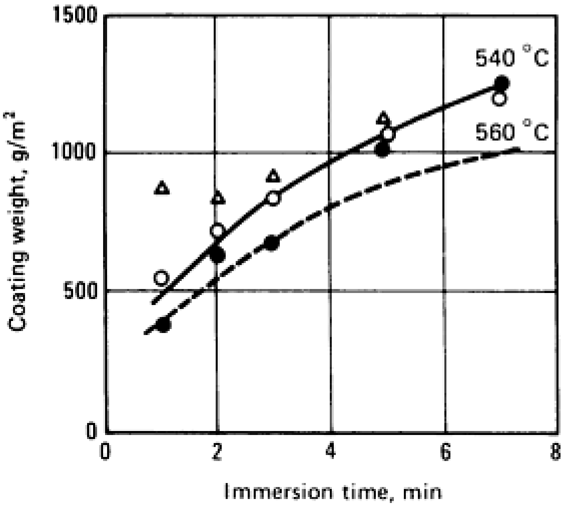


Fig. 12 Coating weight versus immersion time for three steels with varying silicon contents galvanized in a high-temperature bath containing 0.22% Fe. d , steel containing 0.02% Si; •, steel containing 0.22% Si; V, steel containing 0.42% Si

Because of the high reactivity between molten zinc and steel at these temperatures, a ceramic-lined steel kettle is used. While the available ceramic kettle technology is adequate for this application, the state of the art of ceramic kettle heating currently lacks the efficiency of flat flame burners used to heat steel kettles. The development of immersion heaters to heat the ceramic baths is proceeding and offers good promise of improved efficiencies. Pending development of an operationally suitable immersion heater system, ceramic galvanizing kettles are top heated. This technique is relatively inefficient and interferes with the handling of materials into and out of the kettle.

In the bath, the solubility of iron increases from 0.03% at 450 °C (840 °F) to 0.3% at 550 °C (1020 °F). By controlling the iron content, the coating weight can be controlled. As shown in Fig. 13, increasing the iron content from zero to 0.3%, the solubility limit at 550 °C (1020 °F) increases the coating thickness by a factor of 2. Controlling the iron content within the range 0.1 to 0.2% produces coating weights which meet specifications and are not excessively heavy.

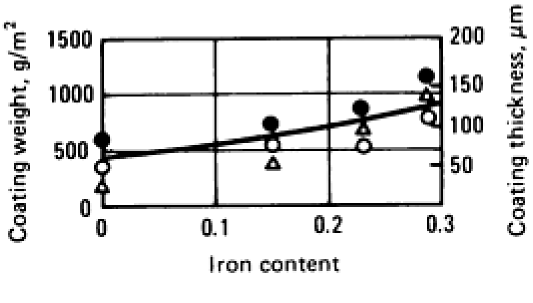


Fig. 13 Coating weight as a function of galvanizing bath iron content for three steels with varying silicon contents. Galvanizing time, 3 min at 550 °C (1020 °F). d , steel containing 0.02% Si; •, steel containing 0.22% Si; V, steel containing 0.42% Si

In a high-temperature galvanizing bath, aluminum up to 0.5% does not appear to have any systematic effect on coating weight. However, above 0.3%, it produces a floating dross which can mar the coating appearance. An aluminum addition of 0.03% is sufficient to brighten the coating if this is desired.

There have been reports of occasional adherence deficiencies of high-temperature galvanized coatings. At this time, it is believed that this is the result of a lead-deficient bath. As a result, the bath lead level should be maintained at 1%. Therefore, the following bath conditions are considered ideal:

- Temperature at 560 °C (1040 °F)
- Iron content between 0.1 and 0.2%
- Lead content about 1%
- Aluminum content of 0.05%

The coating has a light gray, uniform appearance that does not vary with silicon content of the basis steel. Brighter coatings can be obtained by the aluminum addition to the bath described above and by quenching instead of air cooling. Coating adhesion and ductility are equivalent to coatings galvanized at conventional temperatures. The metallographic structures of all high-temperature coatings are similar, the only variation being in the constituent proportions of some of the layers (Fig. 14).

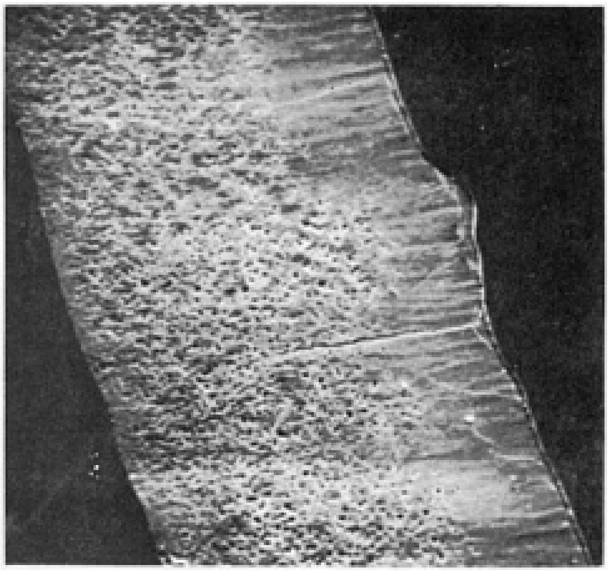


Fig. 14 Electron-scanning image of a high-temperature galvanized coating

Mechanical property tests of the basis steel subjected to high-temperature galvanizing reveal no significant differences from the results obtained using conventional galvanizing techniques. These tests include tensile properties on plain, punched, and welded specimens, reverse bend tests for strain age embrittlement, ductility bend tests, and pulsating tension fatigue tests.

Because of the recent development of high-temperature galvanized coatings, their performance is not as well documented as that of conventional coatings. Based on a limited body of longer term exposure data and accelerated weathering tests in marine, urban, and industrial environments, it appears that the performance of these coatings is at least equal to that of coatings produced by conventional techniques.

Nickel Addition to the Bath. It has been known since the 1960s that the addition of certain alloying elements to the bath will minimize the reactive effect of silicon-killed steels.

European galvanizers have been adding nickel to kettles since the 1970s. The process was brought to North America in the early 1980s and has been used in Canada with some success; it has also been in limited use in the United States since that time.

In this process, nickel is added to the bath as part of the zinc, as a special additive similar to brightener bars, or as a powder. The bath nickel concentration should be 0.05 to 0.09%; experience has shown that maximum effectiveness is achieved in this range. This technique has maximum effectiveness for steels with silicon levels below 0.25%. For steels with higher silicon contents, it provides only minimal coating improvements.

Nickel generally decreases the reaction between the zinc and steel for all steels. It is possible that nickel additions may produce low coating thicknesses on some steels. Care must be taken to ensure adequate zinc thicknesses. Figures 15 and 16 show the effects of nickel additions in the galvanizing bath.

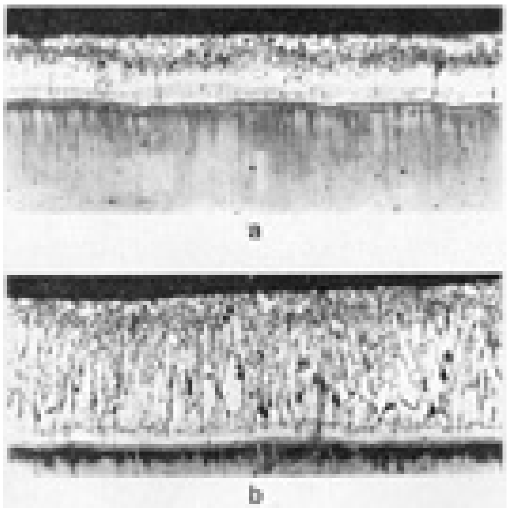


Fig. 15 Effect of nickel additions to the galvanizing bath. (a) Typical hot dip galvanized coating on mild steel. (b) Coating on silicon-killed steel, galvanized in bath containing nickel additions. Note the relatively thin delta layer and the thick, coarse zeta layer in (b). Both 250×. Source: Ref 6

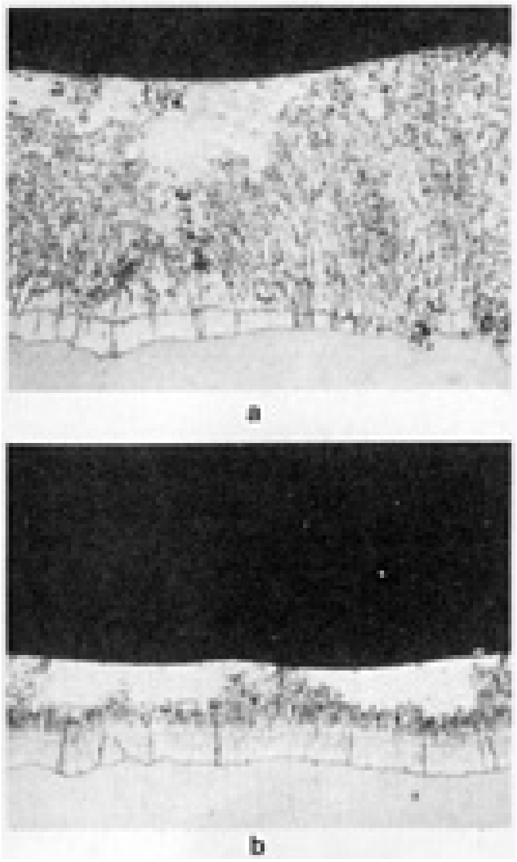


Fig. 16 Effect of nickel additions in the galvanizing bath for a steel containing 0.15% Si. (a) Galvanized in nickel-free bath. (b) Galvanized in bath containing 0.095% Ni. Source: Ref 6

Additions of vanadium, 5% Al, and rare earth metals have also shown positive effects on galvanizing of silicon-killed steels.

Reference cited in this section

6. Richard F. Lynch, Hot-Dip Galvanizing Alloys, *J. Met.*, Vol 39 (No. 8), Aug 1987, p 39-41

Batch Galvanizing Equipment

Because the galvanizing kettle is the most important piece of equipment used in galvanizing, its selection should be based on the careful evaluation of several major variables, such as size, shape, wall thickness, tank material, source of heat, and auxiliary equipment requirements.

Size and Shape. Although the size and shape of the galvanizing kettle are governed primarily by the parts to be galvanized in it, other factors must also be considered. The kettle must be large enough to contain an adequate thermal mass; that is, it must possess sufficient heat capacity in the molten zinc to compensate for the loss of heat encountered when cold workpieces are immersed in the tank. The minimum and maximum operating temperatures that must be maintained depend on production requirements; usually, the weight of zinc in the tank should be equivalent to 15 to 20 times the weight of parts that are to be galvanized in 1 h. In many production installations, the weight ratio of zinc to workpieces is more likely to approach 40 to 1.

Although the shape of the kettle must accommodate the workpieces that are to be immersed, it should also be designed to expose a minimum of bath surface. If the size of a kettle is to be increased to accommodate a particular part, the depth of the kettle rather than its length or width should be increased to minimize the exposed surface area of the bath. A minimum surface area conserves heat and produces less surface oxide than a larger area. Kettles of complicated shape should be avoided because they are susceptible to damage by severe thermal stresses. Simple, rectangular kettles are most widely used.

Wall Thickness. Theoretically, the selection of wall thickness of a galvanizing kettle should be governed by:

- The rate of corrosive attack by liquid zinc
- The hydrostatic load imposed against the kettle walls by the volume of the zinc bath
- The strength of the kettle wall material at the operating temperature of the bath
- The support afforded the kettle walls by the surrounding brickwork or by other reinforcing elements

Because the variables are so numerous and complex, accurate calculation of a required wall thickness is not practical, and selection is based entirely on empirical data. Depending on the size of the kettle and its reinforcing elements, wall thickness usually varies from 20 to 50 mm ($\frac{3}{4}$ to 2 in.).

Kettle Material. Aside from strength, the principal requirement of a galvanizing tank material is the ability to resist the corrosive attack of molten zinc. The most widely used material is boiler plate of firebox quality with low silicon. The chemical composition of this steel ensures a minimum rate of attack by molten zinc; also, the good welding and bending characteristics of this material are essential features in kettle fabrication. The chemical composition of the welding rods used in kettle fabrication should also be of low carbon and low silicon. Composition of the rod is very critical; obtaining the advice of welding experts is strongly recommended.

If a flux layer is to be maintained on the bath surface, a collar of firebrick or other suitable ceramic material should surround and abut the top 150 or 180 mm (6 or 7 in.) of the tank to retard heat transfer in this area and thus reduce attack by the flux on the steel kettle wall. A similar brick or insulated area of 150 to 205 mm (6 to 8 in.) should exist at the bottom of the kettle to reduce dross attack.

Source of Heat. Galvanizing kettles can be suitably heated by combustion of oil or gas, by electrical resistors, or by electromagnetic induction. The source of heat is of minor importance provided the heating installation satisfies the following requirements:

- High efficiency factor
- Good adjustability and control to maintain an even temperature
- Ability to maintain the minimum temperature required on the outside walls of the kettle
- Uniform heating along the outer walls, without hot or cold spots

Failure to satisfy all these requirements severely curtails the life of the kettle and may result in unexpected kettle failure. Due to energy costs, electric heat and induction heat are not widely used for job shop kettles.

Temperature Controls. When a new galvanizing tank is installed, a complete temperature survey should be made of the molten zinc bath. Based on this survey, control thermocouples may be located in the bath to maintain temperature uniformity and control.

Post Treatments

Wet Storage Film Inhibitors. A white film (sometimes called white rust or wet storage stain) may appear on zinc surfaces during storage or shipment. The film is found on material with newly galvanized, bright surfaces and especially in such areas as crevices between closely packed sheets and angle bars. Wet storage film can form if the surfaces come into contact with condensate or rainwater and the moisture does not dry quickly. Zinc surfaces that have developed a normal protective layer of corrosion products are seldom attacked.

When zinc coatings corrode openly in air, zinc oxide and zinc hydroxide are normally formed. In the presence of atmospheric carbon dioxide, these compounds are transformed to basic zinc carbonate. If the supply of air to the surface of the zinc coating is restricted, as in a narrow crevice, then sufficient carbon dioxide is not supplied for the formation of the normal layer of zinc carbonate.

The layer of zinc oxide and zinc hydroxide is voluminous and porous and adheres loosely to the zinc surface. Consequently, it does not protect the zinc surface against oxygen in the water. Corrosion can therefore proceed as long as there is moisture left on the surfaces. When wet storage film occurs, the objects should be arranged so their surfaces dry rapidly. The attack ceases, and with a free supply of air to the surfaces, the normal protective layer of corrosion products forms. The white corrosion products gradually wash off, and the surface of the coating takes on the normal appearance of a hot dip galvanized, exposed object.

Because the corrosion products are very voluminous (about 500 times that of the zinc that has been consumed), any attack may appear serious. Usually, however, such an attack of wet storage film is of little or no importance to the durability of the corrosion protection.

Wet storage film is best avoided by preventing newly galvanized surfaces from coming into contact with rain or condensate water during storage and transport. Materials stored outdoors should be arranged so that water can easily run off the surfaces and so that all surfaces are well ventilated (Fig. 17).

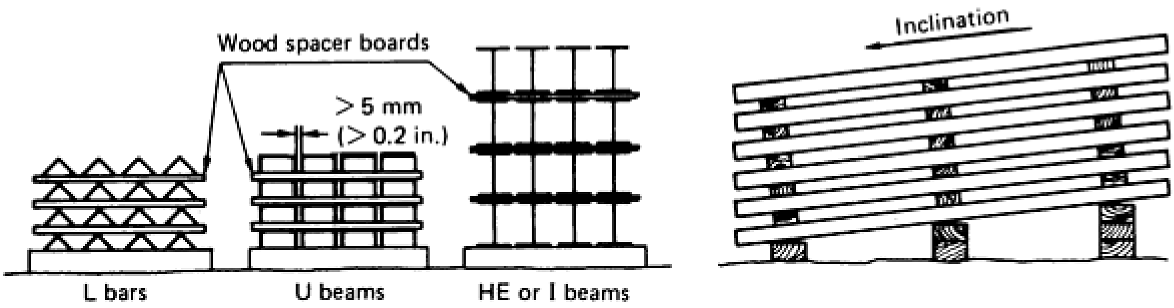


Fig. 17 Galvanized materials stacked with spacers and on an incline to prevent the formation of wet storage film

Temporary protection against wet storage film is obtained by chromating or phosphating. Painting after galvanizing also provides effective protection. Acrylic films containing corrosion inhibitors can also be applied to prevent the formation of wet storage film.

Where the surface staining is light and smooth without growth of the zinc oxide layer as judged by lightly rubbing fingertips across the surface, the staining will gradually disappear and blend in with the surrounding zinc surface as a result of normal weathering in service. When the affected area will not be fully exposed in service or when it will be subject to a humid environment, wet storage film must be removed, even if it is superficial, to allow formation of the basic zinc carbonate film which normally contributes to the corrosion resistance of galvanized coatings.

Medium to heavy buildup of white corrosion product must be removed, otherwise the essential protective film of basic zinc carbonates cannot form in affected areas. Light deposits can be removed by brushing with a 2% solution of sodium or potassium dichromate with the addition of 0.1 vol% of concentrated sulfuric acid. This is applied with a stiff brush and left for about 30 s before thoroughly rinsing and drying.

Paint Over Galvanizing. Hot dip galvanized steel may need to be painted for the following reasons:

- Additional corrosion protection for exposure to aggressive environments is needed, especially if future maintenance will be difficult or if the zinc coating is thin, such as on sheet metal.
- Another color of coating is desired for aesthetic reasons, for warning purposes, or for camouflage.
- Protection against galvanic corrosion is needed because the hot dip galvanized steel is to be in contact with another metal such as copper.

Hot dip galvanizing combined with painting offers good corrosion protection, even in very aggressive environments. The durability of such a duplex system is 1.5 to 2.7 times that of the durability of either the painted bare steel or the zinc coating alone.

The zinc coating can be painted immediately after hot dip galvanizing or after some time of exposure (Table 5). In most cases, painting immediately after hot dip galvanizing is preferable, since the surfaces are least contaminated.

Regardless of whether the paint is applied to a fresh, bright coating surface or to an exposed surface with corrosion products, the surfaces must be cleaned carefully prior to painting. The paint on zinc surfaces is more sensitive in this respect than many other materials, because even small quantities of impurities on the surfaces can affect the adhesion of the paint film.

However, the surfaces of zinc coatings are often much easier to clean than steel surfaces. It is important that an appropriate cleaning procedure be used for the particular impurities present on the surfaces.

Exposed Matte Surfaces. When zinc coatings are exposed, the surface corrodes and is covered with corrosion products. The basic zinc carbonate that forms in clean air can be painted. This is the reason for the traditional recommendation to wait from 6 months to 1 year before painting hot dip galvanized objects.

Today, however, the air is seldom clean. The layer of corrosion products contains such substances as sulfides, sulfites, sulfates, and chlorides. Many of these compounds are water soluble and some are even hygroscopic. To achieve good results when painting, all water-soluble impurities must be removed.

Cleaning and Surface Preparation. Heavily contaminated surfaces, both fresh and exposed, should be washed with a suitable organic solvent such as white mineral spirits, and then bristle brushed to remove solid particles and corrosion products. This washing should be followed with a thorough rinsing with water at high pressure, if possible.

Moderately contaminated surfaces, for example, fresh newly galvanized surfaces and surfaces that have been exposed for a longer period of time but have not been contaminated with oil and grease, can be washed with water to which 5 to 10% ammonia, caustic soda (NaOH), or acetic acid has been added. Afterwards, the surface should be buffed with a soft brush. This treatment must be followed by very thorough rinsing with water at high pressure, if possible.

Chromated surfaces, on continuously hot dip galvanized sheet, for example, can also be washed with ammonia, caustic soda, or acetic acid in water and buffed, followed by thorough rinsing. The alkaline or acid solution dissolves the chromate layer. In general, when galvanized after fabrication material is to be painted as a post-treatment, it should not be chromate treated.

Surfaces that have been exposed, moderately contaminated surfaces, or newly galvanized surfaces can also be brush blasted, that is, blasted with low pressure and a rapid motion of the nozzle, for example 0.3 MPa (0.04 ksi) at 6 mm (0.2 in.) nozzle diam and 250 to 300 mm (9.8 to 11.9 in.) nozzle distance. Abrasives consisting of silicates and slags of 0.2 to 0.5 mm (0.008 to 0.02 in.) are recommended. Glass beads and fine-grained aluminum oxide can also be used.

Sweep blasting effectively removes any corrosion products and provides an advantageous roughening of the surface of newly applied bright zinc coatings. However, brush blasting must be carried out carefully so that the zinc coating is not destroyed and large stresses are not built into the coating. These stresses may subsequently cause flaking of the paint coat.

General Surface Conditions After Galvanizing. Table 8 provides a general guide to the inspection of galvanized surfaces.

Table 8 Guide for visual inspection of galvanized surfaces

Condition	Causes	Grounds for rejection?
Bare spots	Paint, grease or oil residues	Yes, except where bare spots are small and suitable for patching
	Scale or rust residues	
	Residual welding slag	
	Rolling defects in basis steel	
	Embedded sand in castings	
	Overdrying of preflux	
	Excess aluminum in bath	
	Articles in contact during galvanizing	
General roughness	Analysis or original surface condition of steel	No, except by prior agreement
	Overpickling	
	Uneven cold working	
	High galvanizing temperature and/or long immersion time	

Dross protrusions	Entrapped dross particles	No, unless dross contamination is heavy
Blisters	Surface defects in steel	No
	Absorbed hydrogen	Not if due to steel composition
Lumpiness and runs	Withdrawal speed too high	Only on basis of prior agreement
	"Cold" galvanizing bath	
	Delayed run-off from seams,joints, bolt holes, etc.	
	Articles in contact during withdrawal	
Flux inclusions	Stale flux burnt on during dipping	Yes
	Surface residues on steel	Yes
	Flux picked up from top of bath	Yes, unless removed
Ash inclusions	Ash burnt on during dipping	Yes, if in gross lumps
	Ash picked up from top of bath	
Dull gray coating or mottled appearance	Steel composition (high silicon, phosphorus, or carbon) or severe cold work	Not if due to steel composition or condition, or limited to occasional areas
	Slow cooling after galvanizing	
Rust stains	"Weeping" of acid, etc., from seams and folds	No
	Storage on or near rusty material	No
Wet storage film ("white rust")	Confinement of close-packed articles under damp conditions	No, unless present prior to first shipment or unless severely pitted.
	Packing of articles while damp	Customer to exercise caution during transportation and storage

Choice of Paint. Paints suitable for direct application to properly cleaned hot dip galvanized steel are discussed below. As with most other paints, first apply a suitable primer to the zinc surface.

Paints consist of 10 to 20 different components and each different manufacturer has its own formula for a certain type of paint. Paints of the same type but from different manufacturers can have different properties. Detailed recommendations can be obtained from the manufacturer. Table 9 compares characteristics of some of the most common paints used with galvanized coatings.

Table 9 Comparative characteristics of paints and paint films used on hot dip galvanized steel

E, excellent; G, good; F, fair; P, poor. Other symbols used are defined in the table footnote.

Paint (film) characteristics	**Numbers of paints in Table 5**														
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Application method[(a)]	B	B	B	S	S	S/B	S/B	S	S	S	S/B	S	S	S	S
Drying time[(b)]	Lo	Lo	Mi	Sh	Sh	Mi	Mi	Mi	Sh	Sh	Mi	Mi	Mi	Mi	Mi
Hardening-through time[(c)]	Lo	Lo	Mi	Mi	Mi	Lo	Lo	Mi	Mi	Mi	Lo	Mi	Mi	Lo	Mi
Hardness	F	F	F	G	G	F	F/G	G/E	G	G	F	G	F/G	F	G/E
Flexibility	E	E	E	F/G	G	G	G	G	G	G	G	F/G	F/G	G	G
Impact resistance	E	E	E	G	E	G	G/E	E	G	E	G	G	G	G	E
Gloss retention[(d)]	G	E	E	P	F	F	F	E	P	F	F	P	F	P	E
Color retention[(e)]	P	F	G	P	F	E	E	E	P	F	F	F	F	. . .	E
Can stability[(f)]	G	G	E	E	E	G	G	P	E	E	G	P	G	P	P
Thermal resistance[(g)]	P	P	F	P	P	F	F	G	P	F	F	F	F	P	G
Weather resistance[(h)]															
Rural	E	E	E	E	E	E	E	E	E	E	E	E	E	P	E
Marine	G	G	G	E	E	F	E	E	E	E	G	E	G	G	E
Industrial	G	F	G	G	E	F	F	G	G	E	G	E	F	E	G
Resistance[(i)]															
Acid solutions	F	P	F	E	E	P	F	G	G	G	F	E	F	E	G

Alkaline solutions	P	P	P	E	E	P	P	F	G	G	P	G	P	E	E

Note: Paint and film characteristics may show differences because of variations in paint formulations; therefore, all indications are relative.

Source: Ref 3

(a) B, mainly by brush; S, mainly by spraying (air or airless).

(b) Drying time to tack-free: Sh, short (<1 h); Mi, intermediate (1 to 4 h); Lo, long (4 to 12 hours).

(c) Hardening-through time: Sh, short (3 h); Mi, intermediate (1 to 7 days); Lo, long (>7 days).

(d) Poor and fair ratings are mainly due to chalking.

(e) Poor and fair ratings are mainly due to yellowing.

(f) E, stable for more than 6 months; G, stable for approximately 6 months; F, stable for approximately 1 month; P, stable for less than 36 h (after adding hardeners).

(g) E, permanent resistance to temperatures between approximately 50 and 150 °C (120 and 300 °F); G, resistance to temperatures between approximately 50 and 75 °C (120 and 165 °F); F, resistance to temperatures between approximately 50 and 75 °C (120 and 165 °F) for short periods only; P, practically no thermal resistance above 50 °C (120 °F).

(h) Not counting changes in gloss and/or color.

(i) Indications depend on time of exposure and concentration and temperature of aqueous solutions.

In moderately corrosive atmospheres paints based on acrylate and PVAc-latex are suitable. However, it takes about 10 to 14 days for these paints to achieve maximum hardness and adhesion. If the objects are to be handled or transported within this time, special care must be observed to avoid damage.

Under severe chemical conditions, such as in industry, and in aggressive atmospheres, paints with better chemical resistance than latex paints are required. Such paints are based on PVC, vinyl copolymers, chlorinated rubber, polyurethane, and epoxy.

In water and soil, tar/bitumen paints are recommended, preferably in combination with epoxy. and polyurethane. Certain aluminum-pigmented asphalt solutions can also be used for structures in water, but they have relatively poor mechanical strength.

Additional information is available in the article "Painting" in this Volume.

Reference cited in this section

3. Frank Porter, *Zinc Handbook: Properties, Processing, and Use in Design,* International Lead Zinc Research Organization, 1991

Babbitting

William P. Bardet and Donald J. Wengler, Pioneer Motor Bearing Company

Introduction

BABBITTING is a process by which relatively soft metals are bonded chemically or mechanically to a stronger shell or stiffener, which supports the weight and torsion of a rotating, oscillating, or sliding shaft. The babbitt, being softer than the shaft and having excellent antifrictional qualities, prevents galling and/or scoring of the shaft over long periods of use. Compositions and selected properties of babbitts are summarized in Tables 1 and 2 and Fig. 1.

Table 1 Compositions and physical properties of tin-base babbitts

ASTM B 23 alloy No.	Specific gravity	Composition, %				Compressive yield point(a)(b)				Ultimate compressive strength(a)(c)				Hardness, HB(d)		Melting point		Complete liquefaction		Proper pouring temperature	
						At 19 °C (66 °F)		At 100 °C (212 °F)		At 19 °C (66 °F)		At 100 °C (212 °F)		At 20 °C (68 °F)	At 100 °C (212 °F)						
		Cu	Sn	Sb	Pb	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi			°C	°F	°C	°F	°C	°F
1	7.34	4.56	90.9	4.52	None	30.3	4.4	18.5	2.7	88.6	12.9	41.7	6.1	17.0	8.0	223	433	371	700	440	825
2	7.39	3.1	39.2	7.6	0.03	42.1	6.1	20.7	3.0	103	14.9	60.0	8.7	24.5	12.0	241	466	354	669	425	795
3	7.46	8.3	83.4	8.3	0.03	46.9	6.8	21.4	3.1	121	17.6	68.3	9.9	27.0	14.5	240	464	423	792	490	915

(a) The compression test specimens were cylinders 38 mm (1.5 in.) long, 13 mm (0.5 in.) in diameter, machined from chill castings 50 mm (2 in.) long, 19 mm (0.75 in.) in diameter.

(b) Values were taken from stress-strain curves at a deformation of 0.125% reduction of gage length.

(c) Values were taken as the unit load necessary to produce a deformation of 25% of the length of the specimen.

(d) Tests were made on the bottom face of parallel-machined specimens that had been cast at room temperature in a steel mold, 50 mm (2 in.) in diameter by 16 mm (0.625 in.) deep. Values listed are the averages of three impressions on each alloy, using a 10 mm (0.4 in.) ball and applying a 500 kg load for 30 s.

Table 2 Compositions and physical properties of lead-base babbitts

ASTM B 23 alloy No.	Specific gravity	Composition, %					Compressive yield point(a)(b)				Ultimate compressive strength(a)(c)				Hardness, HB(d)		Melting point		Complete liquefaction		Proper pouring temperature	
							At 19 °C (66 °F)		At 100 °C (212 °F)		At 19 °C (66 °F)		At 100 °C (212 °F)		At 20 °C (68 °F)	At 100 °C (212 °F)						
		Cu	Sn	Sb	Pb	As (max)	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi			°C	°F	°C	°F	°C	°F
7(e)	9.73	0.50	10	15	75	0.60	24.5	3.6	11.0	1.6	108	15.7	42.4	6.2	22.5	10.5	240	464	268	514	338	640
8	10.04	0.50	5	15	80	0.20	23.4	3.4	12.1	1.8	108	15.7	42.4	6.2	20.0	9.5	237	459	272	522	340	645
15(f)	10.05	0.5	1	15	82	1.40	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	21.0	13.0	249	469	281	538	350	662

Source: Sleeve Bearing Materials, *Metals Handbook*, 8th ed., Vol 1, ASM, 1961, ASTM B 23-83, and Ref 1

(a) The compression test specimens were cylinders 38 mm (1.5 in.) long, 13 mm (0.5 in.) in diameter, machined from chill castings 50 mm (2 in.) long, 19 mm (0.75 in.) in diameter.

(b) Values were taken from stress-strain curves at a deformation of 0.125% reduction of gage length.

(c) Values were taken as the unit load necessary to produce a deformation of 25% of the length of the specimen.

(d) Tests were made on the bottom face of parallel-machined specimens that had been cast at room temperature in a steel mold, 50 mm (2 in.) in diameter by 16 mm (0.625 in.) deep. Values listed are the averages of three impressions on each alloy, using a 10 mm (0.4 in.) ball and applying a 500 kg load for 30 s.

(e) 0.10% max Fe.

(f) Range of arsenic content 0.80 to 1.40% with 1.0% preferred.

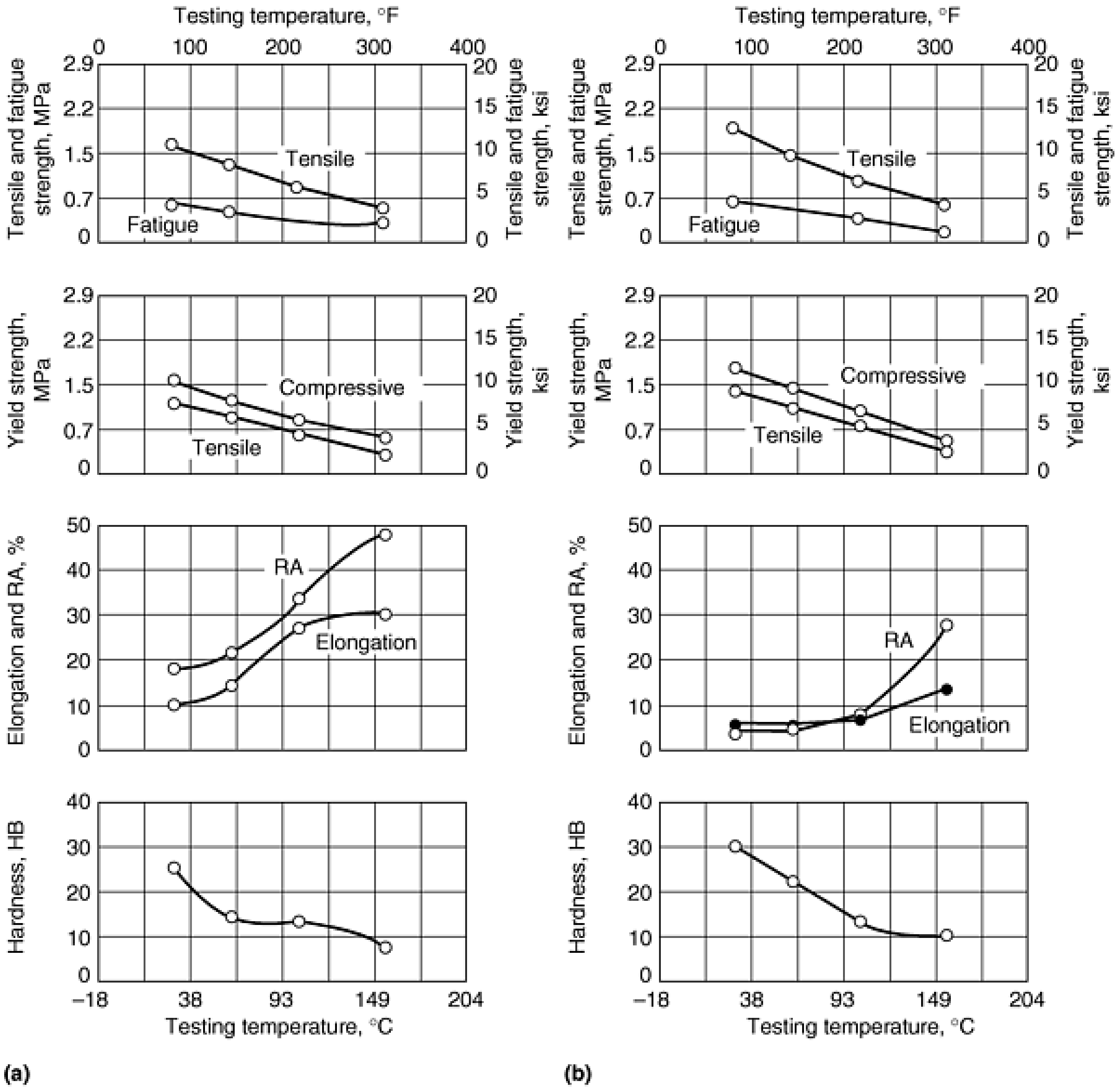


Fig. 1 Effect of testing temperature on mechanical properties of ASTM B 23 tin-base babbitt. (a) Grade 2 (75%

Sb, 3.5% Cu). (b) Grade 3 (8% Sb, 8% Cu). RA, reduction in area

Babbitting is named for Isaac Babbitt, who patented the process in the United States in 1863. Babbitt metals, which are more widely known as *white metals*, are comprised principally of tin alloys (hardened with copper and antimony) or lead alloys (hardened with tin and antimony and, in some cases, arsenic). In the babbitting process, the relatively soft bearing material (babbitt) is bonded to a stronger supporting base metal, typically mild steel, cast iron, or bronze. The base metal may be in the form of mild steel strip unwound from a coil, a half-round mild steel pressing or bushing, or a bronze or iron casting. The bonded bimetal material is shaped and machined to make plain, fluid film lubricated bearings for a wide variety of automotive, industrial, and marine applications.

Babbitt is used in small bearings for high-volume applications, such as electric motors and internal combustion engines, and for large rotating and reciprocating machinery with low to modest volume requirements, such as high-speed turbines and low-speed marine diesel engines. In addition, babbitt has been used for jewelry, shot, filler metals, and various other applications. Lead-base alloys enjoy a cost advantage, while tin alloys offer modest technical advantages, particularly in high-speed centrifugal equipment. It should be noted that government regulations now discourage the use of lead-base alloys for health and hazardous waste disposal reasons.

Babbitting of bearing shells can be accomplished by three methods:

- Static babbitting (hand casting)
- Centrifugal casting
- Metal spray babbitting

Centrifugal casting and static (gravity) casting are the two babbitting methods used in the manufacture and repair of large, low-volume journal (radial) and thrust bearings. Centrifugal casting of journal bearings offers both technical and economic advantages if special spinning equipment is available. Flat shapes (thrust bearings) are usually statically cast.

Repairing of industrial and marine babbitted bearings is routinely accomplished by melting off the old metal and rebabbitting the shells with new metal, following the same basic casting methods described below for producing new products. Emergency repair methods using proprietary tinning compounds, babbitt spray, or welding techniques can be employed. Suppliers of such repair equipment should be consulted for operating instructions.

Thin-wall babbitted half bearings, rolled bushings, and flat thrust washers are mass produced from bimetal strip stock. The strip stock is produced by continuously feeding coils of low-carbon steel in ribbon form first through appropriate cleaning and tinning baths and then through a stream of molten babbitt, which is gravity cast on the moving strip. The strip is immediately water-chilled from below. After excess babbitt is removed, the stock is recoiled and is ready for press blanking, forming, and finish machining operations. Details of mass production methods for making babbitted bearings are proprietary to the manufacturers involved, and beyond the scope of this article.

Regardless of the method used to produce the babbitt, bond quality is an important factor, particularly when heat transfer through the babbitt into the shell is expected to contribute to extending the life of the bearing. In all cases, a metallurgical (chemical) bond must be achieved to ensure good heat transfer and satisfactory babbitt fatigue life. Mechanical retention, through the use of design details such as dovetail grooves and tapped holes, does not meet this requirement, but is sometimes still used in large metallurgically bonded bearings as a form of backup insurance against bond failure. This approach (see the section "Mechanical Bonding" in this article) is more likely to be found in cast iron shells, which are more difficult to prepare for babbitting.

Acknowledgement

The sections "Cleaning by Degreasing or Pickling" , "Fluxing" , and "Single-Pot Tinning" were adapted from D.J. Maykuth, Hot Dip Tin Coating of Steel and Cast Iron, *Surface Cleaning, Finishing, and Coating*, Volume 5, 9th Edition, *Metals Handbook*, American Society for Metals, 1982, p 351-355

Reference

1. *Manual of Bearing Failures and Repair in Power Plant Rotating Equipment,* EPRI GS-7352, Electric Power Research Institute, July 1991

Preparation

Prior to casting by any method, the workpiece must be scrupulously prepared by various cleaning, fluxing, and tinning steps. The preferred methods for accomplishing these steps are described below.

After the single-pot immersion tinning step, the surface must visually demonstrate 100% wetting as evidence it is ready for babbitting by either centrifugal or static casting methods. If the surface is not 100% wetted, faulty bond areas are likely to result. Small "dry" spots can be eliminated while the tinning is still molten by application of flux scrubbed in with a stainless steel brush and retinning of the questionable areas with tin sticks. If the workpiece is still not satisfactory, it must be reprocessed by mechanically removing all tinning and starting over with basic cleaning steps described below.

The babbitting procedures described in the sections "Centrifugal Casting" and "Static Casting" in this article assume that a substrate material of low- or medium-carbon steel is being babbitted with ASTM B 23 alloy 2, the 89% Sn alloy widely used in industrial and marine machinery. Base metals other than mild steel (bronze, cast iron, etc.) are babbitted using the same procedures, although the preparatory cleaning, fluxing, and tinning steps may differ.

Typical tin bronze and leaded bronze alloys are readily tinned (Ref 2) using methods very similar to those for mild steels, but at reduced temperatures and tinning times to minimize dissolution of the bronze and growth of brittle copper-tin intermetallic compounds. As noted before, the final step before babbitting should be a visual in-process inspection of the tinned shell to confirm that it is 100% wetted by the tinning material. The tinning material is usually commercially pure tin or a tin-lead solder; pure tin produces somewhat stronger bonds, but is more expensive.

Cleaning by Degreasing or Pickling. Iron and steel parts must be free of surface contaminants such as oil, grease, drawing lubricants, and mill scale before fluxing and immersion in molten tin. Inadequate or improper surface preparation is a frequent cause of defects such as poor adhesion.

Degreasing. Oil, grease, soap, and other lubricants used in machining, drawing, and forming can be removed by one or more of several methods, including vapor degreasing, solvent cleaning, alkaline cleaning, and emulsion cleaning. Some details of various processes are given below.

The organic solvents generally used are trichloroethylene or, occasionally, perchloroethylene. Degreasing is effected by placing the articles in the hot liquid, or in the vapor, or in both in turn. In the liquid process, the solvent is continuously circulated and purified by distillation. In the vapor process, the cold articles are cleaned by the condensed vapor of the boiling solvent condensing on them. Commercial equipment for solvent degreasing is available.

Solvent procedures are ideal for removing mineral oils, greases, and many types of vegetable oils, but are less effective with certain types of drawing compounds and spinning soaps which leave behind solid constituents. In a liquor-vapor plant, a short cooling period should follow immersion in the boiling solvent to ensure that adequate condensation of solvent occurs on the articles which should be so racked or supported that the condensed solvent runs off them completely and does not collect in recesses.

Wet articles must not be loaded into a solvent degreaser, because corrosion of the units may cause decomposition of the solvent. Smoking and naked flames must be prohibited close to trichloroethylene degreasing plants to avoid the risk of phosgene poisoning.

Alkaline detergents act be penetrating the contaminant layer and removing it by emulsification, saponification, or flocculation. Appropriate commercial salts are available in powder or crystal form, which are dissolved in water at a concentration of from 1 to 10%, according to the instructions. Alkaline cleaning solutions may be made more effective by employing electrolysis at the same time, but this is not commonly practiced.

Alkaline cleaners usually contain sodium hydroxide with other constituents added to render the grease soluble. Proprietary cleaners are recommended because they are formulated to deal with specific types of contaminants and basis metal. The temperature of alkaline solutions should not be below 85 °C (185 °F).

A simple 5% sodium hydroxide solution at 80 to 90 °C (185 to 195 °F) often is adequate for the anodic electrolytic cleaning of steel, but a specifically formulated proprietary solution is preferred. The articles are suspended to form one

electrode, and a plain steel tank containing the alkaline solution is the other electrode. A 6 to 12 V direct current is applied between busbar and tank to obtain a current density on the work of between 2 and 5 A/dm^2 (20 to 50 A/ft^2) of surface. Generally, the use of electrolysis allows more latitude in the temperature of the alkaline bath, but the hotter the solution, the more efficient the cleaning. Tenacious oil films causing slow pickling and tinning difficulty are sometimes best removed by an electrolytic cleaning treatment.

Articles should be rinsed immediately as they are removed from alkali to avoid deposition of salts or de-emulsification of the grease on the surface. The best procedure consists of a hot water rinse, followed by a final rinse in a cold water tank provided with running intake and overflow. The rinse water should not contain acids or salts likely to bring about the breakdown of emulsions adhering to articles removed for rinsing. For this reason, avoid using the same rinse tank for degreasing and pickling.

Ultrasonic cleaning involves the use of high frequency mechanical vibrations from a transducer device in a cleaning solution to achieve a higher degree of cleanliness and at a much faster rate than is possible by conventional methods. Frequencies of 20 to 40 kHz are frequently used. The scouring effect penetrates into crevices, holes, and complex contours that are inaccessible to mechanical action such as brushing.

The temperature of the cleaning liquid is important as it affects density and volatility. Aqueous solutions are used at about 50 °C (120 °F) instead of the more conventional 80 to 95 °C (175 to 205 °F), and emulsifying agents may be present which are effective at lower temperatures. Organic-solvent, ultrasonic, degreasing plants usually have a special compartment containing cool solvent in which the transducers are fitted. Articles are initially degreased in boiling solvent before passing to the ultrasonic treatment chamber. A final degreasing in vapor alone may be used.

The use of many degreasing solvents is being restricted due to environmental concerns. Additional information is provided in the article "Vapor Degreasing Alternatives" in this Volume.

Pickling of steel, usually done in aqueous solutions of hydrochloric or sulfuric acid, can be used to remove mill scale and rust before hot tinning. Hydrochloric acid pickles efficiently at room temperature, and in most applications, no provision is made for heating it. Dilutions range from one part acid in two parts water to three parts acid in one part water. Immersion times range from 10 to 60 min. When pickling for hot dip tinning, immersion in the pickling bath should be prolonged for a few minutes beyond the time required for the total removal of visible scale and rust. This gives the steel a light etch, which will promote wetting of the base metal during the tinning process.

Depending on the condition of the surface being treated, the composition of the aqueous sulfuric acid pickling solution varies from about 4 to 12% sulfuric acid. The recommended operating temperature range for these solutions is 80 to 85 °C (175 to 185 °F). Removing light scale or rust normally requires an immersion time of $\frac{1}{2}$ to 2 min; even heavy scale should not require an immersion time of more than 15 min. In sulfuric acid pickling baths, inhibitors are commonly added to concentrate the attack on the scale and reduce acid consumption, metal loss, spray, and risk of hydrogen absorption by the steel.

Difficult steels, such as those having surface layers formed by decomposing lubricants, often require oxidizing conditions and a hydrochloric or sulfuric acid immersion sufficient to remove surface oxides followed by 1 to 3 min in 10 to 25 vol% nitric acid to achieve a tinnable surface.

Cast iron should not be acid pickled for tinning, because a heavy carbon smut derived from graphite forms over the whole surface and prevents tinning.

Details of operating procedures and equipment required for pickling in hydrochloric and sulfuric acid, as well as the use of inhibitors to minimize acid attack, are given in the article "Pickling and Descaling" in this Volume.

Abrasive blast cleaning must be done on castings and all assemblies of cast iron, cast steel, and malleable iron with wrought steel prior to hot dip tinning. Iron castings to be tinned by the direct chloride method or by wiping should be blasted with fine (70-mesh) angular chilled iron grit. Blasting should be thorough with all surfaces to be tinned treated for 30 to 60 s. For a description of the equipment and techniques used in abrasive blasting, see the article "Mechanical Cleaning Systems" in this Volume.

Fluxing facilitates and speeds the reaction of molten tin with iron or steel, promoting the formation of a continuous thin layer of tin-iron or other intermetallic phases on which the liquid tin coating can spread in an even, smooth, continuous film. In hot dip tinning, fluxes may be used in three different ways:

- As aqueous solutions in which the work is briefly dipped before it is immersed in the molten tin
- As a molten fused layer or cover on the top of the molten tin bath
- As a solution, paste, or admixture to tin powder that is applied to the surface of the work prior to wipe tinning

The material compositions of two aqueous flux solutions are given in Table 3.

Table 3 Compositions of flux solutions used in hot dip tinning

Solution	Constituents									
	Zinc chloride		Ammonium chloride		Sodium chloride		Hydrochloric acid[(a)]		Water	
	kg	lb	kg	lb	kg	lb	cm^3	oz	L	gal
A	11	25	0.7	1.5	. . .	. . .	296-591	10-20	38	10

(a) Commercial grade, 28%

A cover of molten flux should be maintained on the surface of the first tin dipping bath. The flux cover, which must be molten at the operating temperature of the bath, is normally regenerated by absorbing aqueous flux solutions on the surface of the incoming work. The addition of water as a fine spray to the surface of the flux may still be necessary at intervals to rejuvenate it. Compositions of two effective flux covers are given in Table 4. The salt components of the various flux solutions given in Table 3 form suitable flux covers.

Table 4 Compositions of flux covers for hot dip tinning baths

Mixture	Melting point		Constituent	Content, wt%
	°C	°F		
A	260	500	Zinc chloride	78
			Sodium chloride	22
B	260	500	Zinc chloride	73
			Sodium chloride	18

			Ammonium chloride	9

After being pickled, rinsed, and dried of excess rinse water, the steel (or in the case of iron castings, the dry, shot-blasted workpiece) is immersed in an aqueous flux solution. Workpieces may require some movement in the flux bath to remove all air locks and to ensure that all surfaces are fully wetted by the flux. Work should be immersed in the flux only long enough to ensure complete coverage; nothing is gained by prolonged immersion. When the workpiece is withdrawn from the bath, the excess flux should be allowed to drain briefly. The workpiece is then ready for immediate immersion in the tin bath.

Single-pot tinning is used to provide a preliminary coating for bonding. The tinning operation does two things: It establishes a bond between the base material, and it raises the temperature of the backing to a level where it will maintain the tinning in a molten state ready to bond with molten babbit when casting commences.

The process involves a single immersion of fluxed workpieces in a molten tin bath heated to 280 to 325 °C (535 to 615 °F). The average operating temperature of the bath is maintained at about 300 °C (575 °F). When the workpiece is withdrawn from the bath, the surface of the work may have spots of flux, which must be removed by suitable washing.

Flux is placed on the surface of the molten tin bath in an amount sufficient to provide a molten flux layer that covers about two-thirds of the surface area. The use of partial rather than total flux coverage helps eliminate excessive pickup of flux when the work is withdrawn.

After being coated with aqueous flux, the workpieces are picked up by pretinning tongs, hooks, or perforated baskets and lowered gently into the molten tin, passing through the portion of the bath that is covered with flux. The optimum immersion rate normally ranges from 13 to 51 mm/s ($\frac{1}{2}$ to 2 in./s). Heavy sections are immersed at a slower rate than light sections. The work need only be immersed long enough to reach the temperature of the bath.

In order to minimize flux pickup and to shed any particles of iron-tin compound that have accumulated in the bath, workpieces are withdrawn from the bath with a clean, rapid movement through an area not covered with flux. Flux may be moved to one side with a paddle.

The operations that follow withdrawal from the tin bath vary considerably. The work may be shaken or swung by hand to remove excess tin. To remove tears or droplets of tin that collect at lower or outer edges of the workpiece, the teared edge can be allowed to touch barely the surface of the clean metal in the pot. This slight contact pulls the droplets away from the work by surface tension. Centrifuging or spinning of jigged work is also used to remove excess molten tin.

After the excess tin has been removed, the work is cooled in air, then flux residues are removed by rinsing in cold water acidified with about 1 vol% hydrochloric acid or 5 to 10 vol% citric acid. A water rinse follows. Quenching the work in water or kerosene is also possible.

Mechanical bonding of a babbitt to a shell is a simple fastening process. Mechanical methods used in babbitting shops include anchor groove dovetails and drilled and tapped holes into which molten babbitt flows, locking the babbitt in place. Copper or brass screws inserted into threaded holes also help hold the babbitt to the shell. In some instances, brass or copper bars are tinned and recessed into the bore and bolted or screwed into the bore of the casting. In most cases, these methods are used on cast iron when caustic treatment is not available. The heads of the screws must be recessed into the babbitt to prevent the screw head from becoming exposed when the babbitt is machined to a final bore size.

Reference cited in this section

2. C.J. Thwaites, "Practical Hot Tinning," Publication No. 575, International Tin Research Institute

Centrifugal Casting

Centrifugal casting is the preferred method for babbitting medium- and thick-wall, half-shell or full-round (nonsplit) journal bearings because it virtually eliminates porosity and allows close control of the cooling process to promote a

strong bond. Disadvantages are the need for more extensive equipment and tooling than static casting requires and minor segregation of the intermetallics in the babbitt across its thickness. (It should be noted, however, that segregation along the axial length of a statically cast bearing can be more serious, and is more difficult to detect). The spinning axis is usually horizontal, but vertical orientation is sometimes employed for unusual sizes (e.g., large diameters or short lengths). The descriptions of equipment and procedures below apply only to horizontal casting.

Equipment. Centrifugal babbitting requires a machine expressly designed or modified for this purpose (Fig. 2). No mandrel is used in horizontal applications. A variable-speed centrifugal casting (spinning) machine is fitted with a safe means for supporting and rotating a reasonably well-balanced workpiece clamped between recessed sealing plates. With the shell rotating, molten babbitt is fed to the inside of the prepared bearing through a hole in the outboard spinning plate, then solidified by air and/or water sprayed on the outside diameter of the shell while it is spinning. A speed is selected that produces a centrifugal force high enough to eliminate porosity but low enough to minimize metal segregation. Too low a speed causes metal "tumbling," while too high a speed causes segregation. Table 5 shows a range of spinning speeds for various bearing sizes (inside shell diameter), based on minimum centrifugal forces of 20 g for tin-base alloys. The minimum for lead-base babbitts is 16 g. To promote directional solidification after the babbitt is poured, the tooling plates must be preheated to 200 °C (390 °F) minimum and faced with gaskets cut from sheets of environmentally approved insulating materials, such as Inswool, to seal and insulate both ends of the bearing when it is clamped between the support plates by hydraulic pressure. The centrifugal casting machine must be of fail-safe design in the event of a loss of power and/or clamping pressure.

Table 5 Centrifugal casting speeds for tin-base babbitt bearings

Optimum speed is slowest speed that will produce sound (porosity-free) castings with minimum segregation.

Inside diameter of bearing shell		Centrifugal casting speed, rev/min
mm	in.	
51	2	850-975
76	3	700-800
102	4	600-700
127	5	535-610
152	6	485-550
178	7	450-525
203	8	420-500
229	9	395-470
254	10	375-450
279	11	360-430
305	12	345-410

330	13	330-395
356	14	320-370
381	15	305-360
406	16	295-350
432	17	285-340
457	18	280-330
483	19	275-325
508	20	265-315
533	21	260-310
559	22	250-300
584	23	245-295
610	24	240-290
635	25	235-285
660	26	230-280
686	27	230-275
711	28	225-270
737	29	220-265
762	30	215-260
787	31	215-255
813	32	210-250
838	33	205-245

864	34	200-245
889	35	200-240
914	36	195-235
965	38	190-230

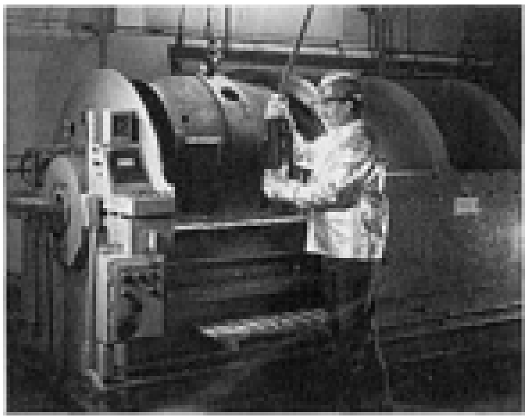


Fig. 2 Loading of a large steam turbine generator bearing into a centrifugal babbitting machine. Courtesy of Pioneer Motor Bearing Company

Procedure. After tinning, full-round (nonsplit) shells require no further preparation and can be immediately loaded into the casting machine. Split-type bearings (in halves) or segmented (tilting pad) style journal bearings require fixturing after the pretinning of each component to make up an assembly ready for spinning. The fixturing consists of laminated spacers for each parting face. These spacers must prevent both radial and axial leakage without unduly restricting the smooth flow of the molten rotating metal.

Spacers can be cut from steel sheet with a minimum thickness of 1.0 mm (0.04 in.) and faced on both sides with 3 mm (0.12 in.) gaskets that are cut to fit. Total spacer thickness should be at least 7 mm (0.28 in.) before assembly to allow for the later separation of the halves or segments by saw cutting through the babbitt without damage to the steel parting faces.

When the spacers are in place and the halves or segments are retained by bolting or other means of safe clamping, the assembly must be reheated in the tinning bath, if necessary, to ensure a minimum temperature of 300 °C (570 °F) before loading in the casting machine. Alternatively, the cold assembly can be mounted in the machine and slowly rotated while gas torches are applied along the outside of the bearing until it reaches tinning temperatures. This latter method, however, does not allow visual in-process inspection to ensure complete wetting (tinning) before casting commences. In any case, there must be little time lost after tinning temperatures are reached, and before babbitt metal is poured, to achieve a satisfactory bond; tinning must be molten when the babbitt is poured.

The babbitt alloy should be melted in a temperature-controlled cast iron pot that is held at its recommended pouring temperature (Tables 1 and 2) and stirred with a vertical motion to promote uniform metal temperature and to avoid metal segregation. Dross on the surface of the pot is skimmed aside while a preheated ladle, preferably of the bottom-pour style, is filled with a predetermined volume of metal. The volume of metal poured should be sufficient to provide a minimum of 4 mm (0.16 in.) machining stock per side after babbitting so that impurities, which float to the inside during centrifugal casting, can be removed.

With the bearing shell rotating at a preselected speed (Table 4), the metal is ladled in one continuous pour directly, or through a preheated trough, into the spinning shell. Water cooling should be started immediately after pouring is completed, and the bearing rotation should continue until the assembly temperature drops to around 150 °C (300 °F). At

this point, the water should be shut off and the bearing allowed to air cool more slowly while spinning. This cooling regime minimizes the stress imposed on the bond by the difference in thermal coefficients between typical babbitts and backing materials. (The ratio is almost 2:1 between babbitt and steel, and 1.5:1 between babbitt and bronze.) A controlled flow of coolant along the length of the bearing ensures directional solidification. That is, the babbitt freezes (solidifies) uniformly along the bond line first, then progressively toward the inside of the casting. This ensures that molten metal under pressure is available to feed the shrinkage and to squeeze out trapped gases and dross. When a shell has a nonuniform cross section, the coolant flow should be adjusted to promote uniform solidification from end to end.

Nonsplit journal bearings follow the same basic procedures as above without the need for assembling half shells or tilting pad segments and reheating them before they are loaded into the casting machine.

Static Casting

The static casting method is used for babbitting of flat surfaces (thrust plates or pads, etc.) and journal bearings. The latter may not lend themselves to centrifugal casting because of odd shapes, equipment requirements, or tooling costs. Static babbitting requires a babbitting mandrel to form the babbitt in the bearing shell. Mandrels can be designed for use in a vertical or horizontal position. Plates are placed at each end when the mandrel is designed for use in a horizontal position. Vertical casting is preferred when possible.

Flat workpieces are cleaned and tinned and fitted with a preformed steel fence clamped around the perimeter of the part. The fence must be sufficiently high to provide a 6 mm (0.25 in.) riser for the mold. The assembly is supported on insulated blocks in an open pan. Once it has reached a minimum temperature of 300 °C (570 °F), the babbitt is poured in a steady stream to fill the mold. The pan is then flooded with tap water to just above the bottom of the workpiece; this must be done immediately to ensure directional solidification. Heat may be added by gas torch to the babbitt surface while the metal is gently agitated to promote the release of any trapped air or dross. Additional metal may be added to feed the shrinkage.

Split-type journal bearings can be statically cast by assembling both halves together with spacers around a vertical mandrel (core) on a level table. Alternatively, each half may be cast separately by clamping parting faces against flat wings projecting from each side of a vertical half-round core. A steel riser ring is placed over an appropriate gasket on top of the half shell or assembled pair of shells to provide a minimum 12 mm (0.5 in.) height of excess molten metal to feed the shrinkage during solidification. The inside diameter of the riser and gasket should be somewhat larger than the tinned inside diameter of the shell(s). The radius of the mandrel or core should be at least 5 mm (0.20 in.) smaller than half the finished bore diameter of the bearing to allow for later stock removal. Large bearings may require a greater allowance for machining stock because of inaccuracies in locating the core of the bearing shell when the babbitt is poured. The mandrel/core height should preferably be at least 50 mm (2 in.) higher than the riser to act as a backboard against which the babbitt can be ladled into the cavity with minimum turbulence.

The mandrel, riser ring, and casting table are preheated to 290 °C (550 °F) to promote directional solidification. The casting must solidify progressively from the bond line inward toward the core, and up from the bottom of the shell(s) to the top of the riser. If not, shrinkage cavities will occur at the interface and the bond will be weakened. The mandrel can be "smoked" with a reducing flame from an acetylene torch or coated with an appropriate stop-off material before heating to promote easy release of the bearing from the mandrel after solidification.

After tinning, the bearing assembly or half shell is immediately clamped against the half core or around the mandrel. If the shell is being rebabbitted, any openings (holes, slots, etc.) must be quickly and effectively plugged with a dry high-temperature packing material. The bottom of the bearing assembly or shell should be sitting on a sheet of gasketing material to insulate it and to prevent leakage; strips of gasket material can be used to seal the joint faces.

The bearing shell temperature should be a minimum of 260 °C (500 °F). Once the babbitt metal is heated to its recommended pouring temperature, it is stirred and skimmed and then the cavity is filled in one continuous pour to the top of the riser ring.

Castings can be cooled by air or by having water spray directed uniformly against the outside of the shell(s) from the bottom up while heat is added to the mandrel and/or riser with a gas torch. The molten metal can be gently agitated by continuous vertical stroking with a small-diameter stainless steel rod to promote the release of trapped gases while the cooling progresses upward and inward toward the core. Molten metal is added to feed the shrinkage. When the riser solidifies, the bearing can be separated from the core and air-cooled to room temperature.

Bond Quality

Bond integrity is arguably the most important manufacturing feature of any bimetal bearing. A bond failure can be very expensive to correct, particularly considering the cost of lost production while the bearing is repaired or replaced. The bond tensile strength of a metallurgically well-bonded steel-backed babbitted bearing should exceed 60 MPa (8700 psi); bronze-backed bearings should exhibit a minimum bond strength of 40 MPa (5800 psi). In other words, the bond strength should comfortably exceed the ultimate tensile strength of the babbitt.

Bond strength is determined by destructive tests for evaluating tensile strength and ductility (Ref 3). Nondestructive ultrasonic bond testing, when conducted and evaluated by an experienced and qualified operator, does not determine strength but does reveal the location and extent of any significant unbonded areas. An unblemished surface is a very good indication that proper preparation and casting techniques have been employed throughout the babbitting process and that at least minimum bond strengths can be reasonably expected.

Defective bonds can most often be traced to poor preparation (i.e., inadequate cleaning of the base metal). The second most prevalent cause is allowing the tinned shell to cool such that the tinning is not molten when the babbitt is centrifugally or statically cast. To correct either problem, the babbitt and tinning must be removed and the shell reprocessed, starting with the basic cleaning steps and following recommended temperature guidelines.

Reference cited in this section

3. Bond Testing, Babbitt-Lined Bearings, Military Standard DOD-STD-2183SH, 1985

Metal-Spray Babbitting

Babbitting by the metal-spray method requires special equipment consisting of an acetylene/oxygen flame spray gun that uses a high tin-base babbitt in wire form. The molten alloy is sprayed on a bond coating, which has been previously sprayed on the bearing shell. The buildup of the babbitt is relatively slow, and bond strengths are somewhat lower than with other methods; however, voids are eliminated and a high-quality product results. Spray babbitt thicknesses to 26 mm (1.02 in.) are possible, and spray control is sufficient to require only a small excess of deposit for subsequent machining. Overspray losses are minimal. Mechanical aids to hold the babbitt to the bearing shell are not necessary and are not recommended for this process, and skill levels for operators are not as high as those required for static babbitting.

Phosphate Coatings

Introduction

PHOSPHATE COATING is the treatment of iron, steel, galvanized steel, or aluminum with a dilute solution of phosphoric acid and other chemicals in which the surface of the metal, reacting chemically with the phosphoric acid media, is converted to an integral, mildly protective layer of insoluble crystalline phosphate. The weight and crystalline structure of the coating and the extent of penetration of the coating into the base metal can be controlled by:

- Method of cleaning before treatment
- Use of activating rinses containing titanium and other metals or compounds
- Method of applying the solution
- Temperature, concentration, and duration of treatment
- Modification of the chemical composition of phosphating solution

The method of applying phosphate coatings is usually determined by the size and shape of the article to be coated. Small items, such as nuts, bolts, screws, and stampings, are coated in tumbling barrels immersed in phosphating solution. Large fabricated articles, such as refrigerator cabinets, are spray coated with solution while on conveyors. Automobile bodies are sprayed with or immersed in phosphating solution. Steel sheet and strip can be passed continuously through the phosphating solution or can be sprayed.

Phosphate coatings range in thickness from less than 3 to 50 μm (0.1 to 2 mil). Coating weight (grams per square meter of coated area), rather than coating thickness, has been adopted as the basis for expressing the amount of coating deposited.

Phosphate Coatings

Three principal types of phosphate coatings are in general use: zinc, iron, and manganese. A fourth type, lead phosphate, more recently introduced, is operated at ambient temperatures.

Zinc phosphate coatings encompass a wide range of weights and crystal characteristics, ranging from heavy films with coarse crystals to ultrathin microcrystalline deposits. Zinc phosphate coatings vary from light to dark gray in color. Coatings are darker as the carbon content of the underlying steel increases, as the ferrous content of the coating increases, as heavy metal ions are incorporated into the phosphating solution, or as the substrate metal is acid pickled prior to phosphating. Zinc phosphating solutions containing active oxidizers usually produce lighter-colored coatings than do solutions using milder accelerators.

Zinc phosphate coatings can be applied by spray, immersion, or a combination of the two. Coatings can be used for any of the following applications of phosphating: base for paint or oil; aid to cold forming, tube drawing, and wire drawing; increasing wear resistance; or rustproofing. Spray coatings on steel surfaces range in weight from 1.08 to 10.8 g/m^2 (3.5×10^{-3} to 3.5×10^{-2} oz/ft^2); immersion coatings, from 1.61 to 43.0 g/m^2 (5.28×10^{-3} to 0.141 oz/ft^2).

Iron phosphate coatings were the first to be used commercially. Early iron phosphating solutions consisted of ferrous phosphate/phosphoric acid used at temperatures near boiling and produced dark gray coatings with coarse crystals. The term *iron phosphate coatings* refers to coatings resulting from alkali-metal phosphate solutions operated at pH in the range of 4.0 to 5.0, which produce exceedingly fine crystals. The solutions produce an amorphous coating consisting primarily of iron oxides and having an interference color range of iridescent blue to reddish-blue color.

A typical formulation for an iron phosphate bath is (Ref 1):

Component	Composition, %
Phosphate salts	12-15
Phosphoric acid	3-4
Molybdate accelerator	0.25-0.50
Detergents (anionic/nonionic)	8-10

Basically, then, iron phosphate formulations consist of primary phosphate salts and accelerators dissolved in a phosphoric acid solution. It is the acid that initiates the formation of a coating on a metal surface. When acid attacks the metal and begins to be consumed, solution pH at the metal surface rises slightly. This is what causes the primary phosphate salts to drop out of solution and react with the metal surface, forming a crystalline coating.

All iron phosphate conversion coatings are composed of partially neutralized phosphoric acid. But all iron phosphates are not created equal. Other ingredients, such as the specific accelerator used (Table 1), hold part of the key.

Table 1 Effect of accelerators on the weight of an iron phosphate coating

Accelerator	**Surface treated**	**Coating weight**	
		g/m²	**oz/ft² × 10⁻³**
. . .	Steel only	0.11-0.27	0.35-0.88
Metallic	Mixed metal loads, ferrous, zinc, and aluminum	0.22-0.38	0.71-1.24
Oxidizer	High-quality steel only	0.43-0.86	1.41-2.82

Source: Ref 2

Although iron phosphate coatings are applied to steel to provide a receptive surface for the bonding of fabric, wood, and other materials, their chief application is as a base for subsequent films of paint. Processes that produce iron phosphate coatings are also available for treatment of galvanized and aluminum surfaces. Iron phosphate coatings have excellent adherence and provide good resistance to flaking from impact or flexing when painted. Corrosion resistance, either through film or scribe undercut, is usually less than that attained with zinc phosphate. However, a good iron phosphate coating often outperforms a poor zinc phosphate coating.

Spray application of iron phosphate coatings is most frequently used, although immersion application also is practical. The accepted range of coating weights is 0.21 to 0.86 g/m^2 (6.9 × 10^{-4} to 0.26 oz/ft^2). Little benefit is derived from exceeding this range, and coatings of less than 0.21 g/m^2 (6.9 × 10^{-4} oz/ft^2) are likely to be nonuniform or discontinuous. Quality iron phosphate coatings are routinely deposited at temperatures from 25 to 65 °C (80 to 150 °F) by either spray or immersion methods.

Manganese phosphate coatings are applied to ferrous parts (bearings, gears, and internal combustion engine parts, for example) for break-in and to prevent galling. These coatings are usually dark gray. However, because almost all manganese phosphate coatings are used as an oil base and the oil intensifies the coloring, manganese phosphate coatings are usually black in appearance. In some instances, a calcium-modified zinc phosphate coating can be substituted for manganese phosphate to impart break-in and antigalling properties.

Manganese phosphate coatings are applied only by immersion, requiring times ranging from 5 to 30 min. Coating weights normally vary from 5.4 to 32.3 g/m^2 (1.8 × 10^{-2} to 9.83 oz/ft^2), but can be greater if required. The manganese phosphate coating usually preferred is tight and fine-grain, rather than loose and coarse-grain. However, desired crystal size varies with service requirements. In many instances, the crystal is refined as the result of some pretreatment (certain types of cleaners and/or conditioning agents based on manganese phosphate) of the metal surface.

Manganese-iron phosphate coatings are usually formed from high-temperature baths from 90 to 95 °C (190 to 200 °F).

References cited in this section

1. D. Phillips, Practical Application of the Principles Governing the Iron Phosphate Process, *Plat. Surf. Finish.*, March 1990, p 31-35
2. G.L. Tupper, "Finishing: Where Do You Start," paper presented at Fabtech International '89 (Rosemont, IL), 9-12 Oct 1989, Report No. FC89-572, Society of Manufacturing Engineers

Composition of Phosphate Coating

All phosphate coatings are produced by the same type of chemical reaction: the acid bath, containing the coating chemicals, reacts with the metal to be coated, and at the interface, a thin film of solution is neutralized because of its attack on the metal. In the neutralized solution, solubility of the metal phosphates is reduced, and they precipitate from the

solution as crystals. Crystals are then attracted to the surface of the metal by the normal electrostatic potential within the metal, and they are deposited on the cathodic sites.

When an acid phosphate reacts with steel, two types of iron phosphate are produced: a primary phosphate, which enters the coating; and a secondary phosphate, which enters the solution as a soluble iron compound. If this secondary ferrous phosphate were oxidized to a ferric phosphate, it would no longer be soluble and would precipitate from the bath. Oxidizing agents are incorporated to remove the soluble secondary ferrous phosphate because the ferrous phosphate inhibits coating formation.

Although all phosphating baths are acid in nature and to some extent attack the metal being coated, hydrogen embrittlement seldom occurs as a result of phosphating. This is primarily because all phosphating baths contain depolarizers or oxidizers that react with the hydrogen as it is formed and render it harmless to the metal. In some instances, however, zinc-phosphate processes, intended for use with rust-inhibiting oils for corrosion resistance or manganese-phosphate treatments, can cause hydrogen embrittlement because they may contain a minimum amount of depolarizers and oxidizers. A dwell time before use or mild heating may be needed to relieve embrittlement.

The acidity of phosphating baths varies, depending on the type of phosphating compound and its method of application. Immersion zinc phosphating baths operate in a pH range of 1.4 to 2.4, whereas spray zinc phosphating solutions can operate at a pH as high as 3.4, depending on the bath temperature. Iron phosphating baths usually operate at a pH of 3.8 to 5. Manganese phosphating baths operate in a pH range comparable to that of the immersion zinc phosphating solutions. Lead-phosphate solutions are usually more acidic than any of the others.

Zinc, iron, and manganese phosphating baths usually contain an accelerator, which can range from a mild oxidant, such as nitrate, to one of the more vigorous nitrite, chlorate, peroxide, or organic sulfonic acids (Table 2). The purposes of these accelerators are to speed up the rate of coating, to oxidize ferrous iron, and to reduce crystal size. This is accomplished because of the ability of the accelerators to oxidize the hydrogen from the surface of the metal being coated. Phosphating solution can then contact the metal continuously, permitting completeness of reaction and uniformity of coverage. Accelerators have an oxidizing effect on the dissolved iron in the bath, thus extending the useful life of the solution. Some zinc and iron phosphating processes rely on oxygen from the air as the accelerator. Zinc phosphating baths for aluminum usually contain complex or free fluorides to accelerate coating formation and to block the coating-inhibiting effect of soluble aluminum.

Table 2 Accelerators used in phosphate coating processes

Type of accelerator	Accelerator source	Effective concentration			Optimum operating conditions				Advantages	Limitations
					Ratio	Temperature		Addition		
		%	g/L	lb/gal × 10^{-3}		°C	°F			
NO_3^-	$NaNO_3$, $Zn(NO_3)_2$, $Ni(NO_3)_2$	1-3	. . .	. . .	High $NO_3^- : PO_4^{3-}$	65-93	149-199	. . .	Lower sludge.	Reduction of $FePO_4$ increases the iron content of the coating.
NO_2^-	$NaNO_2$	. . .	0.1-0.2	0.8-1.7	NO_2:NO = 1:1	(a)	(a)	Continuous	Affords rapid processing even at low temperatures.	Corrosive fumes. Highly unstable at high bath temperatures. Frequent addition is required.

ClO_3^-	$Zn(ClO_3)_2$	0.5-1	. . .	. . .	. . .	(a)	(a)	Continuous	Stable in liquid concentrates. Can be used for bath makeup and replenishment. Overcomes the white staining problem.	Corrosive nature of chlorate and its reduction products. High concentrations poison the bath. Removal of gelatinous precipitate from the resultant phosphate coatings is difficult.
H_2O_2	H_2O_2	. . .	0.05	0.4	. . .	(a)	(a)	. . .	Low coating weight. No harmful products. Free from staining.	Bath control tends to be critical. Heavy sludge formation. Limited stability. Continuous addition is required.
Perborate	Sodium perborate	. . .	. . .	. . .	. . .	(a)	(a)	. . .	No separate neutralizer is required. Good corrosion resistance.	Continuous addition is required. Voluminous sludge.
Nitroguanidine	Nitroguanidine	. . .	. . .	. . .	. . .	55	130	. . .	Neither the accelerator nor its reduction products are corrosive.	Slightly soluble. Does not control the buildup of ferrous iron in the bath. Highly expensive.

Source: Ref 3

(a) Low temperature.

Reference cited in this section

3. T.S.N. Sankara Narayanan and M. Subbaiyan, Acceleration of the Phosphating Process: An Overview, *Prod. Finish.,* Sept 1992, p 6-7

Applications

On the basis of pounds of chemicals consumed or tons of steel treated, the greatest use of phosphate coatings is as a base for paint. Phosphate coatings are also used to provide:

- A base for oil or other rust-preventive material
- Lubricity and resistance to wear, galling, or scoring of parts moving in contact, with or without oil
- A surface that facilitates cold forming
- Temporary or short-time resistance to mild corrosion
- A base for adhesives in plastic-metal laminations or rubber-to-metal applications

Phosphate Coatings as a Base for Paint

The useful life of any painted metal article depends mainly on the durability of the organic coating itself and the adherence of the film to the surface on which it is applied. The primary function of any protective coating of paint is to prevent corrosion of the base metal in the environment in which it is used. To accomplish this purpose, the method of preparing the metal should reduce the activity of the metal surface, so that underfilm corrosion is prevented at the interface between paint and metal.

When used as a base for paint films, phosphate coatings promote good paint adhesion, increase the resistance of the films to humidity and water soaking, and substantially retard the spread of any corrosion that may occur. A phosphate coating retards the amount of corrosion creep, because the coating is a dielectric film that insulates the active anode and cathode centers existing over the entire surface of the base metal. By insulating these areas, corrosion of the surface is arrested or at least substantially retarded.

Zinc phosphate coatings of light to medium weight (1.6 to 2.1 g/m^2, or 5.2×10^{-3} to 6.9×10^{-3} oz/ft^2) and lightweight iron phosphate coatings (0.3 to 0.9 g/m^2, or $1 \times 10^{-;3}$ to 3×10^{-3} oz/ft^2) are generally used for paint bases. Examples of products so treated are steel, galvanized and aluminum stampings for automobiles, household appliances, metal cabinets, and metal furniture (Table 3). Enamel that is baked at a temperature of 205 °C (400 °F) or higher can be successfully applied to phosphate-coated steel.

Table 3 Low-carbon sheet steel components spray phosphate coated for paint finishing

Part	**Area**		**Production, pieces/h**
	m^2	**ft^2**	
Zinc phosphate[(a)]			
Automobile body	74	800	50
Dryer shell	4.0	42.5	400
Cabinet back panel	1.18	12.7	700
Cabinet top	0.73	7.9	1400
Compressor housing	0.42	4.5	600
Motor access panel	0.15	1.6	4500
80 mm mortar shell	0.093	1.0	1000

Iron phosphate[b]			
Washing machine shell	4.91	52.9	330
Dryer top	1.18	12.7	660
Range side panel	0.90	9.7	660
Dishwasher door	0.78	8.4	660
Wiring channel	4.5	4.9	4950
Control housing	0.35	3.8	1980
Condenser cover	0.15	1.6	3330
Range gusset plate	0.078	0.84	4950
Conduit cover plate	0.029	0.31	8900

(a) 1.6 to 2.1 g/m^2 (5.2 × 10^{-3} to 6.9 × 10^{-2} oz/ft^2).

(b) 0.4 to 0.9 g/m^2 (1 × 10^{-3} to 3 × 10^{-3} oz/ft^2)

Phosphated surfaces to be painted should not be touched by bare hands or other parts of the body, to ensure good adherence of the paint film. Body salts can contaminate phosphate coatings. Contaminated areas can be reflected as surface imperfections of the paint film and can decrease corrosion and humidity resistance.

Metals Cleaned in Phosphoric Acid versus Those Coated with Phosphate. Phosphoric acid metal cleaners usually consist of phosphoric acid and a water-soluble solvent, with or without a wetting agent. In the preparation of metal with such solutions, the purpose is to complete the following steps in a single operation: remove oil, grease, and rust; and provide a slight etch of the metal to promote the adhesion of paint. The cleaning solution must contain enough acid (15 to 20% H_3PO_4) and solvent to remove rust, oil, and grease. This concentration of phosphoric acid prevents the formation of any substantial phosphate coating.

When metal surfaces are to be phosphate coated, articles are first freed of rust and grease by suitable cleaning methods. Articles are then treated with a balanced dilute acid phosphate salt with a slight excess of acid (0.6 to 1.0% H_3PO_4), so that reaction of the acid with the metal results in the conversion of the surface to a refined crystalline phosphate coating. Tests conducted on steel cleaned with phosphoric acid have revealed that the phosphate film remaining from the cleaning operation averages only 0.05 to 0.10 g/m^2 (1.6 × 10^{-4} to 3.3 × 10^{-4} oz/ft^2) of surface. In contrast, when steel is phosphated for painting by using standard zinc phosphating solutions, coating weights usually range from 1.08 to 4.3 g/m^2 (3.5 × 10^{-3} to 1.4 × 10^{-2} oz/ft^2), depending on the solution and method.

Corrosion Protection

Conversion of a metal surface to an insoluble phosphate coating provides a metal with a physical barrier against moisture. The degree of corrosion protection that phosphate coatings impart to surfaces of ferrous metals depends on uniformity of

coating coverage, coating thickness, density, and crystal size, and the type of final seal employed. Coatings can be produced with a wide range of thicknesses, depending on the method of cleaning before treatment, composition of the phosphating solution, temperature, and duration of treatment. In phosphating, no electric current is used, and formation of the coating depends primarily on contact between the phosphating solution and the metal surface and on the temperature of the solution. Consequently, uniform coatings are produced on irregularly shaped articles, in recessed areas, and on threaded and flat surfaces, because of the chemical nature of the coating process.

The affinity of heavy phosphate coatings for oil or wax is used to increase the corrosion resistance of these coatings. Frequently, phosphate-coated articles are finished by a dip in nondrying or drying oils that contain corrosion inhibitors. The articles are then drained or centrifuged to remove the excess oil.

Medium to heavy zinc phosphate coatings, and occasionally, heavy manganese phosphate coatings are used for corrosion resistance when supplemented by an oil or wax coating. Zinc phosphate plus oil or wax is usually used to treat cast, forged, and hot-rolled steel nuts, bolts, screws, cartridge clips, and many similar items. Manganese phosphate plus oil or wax is also used on cast iron and steel parts.

Phosphate Coating as an Aid in Forming Steel

The contact pressure used in deep drawing operations sets up a great amount of friction between the steel surface and the die. The phosphate coating of steel as a metal-forming lubricant, before it is drawn:

- Reduces friction
- Increases speed of the drawing operations
- Reduces consumption of power
- Increases the life of tools and dies

When phosphate-coated steel is used in drawing seamless steel tubing, the resulting decrease in friction is so pronounced that greater reduction of tube size per pass is possible. This reduction may be as great as one-half.

Reduction in the number of draws and anneals in deep forming results in economy of operation. Conversion of a steel surface to a nonmetallic phosphate coating permits the distribution and retention of a uniform film of lubricant over the entire surface of the steel. This combination of lubricant and non metallic coating prevents welding and scratching of steel in the drawing operations and greatly decreases rejections.

Zinc phosphate coatings of light to medium weight are applied to steel to aid in drawing and forming operations. The phosphated surface is coated with a lubricant (such as soap, oil, drawing compound, or an emulsion of oil and fatty acid) before the forming operation. The zinc phosphate surface, which prevents metal-to-metal contact, makes it practical to cold form and extrude more difficult shapes than is possible without the coating. Table 4 lists and describes some products that are zinc phosphate dip or spray coated before being cold formed.

Table 4 Applications of zinc phosphate dip spray coating to facilitate cold forming

Part[(a)]	**Steel**	**Area**		**Coating weight**		**Production, pieces/h**	**Sequence of operations**
		m^2	**ft^2**	**g/m^2**	**oz/ft^2 × 10^{-2}**		
Spark plug body	1110	0.0002	0.002	4.3-6.5	1.4-2.1	500	[(b)]
Universal-joint bearing cup	1010	0.005	0.05	4.3-6.5	1.4-2.1	2000	[(b)]

Truck wheel nut	1008	0.007	0.08	4.3-6.5	1.4-2.1	1000	(b)
Piston pin	5015	0.009-0.014	0.1-0.15	5.4-7.0	1.8-2.3	2600	(b)
Standard-transmission output shaft	4028	0.009-0.014	0.1-0.15	4.3-6.5	1.4-2.1	300	(b)
Rocket-nozzle plate (69.85 mm or 2.75 in.)	4130, 4140	0.05	0.5	4.3-6.5	1.4-2.1	150	(c)
Mortar shell (80 mm or 3.2 in.)	1010	0.07-0.11	0.8-1.2	4.3-6.5	1.4-2.1	4000	(d)
Cartridge cases (75 mm or 3 in.)	1030	0.08-0.28	0.9-8.0	4.3-6.5	1.4-2.1	1000	(c)

(a) Bath used for all applications listed is zinc phosphate bath accelerated with nitrous oxide.

(b) Alkaline wash, rinse, activating rinse, phosphate, rinse, neutralizing rinse, oil dip.

(c) Sulfuric acid pickle, rinse, rinse, phosphate, rinse, rinse, oil dip.

(d) Alkaline wash, rinse, sulfuric acid pickle, rinse, rinse, phosphate, rinse, oil dip

Wear Resistance

Phosphating is a widely used method of reducing wear on machine elements. The ability of phosphate coating to reduce wear depends on uniformity of the phosphate coating, penetration of the coating into metal, and affinity of the coating for oil. A phosphate coating permits new parts to be broken in rapidly by permitting retention of an adequate film of oil on surfaces at that critical time. In addition, the phosphate coating itself functions as a lubricant during the high stress of break-in.

Heavy manganese phosphate coatings (10.8 to 43.0 g/m^2, or 3.5×10^{-2} to 0.14 oz/ft^2), supplemented with proper lubrication, are used for wear-resistance applications. Parts that are manganese phosphate coated for wear resistance are listed in Table 5.

Table 5 Parts immersion coated with manganese phosphate for wear resistance

Part[(a)]	**Material**	**Coating time, min**	**Supplementary coatings**
Components for small arms, threaded fasteners[(b)]	Cast iron or steel; forged steel	15-30	Oils, waxes
Bearing races	High-alloy steel forgings or bar stock	7-15	Oils, colloidal graphite

Valve tappets, camshafts	Low-alloy steel forgings or bar stock	7-15	Oils, colloidal graphite
Piston rings	Forged steel, cast iron	15-30	Oils
Gears(c)	Forged steel, cast iron	15-30	Oils

(a) Coating weights range from 10.8 to 43.0 g/m^2 (3.5×10^{-2} to 0.14 oz/ft^2).

(b) Coating may be applied by barrel tumbling.

(c) Coating weights range from 5.4 to 43.0 g/m^2 (1.8×10^{-2} to 0.14 oz/ft^2).

When two parts, manganese phosphated to reduce friction by providing lubricity, are put into service in contact with each other, the manganese coating is smeared between the parts. The coating acts as a buffer to prevent galling or, on heavily loaded gears, welding. The phosphate coating need not stand up for an extended length of time, because it is in initial movements that parts can be damaged and require lubricity. For example, scoring of the mating surfaces of gears usually takes place in the first few revolutions. During this time, the phosphate coating prevents close contact of the faces. As the coating is broken down in operation, some of it is packed into pits or small cavities formed in gear surfaces by the etching action of the acid during phosphating.

Long after break-in, the material packed into the pits or coating that was originally formed in the pits prevents direct contact of mating surfaces of gear teeth. In addition, it acts as a minute reservoir for oil, providing continuing lubrication. As work hardening of the gear surfaces takes place, the coating and the etched area may disappear completely, but by this time scoring is unlikely to occur.

Phosphate-Coated Ferrous Alloys

In general, the stainless steels and certain alloy steels cannot be successfully phosphate coated. All other steels accept a coating, with difficulties experienced in the coating process varying with alloy content. Most cast irons are readily coated, and alloy content has little effect on their coatability.

Steels

Whether coatings are applied to steel by spray or immersion, a rule of thumb is that lightweight, amorphous phosphate coatings adhere better, while heavier, crystalline zinc phosphate coatings are more corrosion resistant (Ref 4).

Most phosphate-coated steel is low-carbon, flat-rolled material used for applications such as sheet metal parts for automobiles and household appliances, and phosphating processes have been designed for coating such material. Steels with carbon contents in the range specified for 1025 to 1060 inclusive are suitable for phosphating if the silicon content is held to normal limits. Steels with higher carbon contents, in the range from 1064 to 1095, may require the following modifications of phosphating processes to produce satisfactory results: increasing time; increasing temperature; or increasing solution strength. Copper content up to 0.3% in low-carbon steel, the normal limit for copper-bearing steel, is not a deterrent to phosphate coating. The addition of copper, by itself, at about 0.5% causes surface checking of steel during hot rolling. This acts as a restriction on the amount of copper that may be present to serve as a deterrent to phosphating.

Low-alloy, high-strength steel, provided nickel or chromium does not exceed 1%, can be successfully phosphated. Generally, with some modification, chromium content of up to 9% can be tolerated while still depositing a phosphate coating. Nickel-chromium and chromium stainless steels are not recommended for phosphate coating. For some applications, however, oxalate coating processes are used.

Because electrical steels used in motor laminations and electrical transformers have a silicon content in the range of 1.2 to 4.5%, they are not recommended for phosphate coating by normal phosphating processes. These require processes accelerated by the use of fluoride compounds or special dried-in place salts of phosphates.

Low-carbon steels annealed in a properly controlled atmosphere to provide a clean, oxide-free surface are readily phosphated. Temper-rolled, annealed, low-carbon steels are the most readily phosphated of all steels. Cold-reduced or cold-rolled, full-hard, low-carbon steels readily accept phosphate coatings.

Low-carbon, hot-rolled steel, and normalized and pickled steel, if thoroughly rinsed after pickling, phosphate well. Excessive amounts of residual pickling salts (sulfates) can interfere with normal phosphating. Pickling residue on cold-reduced or cold-rolled steels seldom presents problems, because of the extensive processing that follows the pickling operation. Cold reduction of 30 to 70% spreads the residue over large areas. Cleaning and scrubbing of a cold-reduced strip, followed by annealing and temper rolling, remove or dilute surface contaminants. Phosphating processes that provide for relatively long-time and high-temperature treatments are the least sensitive to small variations in alloy composition and surface conditions.

Stainless Steels (Ref 5). Although phosphate coating of stainless steel is difficult, it is sometimes attempted to protect against pitting in chloride atmospheres. Pretreatment is generally required if an organic coating will be applied.

One study achieved good zinc phosphate coatings using the following bath composition:

Component	Concentration	
	g/L	lb/gal × 10^{-2}
Zinc oxide	16-20	13.3-16.7
Phosphoric acid	13-16	10.8-13.3
Calcium chloride	9-12	7.5-10.0
Ferric chloride	0.5-1.0	0.4-0.8

The researchers tested temperatures from 40 to 80 °C (105 to 175 °F) and immersion times of 15 to 50 min. Various stainless steel pretreatments were tested for their effects on coating adhesion and quality: solvent degreasing, immersion in hydrochloric acid or sulfuric acid solution, and sand blasting.

The results showed that the most effective operating conditions were 60 to 70 °C (140 to 160 °F) with immersion times of 15 to 30 min. Sandblasting with 16-mesh sand proved to be the best pretreatment. The zinc phosphate coatings on stainless steel panels prepared under these conditions were uniform and well adherent. The corrosion resistance of the panels was tested by immersing them in 0.5% NaCl solution and exposing them to a salt-spray chamber, and no rust spots were observed within 15 days for either test. Paint adhered as well to phosphated stainless steel panels as to nonphosphated panels.

Galvanized Steel. Many parts produced from galvanized sheet steel, such as certain automotive stampings and some appliances, require a phosphate coating as a base for a subsequent paint film. Phosphating imparts superior resistance to

corrosion and greater ability to retain paint to galvanized sheet and strip steel by converting the surface to an insoluble phosphate coating. Galvanized steel can be readily phosphated provided the surface of the plate has not been passivated by a chromate-based solution. The passivated surface of the chromate-treated material resists the action of a phosphating solution. Treatment of such passivated surfaces requires the use of an alkali-permanganate solution or, depending on the age and degree of passivation, removal with strong alkaline cleaners.

Cast Irons

Gray, ductile, or malleable iron castings are readily phosphated. The ability of a cast iron to accept a phosphate coating is not affected by alloy content, but hinges primarily on two requirements, a clean surface and a metal temperature approximately equal to that of the phosphating bath. Machined surfaces need no further cleaning; however, cast surfaces can be prepared by removing scale and sand by blasting or other cleaning.

Phosphating bath temperatures are not critical for cast iron. Acceptable coatings can be obtained in baths ranging from 70 to 95 °C (160 to 205 °F). Often, lower temperatures are viable. A problem usually exists in raising the temperature of a casting, particularly one with heavy sections, to approximate the temperature of the bath. Preheating heavy castings to the temperature of the bath minimizes or eliminates excessive pickling action in areas that require a long time to reach the temperature of the phosphating solution.

Manganese phosphate coatings, applied only by immersion, are easily deposited on cast iron surfaces. The normally coarse crystal breaks down readily to provide temporary lubrication during break-in. If this is not sufficient, castings may be given a supplemental oil dip. Interstices between the coarse crystals hold sufficient oil to provide adequate short-time lubrication.

Because manganese phosphate crystals on cast iron build up rapidly to thicknesses of as much as 25 μm (1 mil), machined dimensions carrying close tolerances may be altered significantly by coating. If this is not acceptable, the dimension can be reduced by removing some of the coating thickness. If a fine crystalline structure is necessary, the presence of an appropriate oil on the surface before phosphating, such as film remaining after emulsion cleaning, refines the normally coarse phosphate crystal. Preferably, special manganese phosphate activating chemicals are used in a water rinse preceding the manganese phosphate process.

References cited in this section

4. R. Bridger and P. Burden, Conversion Coating Is Becoming the Norm Prior to Powder Coating, *Prod. Finish.,* April 1988, p 6-8
5. J.A. Guirklis, Surface Finishing, *CAB Curr. Aware. Bull. (200),* April 2-3, 1990, 9012, p 3

Phosphate-Coated Nonferrous Materials

Aluminum. Zinc phosphate coatings, applied via spray, are easily deposited on aluminum surfaces provided fluoride ion is present in the bath. Sodium or potassium salts are also present to prevent the buildup of soluble aluminum in the bath, which inhibits coating formation. In the processing of a metal mix of aluminum, steel, and galvanized steel, separate fluoride additions to the bath may be required if the metal mix consists of greater than 10% aluminum. Coating weights range from 0.27 to 2.2 g/m^2 (8.8×10^{-4} to 7.2×10^{-3} oz/ft^2).

Zinc (Ref 6). For zinc castings, the phosphate coatings used commercially are amorphous phosphate/molybdate coatings and crystalline zinc phosphate coatings. The most widely used are zinc phosphate conversion coatings, which are used primarily as precoats for organic finishes. For example, under paint films, metal surfaces remain conductive, and corrosion will occur if the film is broken. Phosphate coatings give the zinc casting an insoluble nonconductive film that minimizes the spread of corrosion, improves mechanical adhesion, and reduces paint blistering (because the conversion coat is "micro-rough").

Reference cited in this section

6. D. Elliott, Finishing of Zinc Casting Alloys, *Die Cast. Manage.,* Feb 1992, p 28-31

Process Fundamentals

The application of a phosphate coating for paint-based application normally comprises five successive operations: cleaning, rinsing, phosphating, rinsing, and chromic acid rinsing. Some of these operations may be omitted or combined, such as cleaning and coating in one operation. Additional operations may be required, depending on the surface condition of parts to be phosphated or on the function of the phosphate coating. Parts exemplifying these exceptions are:

- Heavily scaled parts, which may require pickling before cleaning.
- Parts with extremely heavy coatings of oil or drawing compounds, which may require rough cleaning before the normal cleaning operation.
- Parts that are tempered in a controlled atmosphere before being phosphated, which may not require cleaning and rinsing before phosphating.
- Parts that are phosphated and later oiled for antifriction purposes, which may have the chromic acid rinse omitted, because corrosion resistance is not required. (Some rust-preventive oils negate the need for a chromic rinse while still providing excellent corrosion resistance.)
- Automotive parts when electrodeposition of a primer is involved. (A deionized water rinse is required after the chromic acid rinse.)

Hexavalent chromic acid for a passivating rinse is no longer used in some plants because of strict effluent controls imposed by the Environmental Protection Agency (EPA). Other, less restricted materials, such as phosphoric acid and various proprietary compounds, are being used.

Cleaning

Because the chemical reaction that results in the deposition of a phosphate coating depends entirely on the phosphating solution's making contact with the surface of the metal being treated, parts should always be sufficiently clean to permit the phosphating solution to wet the surface uniformly. Cleaning may involve chemical action, mechanical action, or both. Precautions must be taken to avoid carryover of cleaning materials into phosphating tanks. This is particularly true for alkaline cleaners, which can neutralize the acid phosphating solutions, rendering them useless. Other cleaning compounds can contaminate the bath, causing poor quality coatings, such as complex phosphates. A typical alkaline cleaner is formulated as follows (Ref 1):

Component	Composition, %
Caustic	8-10
Phosphate	4-5
Sequestering agents	0.5-1.0
Buffer (soda ash)	3-5
Detergents (anionic/nonionic)	8-10

Soil that is not removed can act as a mechanical barrier to the phosphating solution, retarding the rate of coating, interfering with the bonding of the crystals to the metal, or completely preventing solution contact. Some soils can be

coated with phosphate crystals, but adherence of the coating will be poor and affect the ability of a subsequent paint film to remain continuous.

Ordinary mineral oil is usually easy to remove and presents no problem to the phosphating processes. However, with the use of more complex materials in forming metal, in rustproofing metal, in stripping paint, and in removing scale, cleaning has become a major consideration in any phosphating operation. Materials such as cutting oils, drawing compounds, coolants, and rust inhibitors can react with the base metal and form a deleterious film.

Several solutions to phosphating problems that arose because of improper or inadequate surface preparation have been used in actual production situations. In one plant, irregularities occurred in the thickness and crystal size of phosphate coatings on deep-drawn parts. These irregularities varied in severity, but were sometimes acute enough to cause roughness in the subsequently applied paint film. When fresh cleaning solutions were used, the problem was somewhat alleviated, but the irregularities recurred after cleaners had been in use for only a short time. Investigation revealed that a variety of drawing compounds were being used on the parts, and that each contributed in some degree to the contamination of the cleaner and the inability of the cleaner to remove soil. Some drawing compounds react with the steel surface, forming oxides not removable by regular cleaners. Other drawing compounds cause excessive, undesirable foaming when in contact with cleaners. Still other drawing compounds form into small globules in the cleaner and are redeposited on the metal and not completely removed in the subsequent rinse. The degree of cleanness of the parts was reflected in the degree of variation of the phosphate coating. The problem was solved by using a different cleaner with a different detergent system plus an increase in caustic content, and by selecting drawing compounds that, while still performing as required, would be effectively removed by this cleaner without contaminating it.

Another solution was used during an extended production run of 80 mm (3.2 in.) mortar shell cases. In this situation, dip phosphoric acid pickling was replaced by spray sulfuric acid pickling as the final cleaning operation before phosphating for a paint base. Pickling was followed by two rinses. Between pickling and phosphating, a 100% hydrostatic test was required for assurance that the pickling solution had not opened any pinholes through the soldered tail plugs of the shell cases. With sulfuric acid pickling, chromic acid was added to the second rinse as a rust inhibitor to protect parts during test and transfer. The phosphate coatings obtained after this changeover were of poor quality because little or no coating was deposited on the outsides of the shell cases, and inside surfaces rusted badly. All materials and processes were checked and found to be in order. Sample panels that were processed, but not pickled, accepted a satisfactory coating. The problem was traced to a passive film on the shell surfaces, left there by the chromic acid in the final rinse after pickling. Replacing the chromic acid rinse with an alkaline sodium nitrite rinse solved the problem.

In another plant, manganese phosphate coatings had been successfully applied to a variety of machined steel parts. One of these parts, produced in high volume, was a valve tappet of low-alloy steel, for which a surface finish of 0.1 to 0.3 μm (4 to 10 μin.) was required. For no apparent reason, difficulty was suddenly encountered in the form of mottled, noncrystalline coatings and occasional bare spots on the tappets. Other parts were satisfactorily coated. It was discovered that a change in polishing compound had been made to facilitate obtaining the required finish on the tappets. Carrier wax in the new compound contained a larger amount of unsaturated material than was in the wax in the previous polishing compound. These unsaturates are more readily oxidized to insoluble compounds by the heat generated in polishing than are fully saturated material. Reverting to the original polishing compound corrected the difficulty.

In another instance, an alkaline cleaner at a concentration of 7.5 g/L (6.3×10^{-3} lb/gal) was used in the cleaning stage in a zinc phosphating line for processing sheet steel stampings. Stampings were coated with mill oil and drawing oil, and cleaning was satisfactorily accomplished. On certain new parts, however, because of a difficult drawing operation, a pigmented drawing compound was required that consisted of emulsified palm oil and powdered French talc. The cleaner would not remove this drawing compound sufficiently to permit acceptable coatings to be deposited. It was found that the cleaner was removing the oil but leaving the talc on the parts. Increasing the concentration of the alkali in the cleaner to 15 g/L (0.13 lb/gal) resulted in no improvement. However, when the temperature of the cleaner was lowered to 70 °C (160 °F), both oil and talc were removed, permitting satisfactory phosphate coatings. This is counter to the concept that cleaning efficiency increases with the temperature of the cleaner.

Parts that have been tempered in air or a controlled atmosphere, as the last operation before phosphating, usually require no cleaning before being phosphated. The blue oxide film imparted by the normal tempering operation is not detrimental to phosphating. However, if tempering produces a scaly or sooty surface, or if scale or soot is produced in the heat-treating furnace and is not removed before tempering, the parts must be descaled by acid pickling, tumbling, or blasting. Incorporation of crystal refiners (titanation) into the alkaline cleaner promotes the deposition of a dense, finely crystalline zinc phosphate coating. Overheating (greater than 65 °C, or 150 °F) of the activated cleaner stage inhibits the crystal refinement effect.

Rinsing after Cleaning

In the past, water at 70 to 80 °C (160 to 180 °F) ordinarily was used for rinsing parts after cleaning and before phosphating. Hot water is in effect an additional cleaner, serving to remove cleaning compounds that adhere to part surfaces. Ambient temperature rinses are now often used. Parts may be rinsed by immersion or spray. A single rinse tank or spray stage is usually adequate for rinsing simple parts, and a minimum rinse time of 30 s is normally required. An additional spray rinse stage should be added for parts with blind holes or deep recesses.

Immersion Rinsing. Rinse tanks should be equipped to provide adequate agitation of rinse water to increase rinsing efficiency. Agitation may be accomplished using compressed air at low pressure, distributed through evenly spaced holes in pipes laid along the bottom of the tank. However, where compressed air is not available, pumping rinse water through similar pipes can provide suitable agitation. Fresh water may be continuously added to the tank through such pipes to provide agitation, but a siphon-breaker must be installed in the supply line to prevent siphoning contaminated rinse water into the water supply system. The supply of makeup water should be planned to provide adequate rinsing without wasting water. Relatively pure waters, containing less than 150 ppm total solids, require less replacement water than harder or impure waters containing 400 to 600 ppm total solids.

Use of solenoid valves, controlled by conductivity meters in water supply lines to rinse tanks, can maintain adequate rinse water purity at minimum waste. Another effective method of improving rinse water quality is to supply makeup water through spray nozzles. This process causes the fresh water to be the last water to hit the parts as they are being withdrawn from a dip rinse or carried from a spray rinse station. Rinse water makeup added to a water rinse tank other than by the methods discussed above should be supplied. to the end of the tank opposite the overflow trough. Water containing appreciable quantities of chlorides, fluorides, or sulfides may not provide good rinsing. The length of time parts are allowed to remain in the rinse tank depends on their complexity and on the material to be rinsed away.

Spray Rinsing. Vertical and horizontal spacing and size of the nozzles in a spray rinse tunnel are determined by the size and nature of parts being processed and the speed of the conveyor carrying parts through the tunnel. A pressure of 70 to 140 kPa (10 to 20 psi) at the nozzle is normally adequate. Minimum pump volume capacity is determined by multiplying the volume capacity of the nozzle at the desired pressure by the number of nozzles required and adding an allowance for losses required and adding an allowance for losses because of piping length and restrictions. A spray rinse tank should hold a minimum volume of $2\frac{1}{2}$ times the volume of solution piped through the nozzles per minute.

Rinse solutions should be piped from the pump or pumps through large main headers to vertical drop lines containing the nozzles. To assist in scale removal, drop lines should be fitted on the bottom with removable caps. Pressure that is too high may be relieved by drilling suitable holes in the center of bottom caps. This also enables excess rinse solution to flush out scale and sludge continuously. A hot water spray rinse station is shown schematically in Fig. 1. The rinse before phosphating should be maintained slightly alkaline (7.5 to 9.0 pH) to prevent rust-blushing of parts. A rinse containing crystal refiners is recommended just before the phosphate stage.

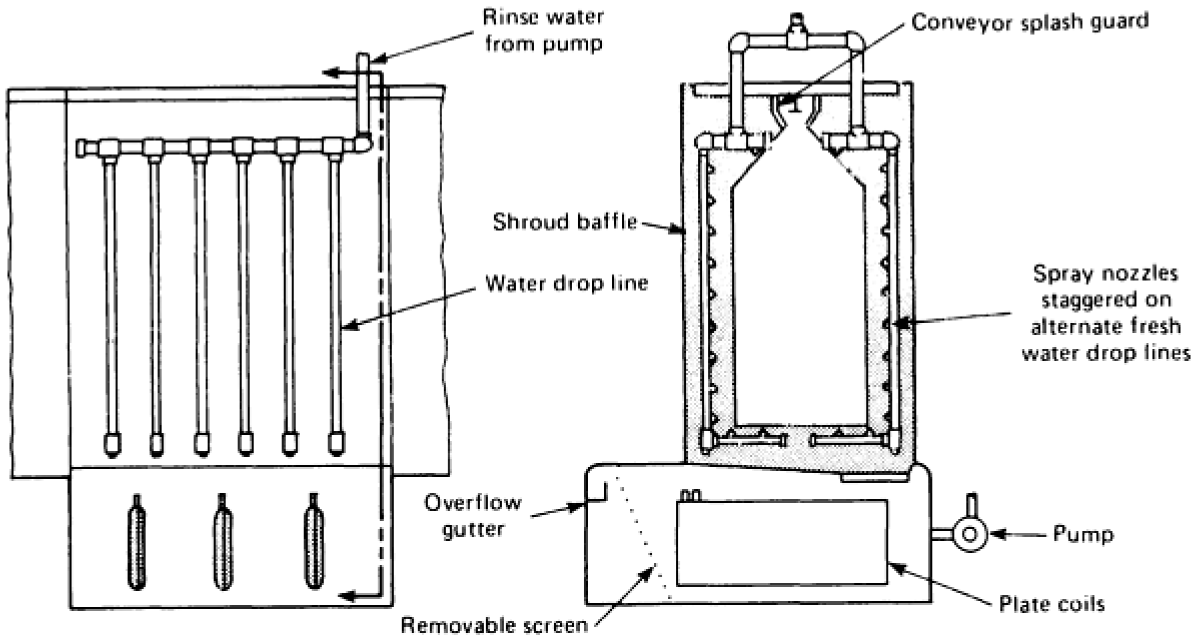


Fig. 1 Schematic of a hot water rinse station in a spray phosphating line

Phosphating Methods

Phosphate coatings may be applied to a surface by either immersion or spray, or a combination of immersion and spray. There has been a modern trend worldwide to the immersion treatment of automobile bodies using zinc-phosphate coating processes. This is usually a combination of spray and immersion. The work is sprayed as it enters the phosphate tank as well as when it exits. Occasionally, a surface may be coated by brushing or wiping, but these methods are seldom used.

Immersion. All three types of phosphate coatings, zinc, iron, and manganese, can be deposited by immersion. Immersion is applicable to racked parts, barrel coating of small parts, and continuous coating of strip. In general, smaller parts are more economically coated by immersion than by spraying. Small parts, such as springs, clips, washers, and screws that are produced in large volume, can be coated efficiently only in an immersion system. Such parts are loaded into drums that are rotated at approximately 4 rev/min after they are immersed in the phosphating solution. Small parts may be placed in a basket and immersed, without rotation, in the bath for coating. This method generally is not completely satisfactory, because no phosphate is deposited where parts contact each other or the basket. It is used as a stopgap method or when volume is too low to justify the use of rotating drums.

Low-volume larger parts are immersed manually in a tank. Certain large parts produced in large volume, but whose shape does not encourage complete coverage by spray phosphating, may be coated by immersion. Intricately shaped parts, such as hydraulic valves or pump bodies that have areas inaccessible to spray, are immersion coated. Either immersion or the spray method may be used to deposit heavy zinc phosphate coatings used as aids in cold extruding or drawing. However, the immersion system usually provides a heavier coating. Shell casings formed by cold extrusion are first coated by the immersion system to produce the heavy coating required for the cold extrusion of the metal. After finish machining, the shell casing can be either spray or immersion coated for a paint base. The immersion system usually is preferred, because of the necessity of coating internal areas.

Although a manually operated immersion system requires very little floor space, a conveyorized immersion system requires more floor space than a conveyorized spray system for comparable production quantities. When parts are of comparable size, the immersion system cannot equal the production output of a spray system. An advantage of an immersion system is that the heat required is much less than for a spray system because of the heat lost from the sprays. The use of an immersion system for automotive bodies provides phosphate coverage in areas not accessible by spraying, namely, box sections. In the immersion process, agitation of the solution accelerates coating formation.

Spray. Zinc and iron phosphate coatings are applied by the spray method, although manganese phosphate is not. The spray method is used to apply a phosphate coating to racked parts, such as panels for household appliances, or to a

continuous strip. Occasionally, baskets of parts are passed through a spray system, but this is not a preferred method. Spray phosphating, because of the equipment required, is usually most applicable to high-volume coating of parts.

It is easier to control the coating solution for iron phosphating in a spray system, and the resulting coating is generally of better quality than the coating obtained from an immersion system. Zinc phosphate coatings produced by a spray system are usually lighter in weight than those produced by immersion. In addition, different zinc phosphate crystalline structures may result from spraying than those that result from immersion.

Phosphating Time. In general, the spray method produces a given coating weight at a faster rate than the immersion method. In spray zinc phosphating, a coating of 1.6 to 2.1 g/m^2 (0.52 to 0.68 oz/ft^2) normally can be obtained in 1 min or less, whereas obtaining a coating of this weight by the immersion method may require as much as 2 to 5 min. For galvanized steel treated in coil lines, zinc phosphate coatings are produced in times as short as 3 to 5 s; for iron phosphate coatings on cold rolled steel, 5 to 10 s. A 1 min spray application of one iron phosphating solution would result in a coating of approximately 0.3 to 0.4 g/m^2 (9.7×10^{-2} to 0.13 oz/ft^2). It is estimated that it would require 2 to 3 min to produce the same coating weight by immersion. Bath parameters are all interrelated, however. In some operations, coatings can be effectively deposited in 3 to 5 s.

The weight of manganese phosphate coatings on steel surfaces is a function of immersion time, as indicated by the curve in Fig. 2. The slope of this curve can vary. The time required to obtain a specific coating weight in a range of 5.4 to 32.3 g/m^2 (1.8×10^{-2} to 0.106 oz/ft^2) can vary from 2 to 40 min, depending on such factors as the type and hardness of the steel being coated and methods of precleaning and pretreatment. Exposure to the phosphating solution for a shorter time than recommended usually results in a coating that is incomplete, too thin, or both.

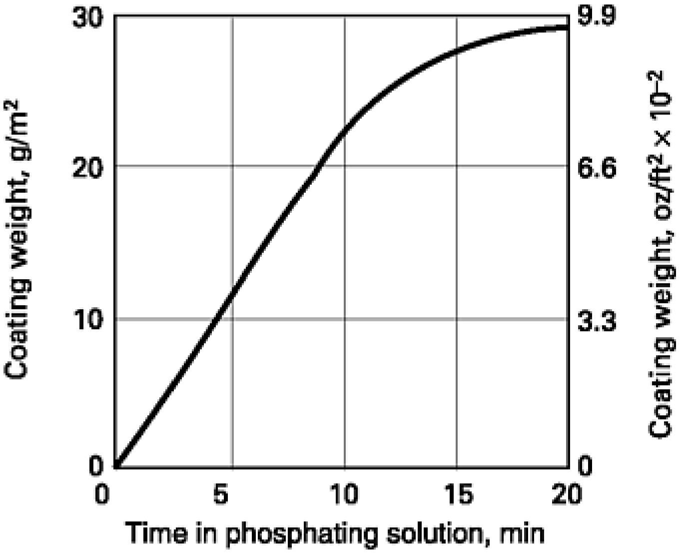


Fig. 2 Plot of manganese phosphate coating weight vs. time of exposure of steel surface to phosphating solution

Operating Temperature. Although operating temperatures of different phosphating solutions may range from 30 to 100 °C, or 90 to 210 °F (Table 6), individual solutions are compounded to operate at maximum efficiency within specific temperature limits. The trend in recent years has been to lower operating temperatures. A phosphating solution should be held within the specified operating temperature range. If the solution is permitted to operate below the minimum recommended temperature, the phosphate coating is thin or nonexistent. If the temperature of the solution exceeds the recommended maximum, the coating builds up excessively and has a nonadherent, powdery surface, and the bath solution may become unbalanced, resulting in excessive sludge and scale. Special low-temperature solutions are available for applying iron or zinc phosphate (see the section "Low-Temperature Coatings" in this article).

Table 6 Operating temperature ranges for phosphating solutions in phosphating applications

Phosphate coating method	Metal treated	Reason for treatment	Operating temperature	
			°C	°F
Medium iron, immersion	Steel	Paint bonding	60-82	140-180
Heavy zinc, immersion	Steel	Corrosion resistance	88-96	190-205
Medium zinc, immersion	Steel	Paint bonding	32-82	90-180
Medium zinc, immersion	Steel plated with zinc or cadmium	Paint bonding	60-82	140-180
Medium zinc, spray	Sheet steel	Paint bonding	38-60	100-140
Medium zinc, spray	Steel	Cold drawing	60-74	140-165
Medium zinc, spray	Galvanized steel	Paint bonding	49-60	120-140
Manganese, immersion	Steel	Wear resistance	93-99	200-210

Solution temperature influenced the results obtained in manganese phosphating small cast iron parts. Coatings deposited at the beginning of each day were thin and red-tinged. However, after the tank had been in operation for about $1\frac{1}{2}$ h, conventional coatings (heavy and dark gray) were obtained, and no further trouble was experienced for the rest of the day. Bath analysis revealed that the phosphating solution had an unusually high concentration of free acid at the start of each day's operation, but the concentration was normal at shutdown time. A review of past records indicated that this condition had not previously existed. Investigation revealed that the condition resulted from improper and excessive preheating of the bath before parts were processed. Only the steam bypass was being turned on, thus circumventing automatic temperature controls, which caused the solution to boil, upsetting composition and thereby affecting coating characteristics. A return to correct preheating procedures ended the problem.

Rinsing after Phosphating

Parts must be rinsed after being phosphated to remove active chemicals from the phosphating solution that remains on the surface of coated parts. Any chemicals not removed may cause corrosion of parts or blistering of a subsequent paint film. Any phosphating chemicals carried over into the chromic acid rinse may contaminate the solution used as a rinse. Rinsing after phosphating never should be hot. The temperature should range from 20 to 50 °C (70 to 120 °F), preferably maintained on the low side. A rinse that is too warm may set the residual chemicals and cause them to adhere to phosphate crystals, resulting in a rough coating, whitish appearance of coating, and lower corrosion resistance. Usually, only one rinse is required. If the water supply is so high in mineral content that a residue remains on the parts after rinsing, a rinse in deionized water may be required.

Chromic Acid Rinsing

Most phosphated parts that are used as a base for paint are given a treatment following the post-phosphating rinse. These post-treatments vary from simple chromic-acid solutions to complex proprietary formulas that may be free of chromium entirely. Because of difficulty experienced when these post-treatments are allowed to dry on a phosphated part, because of concentrations of the post-treatment at the lower edges and around openings such as holes or slots, the excess post-treatment should be removed with a deionized water rinse. Better proprietary post-treatments allow removal of the excess

with deionized water without substantially decreasing the corrosion resistance of the painted system, while retaining good humidity and physical test results associated with conventional post-treatment. Environmental and health concerns have resulted in increasing interest in and the development of improved chromium-free post-treatments for paint-based applications. In the case of heavy zinc-phosphate coating used with oil for corrosion resistance, chromic acid post-treatment may or may not be used, depending on the quality and nature of the rust-preventing oil applied thereafter.

Zinc or manganese phosphate coatings applied to reduce friction usually do not receive a chromic acid rinse, because they are not applied for corrosion resistance. Rather, oil films are normally applied after phosphating to increase antifriction properties of coatings. On parts phosphated to assist in cold extrusion or drawing, application of drawing lubricants usually supplants the chromic acid rinse.

Reference cited in this section

1. D. Phillips, Practical Application of the Principles Governing the Iron Phosphate Process, *Plat. Surf. Finish.*, March 1990, p 31-35

Chemical Control of Phosphating Processes

An efficiently operated phosphating line includes close chemical control of all materials used. Even the mineral content of plain water rinses may need to be controlled to avoid leaving a residue on parts. To obtain satisfactory phosphate coatings on steel surfaces, phosphating solutions must be chemically controlled within limits. These limits vary, depending on the specific phosphating concentrate used. Solutions should be tested on a regular schedule. Frequency of tests is determined by the work load of the phosphating line.

Zinc Phosphating Solutions. When zinc phosphating solutions become unbalanced, the results are poor coatings, excessive sludge buildup, and insufficient coating weights. Several chemical tests are usually made on a zinc phosphating solution used for paint-based application, to determine its suitability for coating. These are tests of:

- Total acid value
- Accelerator content
- Free acid
- In the case of heavy zinc phosphate coatings for use with oil, the iron concentration (ferrous iron)
- Zinc concentration

Total Acid Value. Zinc phosphate solutions have a total acid value established that should be maintained for good performance. One regularly used solution is controlled at 25 to 27 points. To determine the total acid value, a 10 mL (3×10^{-3} gal) sample of the solution is titrated with 0.1 *N* sodium hydroxide (NaOH) (1 mL equals 1 point), 1 using phenolphthalein as an indicator. The end point is reached when the solution changes from colorless to pink.

Free-Acid Value. Zinc phosphate solutions have a free-acid value established that should be maintained for satisfactory performance. To determine the free-acid value, a 10 mL (3×10^{-3} gal) sample of solution is titrated with 0.1 *N* NaOH, using bromphenol blue or methyl orange indicator. The end point is reached when the solution changes from yellow to greenish-blue, for the former.

Accelerator Test. Sodium nitrite is used as an accelerator in some zinc phosphate solutions. It is usually controlled at 30 points. Before the test for sodium nitrite is made, phosphate solution should be tested for absence of iron. This is done by dipping a strip of iron-test paper in phosphate solution. If the paper does not change color, no iron is present in the solution. If the paper changes to pink, however, iron is present, and small additions of sodium nitrite are then made until an iron-test paper shows no change. The sodium nitrite test is made using a 25 mL (6.6×10^{-3} gal) sample of the phosphate solution. From 10 to 20 drops of 50% H_2SO_4 are added carefully to the solution and it is then titrated with 0.042 *N* potassium permanganate. The end point is reached when the solution turns from colorless to pink (1 mL equals 1 point).

The sodium nitrite test may also be performed using a gas evolution apparatus. After the apparatus is filled with the bath solution, sulfamic acid 4 g (0.14 oz) is added to the solution. Evolution of gas into the calibrated section of the apparatus provides the direct reading (in milliliters) of sodium nitrite in the bath. The milliliter of gas is equivalent to the milliliter reading obtained with the potassium permanganate ($KMnO_4$) titration procedure.

Iron Concentration. Because iron is constantly being dissolved from parts being zinc phosphated, the concentration of iron may build up until the efficiency of the solution is impaired. Some zinc phosphating solutions operate best when the iron concentration is maintained between 3 and 4 points. Production experience with a particular solution will indicate whether the iron content can be expanded without affecting the quality of the coating. To determine the iron content, a 10 mL (3×10^{-3} gal) sample of solution is first acidified with a sufficient amount of a 50% mixture of sulfuric and phosphoric acid to ensure a low pH while titrating (2 or 3 drops may be sufficient). The solution is then titrated with 0.2 *N* $KMnO_4$ until a permanent pink color is obtained (1 mL equals 1 point).

This titration is used for immersion zinc phosphating solution. Spray zinc phosphating usually does not involve a buildup of iron in the solution because of the oxidizers that are present. Immersion zinc phosphate solutions generate, in situ, sufficient nitrite to prevent iron buildup. Phosphate coatings formed with iron in the bath usually do not prevent galling during cold-heading processing as well as phosphate baths operated without iron in the bath (Toner side). Immersion zinc phosphating baths are usually controlled by a total and free-acid titration and acid ratio, total acid divided by free-acid values.

Iron Phosphating Solutions. If recommended chemical limits are not maintained in iron phosphating solutions, the results are low coating weights, powdery coatings, or incomplete coatings. To maintain required balance in iron phosphating solutions, titration checks are made to determine the total acid value and the acid-consumed value.

Total acid value is determined by titration of a 10 mL (3×10^{-3} gal) sample of phosphating solution with 0.1 *N* NaOH, using phenolphthalein as an indicator. The end point is reached when the solution changes from colorless to pink. The number of milliliters of the 0.1 *N* NaOH is the total acid value, in points, of the phosphating solution. A normal concentration would be 10.0 points.

Acid-consumed value is determined by titration of a 10 mL (3×10^{-3} gal) sample of phosphating solution with 0.1 *N* HCl, using bromocresol green indicator. The end point is reached when the solution changes from blue to green. A normal range for the acid-consumed value for a solution with a 10-point total acid value would be from 0.0 to 0.9 mL (0 to 2×10^{-4} gal) of 0.1 *N* HCl.

Manganese phosphating solutions used to produce wear-resistant and corrosion-protective coatings are maintained in balance by control of:

- Total acid value
- Free-acid value
- Acid ratio
- Iron concentration

Because the phosphate solutions are acid, these values are determined by titration methods using a standard basic solution. Frequency of control checks on manganese phosphating solutions depends on the amount of work being processed through the tank and on the volume of the solution. However, one to two checks per shift should be sufficient.

Total acid value is determined by titration of a 2 mL (5×10^{-4} gal) sample of phosphating solution with 0.1 *N* NaOH, using phenolphthalein as an indicator. The end point is reached when the solution changes from colorless to pink.

Free-acid value is determined by titration of a 2 mL (5×10^{-4} gal) sample of phosphating solution with 0.1 *N* NaOH, using bromophenol blue indicator. The end point is reached when the solution changes from yellow to blue/violet.

Acid Ratio. To obtain satisfactory coatings, the ratio of total acid to free acid contents of manganese phosphating solutions should be maintained within certain limits. For a solution with a 60- to 70-point total acid value, this ratio should be between 5.5 to 1 and 6.5 to 1. Low-ratio solutions produce incomplete coatings, poorly adherent coatings, or coatings with a reddish cast. High-ratio solutions also result in poor coatings.

Iron Concentration. Because iron is continually dissolved from parts going into the phosphating bath, the concentration of ferrous iron in the bath gradually builds up. Some manganese phosphate coating problems that can be traced to high iron concentrations are: light gray instead of dark gray to black coatings; powdery coatings; and incomplete coatings in a conventional time cycle.

Concentration limits of iron depend on the type, hardness, and surface condition of the steel being treated. A manganese phosphating bath operates satisfactorily with an iron concentration ranging from 0.2 to 0.4%. Production experience indicates whether iron concentration limits can be expanded without affecting the quality of the coating. To determine iron concentration, a 10 mL (3×10^{-3} gal) sample of phosphating solution is used. To this sample 1 mL (3×10^{-4} gal) of 50% H_2SO_4 is added. The solution is then titrated with 0.18 *N* $KMnO_4$. The end point is reached when the solution changes from colorless to pink. One milliliter of the 0.18 *N* $KMnO_4$ is equivalent to 0.1% Fe.

Iron Removal. If iron removal becomes necessary, the ferrous iron in the solution is oxidized with hydrogen peroxide, which causes iron to precipitate as ferric phosphate and also liberates free acid in the bath. Because free acid in the bath increases, lowering the acid ratio, the liberated free acid should be neutralized by adding manganese carbonate. The approximate amount of hydrogen peroxide needed to lower the concentration of iron by 0.1% is 125 mL/100 L (0.16 fl oz/gal) of solution. In this instance, about 450 g (1 lb) of manganese carbonate is needed to neutralize the liberated free acid. Iron removal may be unnecessary if the square footage of steel being processed and the volume of the phosphate bath limit the amount of iron buildup.

Chromic Acid or Other Post-Treatment Solutions. Control of chromic acid or other post-treatment solutions varies considerably because of the wide variety of chemicals and uses. The following procedures are often used with conventional nonreactive chromic-acid post-treatments.

Total acid value is determined by titrating a 25 mL (6.6×10^{-3} gal) sample of chromic acid solution with 0.1 *N* NaOH, using phenolphthalein indicator. The end point is reached when the solution changes from amber to a reddish shade that lasts at least 15 s. Each milliliter of 0.1 *N* NaOH required equals 1 point total acid.

Free-acid value is determined by titrating a 25 mL (6.6×10^{-3} gal) sample of chromic acid solution with 0.1 *N* NaOH, using bromocresol green indicator. The end point is reached when the solution changes from yellow to green. Each milliliter of 0.1 *N* NaOH required equals 1 point free acid. The concentration of free acid in chromic acid solutions is usually maintained between 0.2 to 0.8 mL (5×10^{-5} to 2×10^{-4} gal).

Chromate concentration may be determined by placing a 25 mL (6.6×10^{-3} gal) sample of solution into a 250 mL (6.6×10^{-2} gal) beaker, adding 25 mL (6.6×10^{-3} gal) of a 50% H_2SO_4 solution, 2 drops of orthophenan-throline ferrous complex indicator, and titrating with a 0.1 *N* $FeSO_4$ solution. Each milliliter of 0.1 *N* $FeSO_4$ solution of the amount required to change the solution from blue to reddish-brown is 1 point of chromate concentration. Chromate concentration ranges from 200 to 400 ppm (as chromium) and may also be determined with a test kit containing diphenylcarbazide.

In reactive chromate post-treatments, those that can be post-rinsed with deionized water, pH is often used as a means of determining whether the post-treatment solution is in proper balance.

Each supplier has its own particular means of checking the concentration in chromium-free post-treatments and, in some instances, the acidity of the solution.

Solution Maintenance Schedules

The frequency and extent of solution maintenance is dictated by the materials used and the work load of the line. In one plant, a schedule was established for solution testing, solution maintenance, and tank cleaning. The company revised solution-control procedures to correct problems experienced with zinc phosphate coatings produced in a large automatic line. Coatings periodically were coarse and nonuniform, making it necessary to interrupt production to change phosphating solution. A comprehensive program of testing and checking was inaugurated. Routines for solution maintenance and tank cleaning were established that eliminated defective coatings and downtime for changing phosphating solutions. It was determined that the phosphating bath maintained good coating ability for 9 to 10 weeks. However, tanks required cleaning every 4 to 5 weeks because of sludge buildup. The schedule established includes tank cleaning every 4 weeks and solution change every 8 weeks, coinciding with tank cleaning. Work is done on weekends so that production is not interrupted. The solution is allowed to cool and sit idle for 8 h.

For tank cleaning only, the entire contents of the tank are pumped to a reserve tank, the sludge is removed, and the solution is returned to the phosphating tank. When the solution requires changing, the procedure is as follows: top half of solution is pumped to a reserve tank; bottom half is discarded; and sludge is cleaned from the tank. Salvaged solution is then pumped back into the tank, and sufficient water and phosphating concentrate are added to bring the bath to correct concentration and operating level. Iron, in the form of steel wool, and soda ash are added to the solution to adjust it to proper operating condition, so satisfactory coatings can be produced when production is resumed.

Schedules for operating control and tank and solution maintenance were established by another company for a multistage phosphating process in which automobile bodies were phosphated. The surface area of the bodies approximated 70 to 80 m^2 (750 to 860 ft^2). The production rate could range as high as 75 car bodies an hour. The spray chamber of the phosphating line, including drain area, was 12 m (39 ft) in length. The phosphating solution tank, at operating level, holds 4.2×10^4 L (1.1×10^4 gal). A continuous desludging system is incorporated in the system (hydromation unit). Phosphating and accelerator solutions are replenished continuously and automatically via pH and redox measurements through variable-feed metering pumps. Corrective additions of caustic soda are made manually. Coating weights are maintained at 2.7 to 3.2 g/m^2 (8.8×10^{-3} to 1.0×10^{-2} oz/ft^2).

Operating Control

Table 7 gives a typical schedule of parameters that must be monitored on a daily basis to produce a quality phosphate coating.

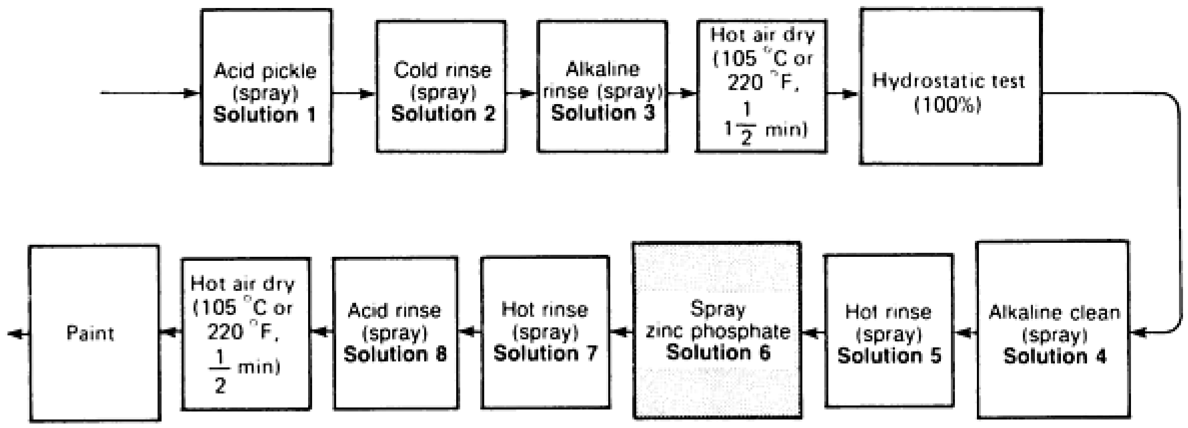
Table 7 Monitoring requirements for quality control of phosphate coating production

Hourly
Phosphating solution titrations Total acid Free acid Visual coating appearance Chemical-supply pumps
All stages Temperature Pressure Solution level
Neutralizing rinse Add 30 mL (0.08 gal) activator, as indicated by visual check of coating continuity Check pH
Check film thickness of soap lubricant
Twice per shift
Alkaline cleaner stage titrations Alkalinity of water rinses before phosphating Acidity of water rinse after phosphating Activating rinse concentration
Once per shift
Conductivity of recirculated deionized rinse, 100 μmho maximum

Tank and Solution Maintenance

The following maintenance schedule should be observed to ensure efficient phosphating operations for the setup described in the flowchart in Fig. 3.

- *Daily*: empty and clean stages corresponding to solutions 4 and 6.
- *Weekly*: empty and clean stages corresponding to solutions 7 and 8.
- *Twice monthly*: empty and clean stages corresponding to solutions 1 and 2.
- *Monthly*: empty and clean stage corresponding to solution 3.
- *Quarterly*: cleaner, water rinse, and phosphate stages should receive heated acidic cleanout. Blocked nozzles should be removed and cleaned or replaced. Heated acidic cleanout may involve inhibited hydrochloric acid.



Solution No.	Type	Composition	Operating temperature		Cycle time, min
			°C	°F	
1	Acid pickle	H_2SO_4, 25 wt%	71	160	2
2	Cold rinse	Water[(a)]	RT	RT	$1\frac{1}{4}$
3	Alkaline rinse	$NaNO_2$, 2.4 g/L (2.0×10^{-2} lb/gal)[(b)]	66	150	$1\frac{1}{4}$
4	Alkaline cleaner	Alkali, 0.7 g/L (5.8×10^{-3} lb/gal)	71	160	$\frac{1}{2}$
5	Hot rinse	Water	66	150	$\frac{1}{2}$
6	Zinc phosphate	NO_2, accelerated[(c)]	60	140	$1\frac{1}{2}$
7	Hot rinse	Water[(a)]	60	140	$\frac{1}{2}$
8	Acid rinse	Chromic and phosphoric acids[(d)]	71	160	$\frac{1}{2}$

(a) Purity maintained by overflow.

(b) Sodium hydroxide added to establish pH of 11.

(c) Total acid, 10 points; free acid, 0.7 to 1.1 points; acid checked using 10 mL (2.6×10^{-3} gal) sample. NO_2 accelerator, 1.5 to 2.0 points, determined using 25 mL (6.6×10^{-3} gal) sample.

(d) Free acid, 0.4 to 0.6 points; total acid, less than 5 points; checked using 25 mL (6.6×10^{-3} gal) sample

Fig. 3 Sequence of operations for spray zinc phosphating of 80 mm (3.2 in.) mortar shell casings before painting. Total area, inside and outside, of each shell was 0.1 m^2 (1 ft^2); coating weight ranged from 1.7 to 2.1 g/m^2 (5.6×10^{-3} to 6.9×10^{-3} oz/ft^2).

Phosphating Tank Maintenance. The phosphate tank should be desludged on a continuous, automatic basis. Depending on work appearance, nozzles and spray pressure at the nozzle may require checking on a monthly basis, rather than quarterly. Phosphate heat exchangers require a heated acidic cleanout to maintain heating efficiency. Acidic cleanout usually involves the following procedure:

1. Pump out solution to holding tank.
2. Flush tank and spray piping with water.
3. Fill to pumping level with water; add hydrochloric acid (1 *N* or 10% volume acid/volume water, V_a/V_w); add inhibitor.
4. Heat to 50 °C (120 °F); circulate spray system for 1 h.
5. Empty tank and flush with water.
6. Fill to pump level; add sodium hydroxide to pH of 10 to 12; circulate 5 to 10 min.
7. Empty tank; flush with water; and restore phosphate solution.

Break-in of Phosphating Solutions. Some zinc and manganese phosphating solutions, although mixed to recommended concentrations, must be broken in by the addition of ferrous salt, such as ferrous sulfate, before they can operate properly. Iron phosphating solutions require no break-in. After being mixed to proper concentration, iron phosphating solutions need only be raised to operating temperature to be ready for use. Most zinc phosphate processes used for paint base or for metal forming operate free of ferrous iron, and the break-in of these phosphating solutions is not a factor.

Zinc Phosphating Solutions. One method of breaking in a zinc phosphating solution is to tolerate a poor phosphate coating until some iron has gone into solution from the chemical reaction between the bath and the parts being coated. Some iron also may be present in sludge that has settled to the bottom of the tank or crusted on the sides from a previous bath. The coatings on first parts are of poorest quality; the coating quality gets progressively better as more iron goes into solution. A simple method is to suspend clean steel wool or scrap in the bath, or to introduce a small quantity of clean iron powder. Another method is to add 170 g (6 oz) of salt, such as ferrous sulfate, to each 380 L (100 gal) of solution. This is applicable to bath spray and immersion baths.

Manganese Phosphating Solutions. Careful attention should be given to breaking in a manganese phosphating bath because of its higher acid concentration in comparison to that of a zinc bath. For the best quality of manganese phosphate coatings, 0.2 to 0.4% Fe^{+2} in solution is the proper range. Usually, breaking in of a new bath is begun by the addition of 170 g (6 oz) of a ferrous salt, such as ferrous sulfate, powder to each 380 L (100 gal) of bath. This is followed by treatments using clean steel wool, powdered iron, or scrap iron to build up ferrous iron content. Manganese phosphating baths operate to best advantage when they have a steady, heavy work load. This permits considerable dissolution of iron, which usually maintains the ferrous iron content at a suitable level.

Equipment for Immersion Systems

An immersion phosphating system for all types of coatings (zinc, manganese, and iron) should include:

- Required number of tanks
- Temperature and solution-level controls
- Overflow and drainage systems
- Vapor-exhaust systems
- Material-handling devices

When drums are used to contain the parts, devices are required at each tank to rotate the drums at approximately 4 rev/min while the drums and the parts within are submerged.

Phosphating tanks are usually made from low-carbon steel plate about 6 mm ($\frac{1}{4}$ in.) thick. A tank and drum for immersion phosphating small parts are shown in Fig. 4. The normal life of a low-carbon steel tank for zinc phosphating solution under average operating conditions is about 1 year. However, some companies report 2 to 3 years of service. One company fabricates zinc phosphating tanks from 9.5 mm ($\frac{3}{8}$ in.) low-carbon steel plate. This tank lasts 4 to 5 years. Stainless steel may give longer life, but its greater cost generally is not justified for a zinc or iron phosphating line, unless acidic solutions contain high levels of chloride. Because of greater acid concentration in manganese phosphating solutions (6 to 10% V_a/V_w as compared with 1 to 3% V_a/V_w in zinc phosphating solutions) and higher operating temperatures used, low-carbon steel tanks for manganese phosphating solutions have a shorter life than those used with zinc or iron phosphating solutions. For this reason, stainless steel tanks may be economically practical for manganese phosphating solutions. Stainless steel should also be considered for the heating coils. Plastic, fiberglass, and rubber-lined tanks have also been used successfully.

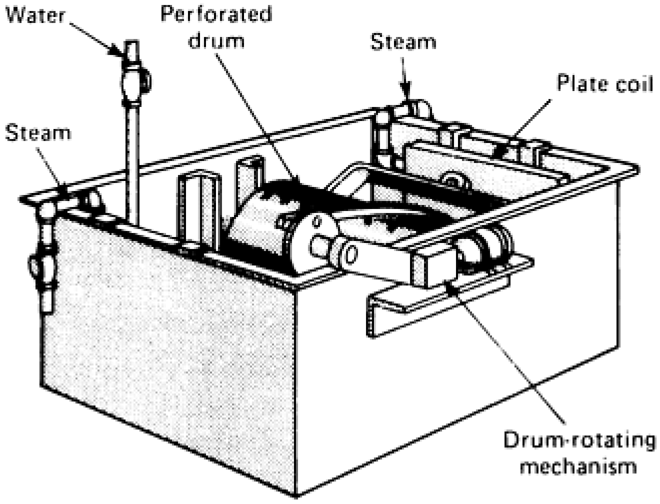


Fig. 4 Immersion phosphating tank for batch coating of small components. Drum into which parts are loaded is shown in immersion position.

Table 8, representing data from the experience of one company, shows a comparison of expected tank life, in years, for the three types of phosphating solutions using both low-carbon steel and type 316 stainless steel. These figures are approximately correct for all solutions. Some solutions permit extended tank life, and others shorten the tank life. One tank made of 6 mm ($\frac{1}{4}$ in.) mild steel has been in continuous operation for 15 years in an iron phosphating line.

Table 8 Expected service life of low-carbon steel vs. type 316 stainless steel phosphating tanks

Process	**Service life, yr**	
	Low-carbon steel	**Type 316 stainless steel**[(a)]
Iron phosphating	10[(b)]	20
Zinc phosphating	4-5[(c)]	10-20

(a) Any thickness that provides mechanical strength required. May be used as liner for low-carbon steel tank.

(b) 6.4 mm ($\frac{1}{4}$ in.) thick.

(c) 9.5 mm ($\frac{3}{8}$ in.) thick

Many phosphating tanks made of low-carbon steel are lined with glass fiber impregnated with polyester resins. Phosphating compounds have no effect on this material, and it will last indefinitely in normal service. It is, however, susceptible to damage from impact, and careless handling of equipment during loading or unloading of the tanks may cause fractures or cracks. Care must be exercised in the placement of heating coils when using polyester-impregnated glass fiber liners. The maximum temperature this material can withstand is about 105 °C (225 °F). Many polyester resins have little resistance to alkaline materials and should not be used where more than casual contact with strong alkaline cleaners is possible.

Tank accessories, including steam coils or other heating mediums, piping, screens, drum trunnions, and drum-rotating mechanisms, may be made of low-carbon steel or stainless steel. Electropolished stainless steel steam coils permit less sludge buildup on the coils.

Tank Design. Tanks should have sufficient capacity to stabilize solution temperature and solution concentration and to prevent rapid buildup of solution contamination. Tanks for the phosphating stage should have a sloping bottom, with at least 0.46 m (1.5 ft) of space below the lowest work level to accommodate sludge buildup.

Rinse Tanks. Water rinse tanks and associated equipment, including steam coils or other heating mediums, piping, and screens, may be constructed of low-carbon steel. Rinse tanks for certain parts sometimes require drum-rotating devices. Immersion rinse tanks should include a method for solution agitation to assist rinsing action. This can be accomplished by use of low-pressure air distributed through evenly spaced holes in pipes laid along the bottom of the tanks. Another method is to recirculate rinse water through a similar piping arrangement. For a clear water rinse, the pump housing, bearings, impeller, and any other part in contact with the water may be of normal material. Acidulated rinses containing chromium preclude the use of brass or bronze in any part of the pump or valving that is in contact with the solution.

Drying equipment for immersion phosphating systems can be of several types. For small parts, such as washers, a centrifuge may be used to spin off moisture. If parts are hot enough, no additional heated air is required. However, if parts are cold, heated air may be introduced into the centrifuge. When parts are centrifuged, the phosphate coating may be damaged on some parts, rendering them unacceptable. Such parts may be dried in a basket or on a rack, in the same manner that larger parts are dried. This is done in a final tank or enclosure in which the parts are held while heated air (at

120 to 175 °C, or 250 to 350 °F) is blown on them. Heat sources may be steam coils, gas burners, or electric heaters. Drying time usually ranges from 2 min for simple parts to 5 min for complex parts. If rinse solutions are retained in pockets or seams, drying requires additional time or temperature, a mechanical aid such as an air blast directed at the pocket or seam, or tilting of the part.

Drums for containing and rotating parts are usually made of low-carbon steel. To obtain longer life, stainless steels may be used; however, one company reports a life expectancy of approximately 10 years from similar drums made from low-carbon steel. This long life is attributed to a hard coating of phosphate that develops on surfaces of the drum. Drums should have a loading-and-unloading door with a positive latch to prevent accidental opening and loss of load during a processing cycle. A drum for containing small parts during batch phosphating is shown in Fig. 5.

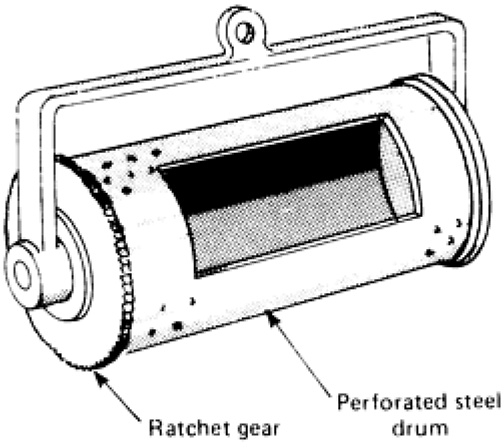


Fig. 5 Drum used in batch phosphate coating of small components

Baskets for handling parts too large for drums or too small or too heavy for racks can be made of either low-carbon or stainless steel. The choice is dictated by cost-life relationships.

Conveying equipment for the immersion process may be of any type that can transport work from the loading to the unloading stage. It must be capable of lowering work into and raising it out of various tanks in the proper sequence and at the proper time, either automatically or manually. Various types of conveying equipment are:

- *Overhead monorail conveyors* with manual or electric hoists. For very small production, the work can be moved manually from tank to tank.
- *Chain-driven conveyors* that lower and raise work into and out of each tank while it is continuously moving
- *Automatic equipment*, similar to automatic plating equipment but without equipment necessary for supplying electric current

Conveying equipment can be of varied design, but it must allow sufficient time for solution to drain from the work as it is raised from the tank. This solution should drain back to the original tank so it will not contaminate the next tank. Drainage and transfer time should not exceed 30 s, or the work may become discolored because of partial or complete drying between stages. The conveyor need not be made of acid-resistant material.

Work-supporting equipment, such as racks, hooks, and baskets, is similar in design and function to that used in electroplating, with the exception that it need not be electrically insulated. For phosphating, however, racks, hooks, and baskets should be resistant to alkaline cleaners, acid phosphating solutions, and other materials used in a phosphating line. Low-carbon steel is usually satisfactory. Stainless steel may be used where its additional life justifies the greater cost. Work-supporting equipment does not need to have tight contact with the work to be phosphated. Light contact with work-supporting equipment is more desirable, particularly on significant surfaces of the work, because coating may be thin or nonexistent at the point of contact, depending on the degree of insulation of the surface by hook, rack, or basket.

Equipment for Spray Systems

Spray systems usually are completely enclosed in a continuous, chambered tunnel or cabinet for better control of the process and cleanliness of the operation. Parts or panels to be processed are hung on racks or hooks, or placed in baskets, and are automatically carried through the various stages of the spray phosphating line (Fig. 6). Temperature and pressure gages and controls are required at all stations, as are pumps of adequate capacity. Time and space intervals between stages, and between the final rinse and the drying oven, must provide sufficient drain time to minimize carryover of solutions to succeeding stages. However, the time must also be as short as possible, because dried-on solutions cause blotchy coatings and can reduce final corrosion resistance or adhesion.

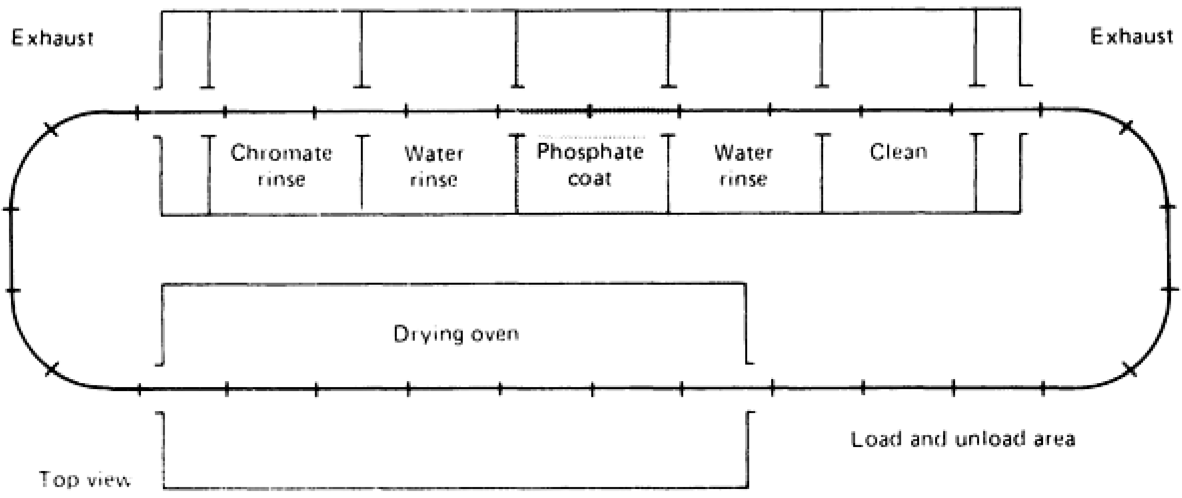


Fig. 6 Typical plant layout for a continuous conveyorized spray line for phosphating

Spray cabinets are usually made from low-carbon steel, as are the reservoirs from which the cleaners, phosphating solutions, and various rinses are pumped. Steam coils or other heating mediums, piping, screens, and valves also may be made of low-carbon steel. Spray nozzles may be made of low-carbon stainless steel, or polypropylene. Pumps may be of all-iron construction with stainless steel impellers. Valves may be all iron. As in immersion systems, because acidulated rinses usually contain chromium, no brass or bronze should be used in contact with these rinses. Also, no brass should be used in contact with alkaline cleaners or phosphate solutions. Potential suppliers of the chemicals should be consulted to ensure compatibility with the specific process to be used.

One large manufacturer doing extensive phosphate coating recommends that all parts and accessories in the phosphating stage of a spray zinc phosphating line be made of stainless steel except the storage tank. These tanks usually give satisfactory service when made from 9.5 mm ($\frac{3}{8}$ in.) thick low-carbon steel. Heating coils should be made from electropolished stainless steel to discourage a buildup of zinc phosphate sludge on the coils.

In a continuous spray phosphating line, baffle ridges on the floor and baffle doors or curtains are essential. Baffling between stages eliminates much of the mixing and contamination from carryover of the solutions. The storage tanks from which various solutions are pumped should have a minimum capacity of 2 to $2\frac{1}{2}$ times the volume pumped out per minute and provide phosphate solution tanks with a minimum capacity of $2\frac{1}{2}$ to $3\frac{1}{2}$ times the volume pumped out per minute, to provide room for sludge to collect.

Drying equipment for spray lines usually consists either of indirect-heated convection ovens, fired by gas or oil, or electric-fired or gas-fired infrared ovens capable of raising the temperature of parts to 150 to 205 °C (300 to 400 °F). If parts tend to hold rinse solutions in pockets or seams, it may be necessary to direct a blast of heated air at the pocket, or to tilt the part automatically to drain off the retained solution. Time required for drying varies from 2 min for simple, thin-

gage parts to 6 min for complex parts. For phosphate coatings used ahead of electropaints, the dry-off oven is often omitted, and parts go into the electropaint tank either air-dried or wet.

Work-Supporting Equipment. The size and design of hooks, racks, and other work-supporting equipment used in spray phosphating depend on the size and contour of the parts being processed. These supports should be designed so that significant surfaces of parts receive the full impingement of phosphating solution as parts are conveyed through the unit. As in immersion phosphating, light or point contact is desirable so as not to mask off any surfaces of parts from the phosphating and rinsing solutions. Intricately contoured parts should be suspended in a manner that eliminates or minimizes the entrapment of solution, so that as little as possible is carried from one tank to another. Parts that, because of their shape, are impossible to suspend with mechanical racks or hooks can be suspended with magnetic hooks.

Work-supporting equipment usually is fabricated from low-carbon steel, although stainless steel can be used. Selection generally is predicated on economics, weighing the greater cost of stainless steel equipment against its longer life. Special care must be exercised in handling finished machined parts and other easily damaged parts in phosphating. Although such parts may be processed in special baskets, this often is unsatisfactory because coatings may be thin or completely absent at the numerous areas of contact. Racks usually are preferable.

Racks must be designed to hold parts in such a way that all significant surfaces are satisfactorily coated and parts are separated to prevent them from bumping and damaging each other during processing. On closely conforming racks, an accumulation of scale can hamper proper hanging or holding of parts or cause the rack to mask more than normal areas, causing imperfect coatings. These racks must be descaled frequently. Descaling can be done either by pickling in an inhibited solution of muriatic acid or by cracking the scale from the rack. Conveyor equipment carrying these racks must have a gentle motion to avoid knocking parts against each other. At the same time, conveyor speed must be rapid enough to prevent solutions from drying on parts as they are being moved between stations.

Conveying equipment used in spray phosphating may be of any type that can transport work through the various processing and draining stages. Continuously moving chain-driven conveyors, either overhead or floor-level, are usually used. Conveyor chains and part-carrying accessories can create problems by dragging out solutions and carrying them from one tank to another or from tank to part. The use of conveyor shielding can minimize some of these problems. In one application, such a problem occurred in a spray zinc phosphating line. Parts were hung on hooks suspended from a conveyor chain and remained on these hooks while being carried through the subsequent painting cycle. In the drying stage, phosphating solution (a proprietary solution containing sodium bifluoride) dripped from the conveyor chain and hooks onto the phosphated parts. Blisters in the paint film occurred in areas on which the solution had dripped. To correct this problem, a thorough system of rinsing, drying, and cleaning of the conveyor chain and hooks was initiated:

- A conveyor-chain washer was added; this consisted of several nozzles to spray fresh water on the conveyor chain between the phosphating stage and the subsequent rinse.
- Additional spray drop lines were added in the rinse stage, including a final drop line that sprayed fresh, rather than recirculated, water.
- Compressed-air nozzles for blowing off the conveyor chain and hooks were added immediately following the acidulated rinse stage.
- A final short rinse with unrecirculated demineralized water was added to remove any remaining contaminants from conveyor and parts.
- The frequency of removing accumulated paint from part hooks was increased to avoid entrapment of contaminants in built-up paint.

Process Selection: Immersion Coating versus Spray Coating

Equipment required for phosphate coating can vary from the simple to the elaborate. Some of the factors that influence equipment requirements include:

- Work load
- Size of products to be phosphated
- Material to be phosphated
- Processing method

Example 1: Manual Immersion Coating of Threaded Fasteners in a Zinc Phosphating Solution.

An example of equipment requirements and process cycles can be found in a company that produces threaded fasteners, zinc phosphates, and oil dips at an average of 3600 kg (8000 lb) of these parts each 8 h shift. One worker operates the entire immersion phosphating line. All parts are cleaned and pickled before being phosphated.

Production requirements for the manual immersion zinc phosphating of fasteners are listed below:

Requirement	Value
Weight of each piece, kg (lb)	0.013 (0.029)
Weight of each load, kg (lb)	193 (425)
Average weight processed per hour, kg (lb)	454 (1000)
Average number of pieces per hour	34,483

Equipment specifications required for manual immersion zinc phosphating are given in Table 9.

Table 9 Equipment specifications for typical manual immersion zinc phosphating coating of threaded fasteners

Component	Quantity	Unit capacity			
		Weight		Volume	
		kg	lb	L	gal
Work-handling equipment					
Workbasket for cleaning[(a)]	2	230	500	. . .	. . .
Perforated drums for phosphating[(b)]	3	230	500	. . .	. . .
Drum loading stand	1	230	500	. . .	. . .
Hoists	2	910	2000	. . .	. . .
Loading chute	1	230	500	. . .	. . .

Cleaning equipment					
Alkali soak tank	1	. . .	. . .	760	200
Acid tank (sulfuric acid)	1	. . .	. . .	760	200
Rinse tank	3	. . .	. . .	760	200
Phosphating equipment					
Phosphating tanks[(c)(d)]	3	. . .	. . .	760	200
Rinse tank	1	. . .	. . .	760	200
Chromic acid rinse tank[(d)(e)]	1	. . .	. . .	760	200
Centrifuge for drying[(f)]	1	. . .	. . .	. . .	. . .
Oil dip tank[(g)]	1	. . .	. . .	380	100

(a) Stainless steel.

(b) Motor-rotated.

(c) Heated by stainless steel steam plate coil.

(d) Automatic temperature control.

(e) Heated by steam plate coil.

(f) Equipped with hot-air blower driven by 2.2 kW (3 hp) motor.

(g) Corrosion resistant

Example 2: Automated Immersion Coating of Cast Iron Cylinder Heads in a Zinc Phosphating Solution.

The equipment requirements for zinc phosphate coating of cast iron cylinder heads include the use of an automatic indexing immersion phosphating machine. These parts, which weigh 121 kg (267 lb) each, are processed in baskets, three to a basket, and are loaded standing on their sides to facilitate drainage of solutions from inner passages. A coating weight of 3.8 g/m^2 (1.2×10^{-2} oz/ft^2) is obtained. The machine includes a phosphating tank that accommodates three workbaskets, thus allowing processing time equal to three times that of any other tank plus the time required to index the

machine twice. Details of the equipment comprised by this automatic machine, together with production requirements and operating conditions for phosphating the cast iron cylinder heads, are given below:

Requirement	Value
Weight of coating, g/m^2 (oz/ft^2)	3.8 (1.2×10^{-2})
Size of each piece, mm (in.)	1143 × 406 × 152 (45 × 16 × 6)
Weight of each piece, kg (lb)	121 (267)
Pieces per load	3
Load weight, kg (lb)	363 (800)
Production per hour	20
Immersion time, min:	
Cleaning (each tank)	2
Cold water rinse	2
Hot water rinse (each tank)	2
Phosphating	8
Cold water rinse	2
Chromic acid rinse	2
Oil dip	2

Equipment specifications are given in Table 10.

Table 10 Equipment specifications for automated immersion zinc phosphate coating of cast iron cylinder heads

Component	Size[(a)]	Material	Method of heating	Bath temperature range	Level control

	mm	in.			°C	°F	Water	Liquid	Oil
Workbasket	1220 × 610 × 660	48 × 24 × 26	[b]	. . .	. . .	. . .	. . .	. . .	. . .
Cleaning tanks (2)	1525 × 890 × 1525	60 × 35 × 60	Low-carbon steel	Steam plate coils	93-96[c]	200-205[c]	. . .	Automatic	. . .
Cold water rinse tank	1525 × 1065 × 1525	60 × 42 × 60	Low-carbon steel	. . .	. . .	. . .	Overflow	. . .	. . .
Hot water rinse tanks (2)	1525 × 890 × 1525	60 × 35 × 60	Low-carbon steel	Steam plate coils	27-93[c]	80-200[c]	Overflow	. . .	. . .
Phosphating tank	1525 × 2720 × 1525	60 × 107 × 60	Stainless steel	Steam pipe coil	93-96[c]	200-205[c]	. . .	Automatic	. . .
Cold water rinse tank	1525 × 890 × 1525	60 × 35 × 60	Low-carbon steel	. . .	. . .	. . .	Overflow	. . .	. . .
Chromic acid rinse tank	1525 × 1065 × 1525	60 × 42 × 60	Low-carbon steel	Steam plate coils	[d]	[d]	. . .	Automatic	. . .
Oil dip tank	1525 × 890 × 1525	60 × 35 × 60	Low-carbon steel	. . .	. . .	. . .	. . .	. . .	[e]
Drip pan[f]	1525 × 890 × 1525	60 × 35 × 60	[b]	. . .	. . .	. . .	. . .	. . .	. . .
Phosphate sludge-settling tank[g][h]	1525 × 2720 × 1525	60 × 107 × 60	Stainless steel	. . .	. . .	. . .	. . .	. . .	. . .

(a) Length, width, and depth, respectively.

(b) Not specified.

(c) Automatically maintained.

(d) As recommended by manufacturer of solution.

(e) Drain out carryover water and add oil as needed.

(f) Attached to oil dip tank.

(g) Method of transfer: centrifugal pump.

(h) Settling time 24 h

Automotive Applications. Automobile or truck fenders and hoods are zinc phosphate coated in an automatic, conveyorized spray phosphating line. Table 11 lists the sequence of processing stages and indicates operating conditions for each station. Although this example is based on a specific application, the data are applicable to the processing of similar parts.

Table 11 Sequence of operations in automatic spray application of zinc phosphate to automobile or truck small parts

Operation		Solution	Concentration	Temperature		Time, s	Pressure	
				°C	°F		kPa	psi
1	Clean	Alkaline titanated cleaner	4-6 mL[(a)]	60-65	140-150	60	100-140	15-20
2	Rinse	Water	1.0 mL max[(b)]	57-60	135-140	30	100-140	15-20
3	Clean	Alkaline titanated cleaner	4-6 mL[(a)]	60-65	140-150	60	100-140	15-20
4	Rinse	Water	1.0 mL max[(b)]	57-60	135-140	30	100-140	15-20
5	Phosphate	Accelerated zinc phosphate	20-25 mL[(c)]	52-55	125-130	60	55-83	8-12
6	Rinse	Water	1.0 mL max[(c)]	35-40	95-105	30	69-100	10-15
7	Acidulated rinse	Partially reduced chromic and/or phosphoric acids	150-250 ppm Cr^{6+}, pH 4.0-5.0	35-40	95-105	30	69-100	10-15
8	Demineralized rinse	Distilled water, deionized 100 μmho max						

(a) Number of milliliters required to titrate a 10 mL (2.6×10^{-3} gal) sample to the phenolphthalein end point using 0.1 *N* hydrochloric acid.

(b) Number of milliliters required to titrate a 10 mL (2.6×10^{-3} gal) sample to the bromocresol green end point using 0.1 *N* hydrochloric acid.

(c) Number of milliliters required to titrate a 10 mL (2.6×10^{-3} gal) sample to the phenolphthalein end point using 0.1 *N* sodium hydroxide.

(d) Or dry at 170 to 180 °C (340 to 355 °F) for 4 min

Consumer Product Applications. The sequence of operations involved in spray iron phosphating panels, brackets, and miscellaneous parts for household appliances is indicated in Table 12. Solutions, operating temperatures, and cycle times are also shown. The entire process is completed in $8\frac{1}{2}$ min. Coating weight ranges from 0.4 to 0.6 g/m^2 (1.3×10^{-3} to 2.0×10^{-3} oz/ft^2).

Table 12 Sequence of spraying operations in iron phosphating of panels, brackets, and other parts for household appliances

Operation		Solution	Concentration		Temperature		Time, s
			g/L	oz/gal	°C	°F	
1	Clean	Alkaline cleaner	5.6-9.40	0.75-1.25	66-74	150-165	60
2	Rinse	Water	. . .	. . .	66	150	30
3	Rinse	Water	. . .	. . .	66	150	30
4	Phosphate	Iron phosphate	50	6.7	68-74	155-165	60
5	Rinse	Water	. . .	. . .	(a)	(a)	30
6	Acidulated rinse	Chromic acid	0.29	0.04	54-86	130-150	30
7	Rinse(b)	Deionized water	(c)	(c)	(a)	(a)	30
8	Dry	. . .	. . .	. . .	150-230	300-450	240

(a) Ambient.

(b) Optional.

(c) 25 ppm (max) impurities

Military Equipment Applications. Manganese phosphate coatings are applied to military equipment to provide increased resistance to scuffing, galling, and corrosion. Table 13 lists the progressive stages of a phosphating indexing line, which is completely automatic, and indicates the operating conditions.

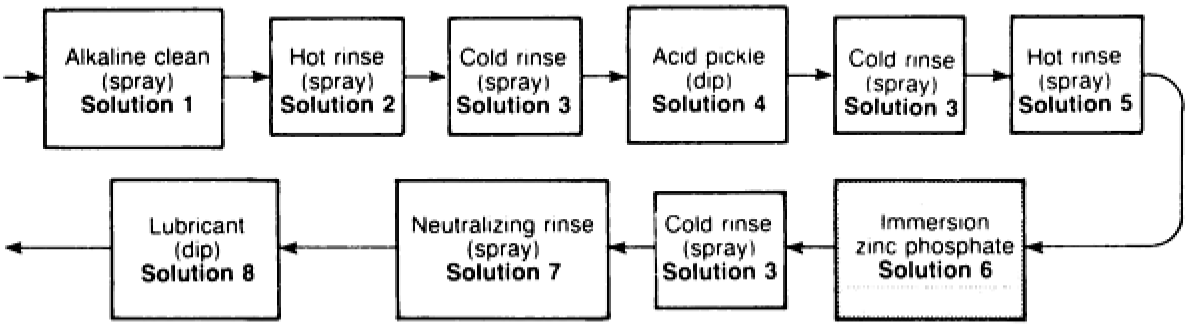
Table 13 Sequence and details of operations for an automatic manganese phosphating indexing line

Operation		Temperature		Time, min	Function	Concentration
		°C	°F			
1	Alkaline cleaner	50	125	5	Degrease, remove soils	6.0-8.0 mL[(a)]
2	Alkaline cleaner	70	160	5	Degrease, remove soils	4.0-6.0 mL[(a)]
3	Water rinse	70	160	0.5	Remove alkali from parts	. . .
4	Water rinse	90	195	0.5	Remove alkali from parts	. . .
5	Water rinse	90	195	0.5	Remove alkali from parts	. . .
6	Water rinse	35	95	0.5	Remove alkali from parts	. . .
7	Pickle	40	105	5	Remove scale or rust	Phosphoric acid, 20%
8	Water rinse	90	195	0.5	Remove acid from part	. . .
9	Activating rinse	35	95	3	Refine phosphate crystal	0.2-4% wt/vol
10	Phosphate	98	210	20	Manganese phosphate coating	FA 1.5-2.0 mL[(b)] TA 9.5-12.0 mL[(b)] Iron, 1.5-2.0 mL
11	Water rinse	35	95	0.5	Remove acidic phosphate solution	. . .
12	Acidulated rinse	35	95	0.75	Remove water salts, provide rust-proofing	. . .
13	Dryer	. . .	. . .	. . .	. . .	. . .

(a) Number of milliliters required to titrate a 10 mL (2.6×10^{-3} gal) sample to the phenolphthalein end point using 0.1 *N* hydrochloric acid.

(b) 2 mL (5.3×10^{-4} gal) sample size for free acid (FA) and total acid (TA) titrations. 10 mL (2.6×10^{-3} gal) sample size for iron titration

Mortar Shell Casings. Figure 7 shows a schematic layout of an automatic, conveyorized line for immersion zinc phosphating and lubricating of blanks from which casings for 80 mm (3.2 in.) mortar shells are cold formed. These blanks, made of 1010 steel, are coated at the rate of 4000 pieces/h. Each blank has an area of approximately 0.1 m^2 (1 ft^2). Conveyor speed is 2.0 m/min (6.6 ft/min). Details of operating conditions and solutions used are presented in the table accompanying Fig. 7.



Solution No.	Solution	Composition	Operating temperature		Cycle time, min
			°C	°F	
1	Alkaline cleaner	Alkali, 3.8 g/L (3.2×10^{-2} lb/gal)	82	180	1
2	Hot rinse	Water[(a)]	77	170	0.75
3	Cold rinse	Water[(b)]	RT	RT	1
4	Acid pickle	H_2SO_4, 15-18 wt%[(c)]	66	150	10
5	Hot rinse	Water	71	160	0.75
6	Zinc phosphate	Chlorate-accelerated[(d)]	82	180	6
7	Neutralizing rinse	$NaNO_2$, 1.1 g/L (9.2×10^{-3} lb/gal)	RT	RT	1
8	Lubricant	Soap, 10 wt%	66	150	6

(a) When lime is present in water, sequestering agent is added in concentration of 1.9 g/L (1.6×10^{-2} lb/gal).

(b) Purity maintained by overflow.

(c) Solution is discarded when iron content reaches 5%.

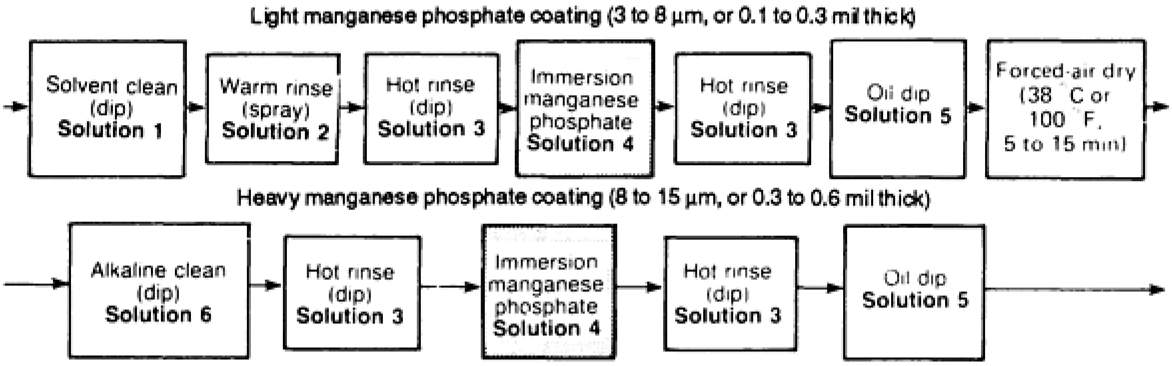
(d) Contains 36 points total acid, 7.5 points free acid, based on titration of 10 mL (2.6×10^{-3} gal) sample; concentration of accelerator, 3.5 g/L (2.9×10^{-2} lb/gal).

(e) (e)NaOH added to establish pH in range of 10 to 11

Fig. 7 Automatic, conveyorized cleaning, immersion zinc phosphating, and lubricating of 80 mm (3.2 in.) mortar shell blanks (1010 steel) before cold forming. Average area of shell blanks was 0.1 m^2 (1 ft^2); coating weight, 16 g/m^2 (5.2×10^{-2} oz/ft^2). Conveyor speed was 0.033 m/s (6.5 ft/min), and the production rate was 4000 pieces/h.

Control of Coating Weight

Figure 8 compares processing stages involved in manganese phosphating to two different ranges of coating thickness, 2.5 to 7.6 μm (0.1 to 0.3 mil) for light coatings and 7.6 to 15 μm (0.3 to 0.6 mil) for heavy, or conventional, coatings. The same phosphating compound is used in each line. Difference in coating weights depends on cleaner used and time in the phosphating solution. For conventional, heavy manganese phosphate coatings, parts are cleaned in an alkaline cleaning solution, providing a surface that permits good contact between metal and the phosphating bath. The resulting coating is heavy and coarse-grain, and it can readily absorb oil. For light coatings, a kerosene-based or similar solvent emulsion cleaner is used. A thin residue of oil left on the metal after two rinses acts as a buffering agent or grain-refiner, to produce a thinner, finer-grain coating. Usually, less lubricating oil is desired in conjunction with a fine-grain coating. Consequently, an additional step is involved for removing excess oil. The additional step is not usually necessary with a coarse-grain coating.



Solution No.	Type	Composition	Operating temperature		Cycle time, min
			°C	°F	

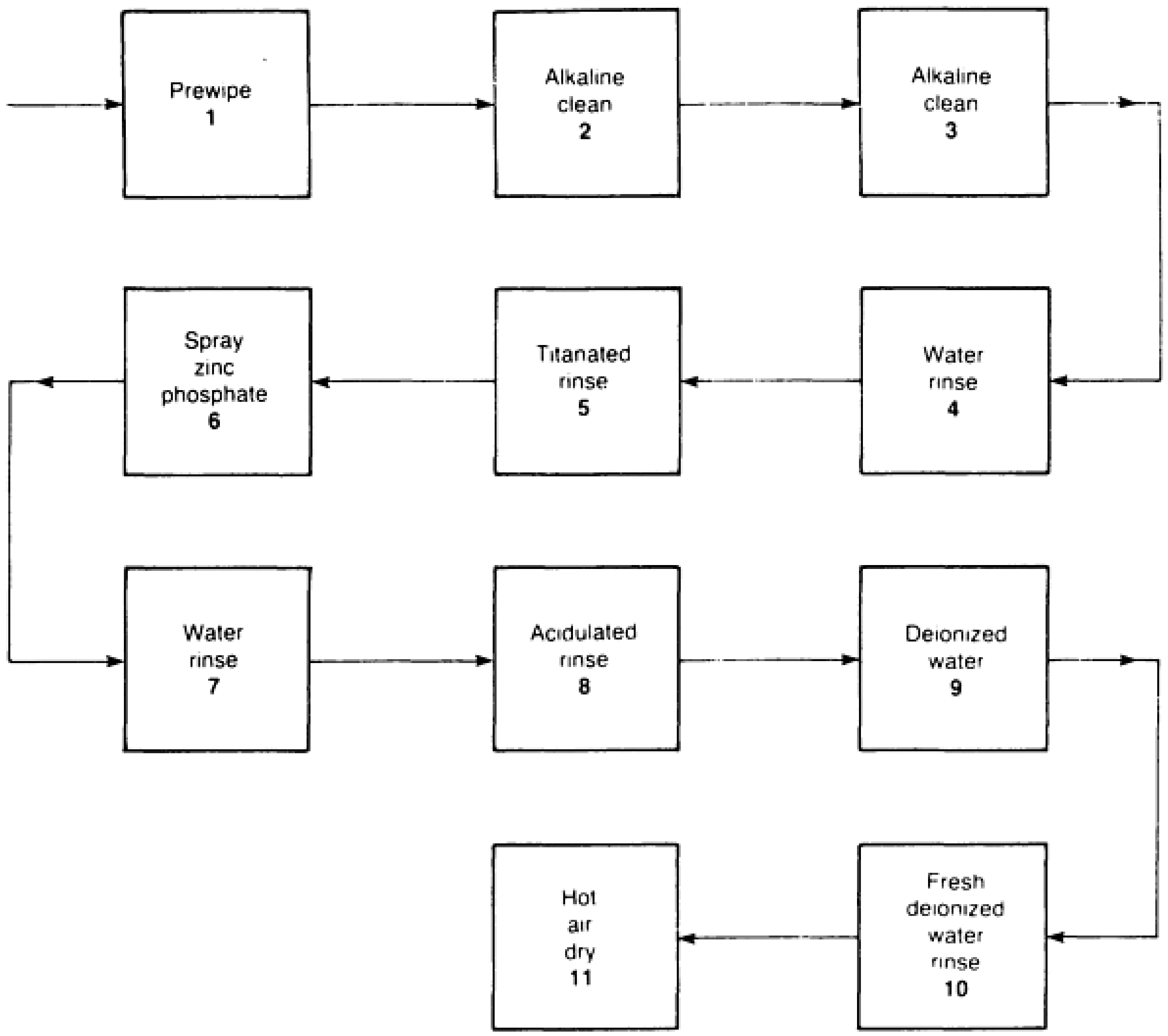
1	Solvent cleaner	. . .	. . .	. . .	3-10
2	Warm rinse	Water	38	100	1-3
3	Hot rinse	Water	82	180	1-3
4	Manganese phosphate	(a)	93	200	(b)
5	Oil	Soluble oil, 5%	60	140	1-3
6	Alkaline cleaner	. . .	93	200	3-10

(a) Contains 12 points total acid, as measured by titration of a 2 mL (5.3×10^{-4} gal) sample.

(b) For light coating, 8 to 12 min; for heavy coating, 10 to 20 min

Fig. 8 Sequence of operations for light vs. heavy applications of manganese phosphate coatings. Coating weight is function of specific cleaner used and immersion time in phosphating solution.

A phosphating line for spray zinc phosphating of automobile bodies is shown in Fig. 9. The bodies average 80 m^2 (860 ft^2) in area and the line speed ranges from 0.12 to 0.14 m/s (24 to 28 ft/min). Coating weights range from 1.6 to 2.4 g/m^2 (5.2×10^{-3} to 7.9×10^{-3} oz/ft^2). Production rate may reach 75 bodies per hour. The table accompanying Fig. 9 gives details of solutions used in this line and lists cycle times for various stages.



Stage	Type	Composition	Temperature		Time,s
			°C	°F	
1	Organic solvent	Mineral spirits	30	86	60
2	Alkaline cleaner	Titanated, alkali 6.0 g/L (5.0×10^{-2} lb/gal)	60-65	140-150	70
3	Alkaline cleaner	Titanated, alkali 6.0 g/L (5.0×10^{-2} lb/gal)	60-65	140-150	70
4	Hot rinse	Water	55-60	130-150	150
5	Activated water rinse	Titanated, 7.5-8.5 pH 0.5 g/L (4×10^{-3} lb/gal)	40-45	104-115	35
6	Zinc phosphate	ClO_3 accelerated[(a)]	50-55	122-130	70

7	Rinse	Water	35	95	15
8	Acidulated rinse	Partially reduced chromic acid (150 to 200 ppm Cr^{6+})	35	95	35
9	Rinse	Deionized water (100 μmho max)	35	95	70
10	Rinse	Deionized water (10 μmho)	35	95	15
11	Dryer	Hot air	. . .	. . .	. . .

(a) Total acid 20 mL (5.3×10^{-3} gal), free acid 0.9 mL (2.4×10^{-4} gal), nitrite accelerator 1.5 mL (4.0×10^{-4}gal); acid checked with 10 mL (2.6×10^{-3}gal) sample, accelerator checked with gas evolution apparatus

Fig. 9 Sequence of operations for spray zinc phosphating of automotive bodies

Tables 3, 4, and 5 present phosphate coating applications and weights. Table 3 deals only with spray application, but it covers both iron and zinc phosphate coatings as bases for paint films. By comparing the area of the parts and the production per hour controlled to obtain the uniform coating weights shown, it is easy to see the interrelation of size, production time, and coating weight. In all applications, the material being coated was low-carbon steel sheet. Table 5 lists applications for manganese phosphate coatings for wear resistance.

As indicated by the curve in Fig. 10, based on the experience of one processor of small threaded parts, the consumption of phosphating solution concentrate is directly proportional to the area and thickness of the coating applied. These parts were immersion zinc phosphated, processed in batches in a rotating drum, to a coating weight of approximately 10.8 g/m^2 (3.5×10^{-2} oz/ft^2). Figure 10 shows that the direct proportionality of area coated to concentrate consumed does not begin until an initial coat is deposited. At the time when parts are immersed, there is an immediate reaction in which an irregular coating is quickly deposited. Because the maximum area of bare steel is exposed to the bath at that time, maximum efficiency takes place. The remaining time in the bath serves to refine the coat by depositing crystals to fill gaps between existing crystals and to increase coating weight to uniform thickness by depositing crystals over previously deposited crystals.

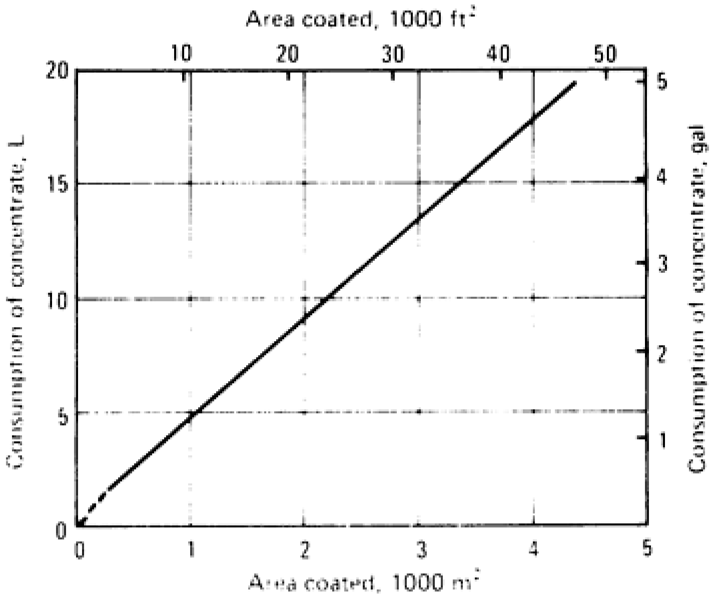


Fig. 10 Plot of zinc phosphating concentrate consumed vs. area covered for small threaded components coated to 10.8 g/m2 (3.5 × 10^{-2} oz/ft^2) with barrel phosphating

Control of Crystal Size

The crystalline structure of the chemically bonded phosphate coating (Fig. 11) provides a suitable base for subsequent paint or oil films. Crystals permit the paint to penetrate, providing the paint with exceptional adherence. When oil is the rust preventive, the interstices of the crystalline structure function efficiently as an oil-retaining reservoir. The adhesion of phosphate coating to the base metal, as determined by flexing of the metal, varies with the type and thickness of the coating. Generally, heavier coatings are composed of large crystals, which do not bond to each other or to the surface of the metal as well as do fine-grain, thinner coatings. Consequently, where adhesion and flexibility may be a problem because of the nature of the application, phosphating material is selected that produces a thin, fine-grain coating. However, this may not result in maximum corrosion resistance. Organic additives, special accelerators, and/or calcium added to a zinc phosphate process provides a microcrystalline structure that exhibits optimum paint adhesion and corrosion resistance.

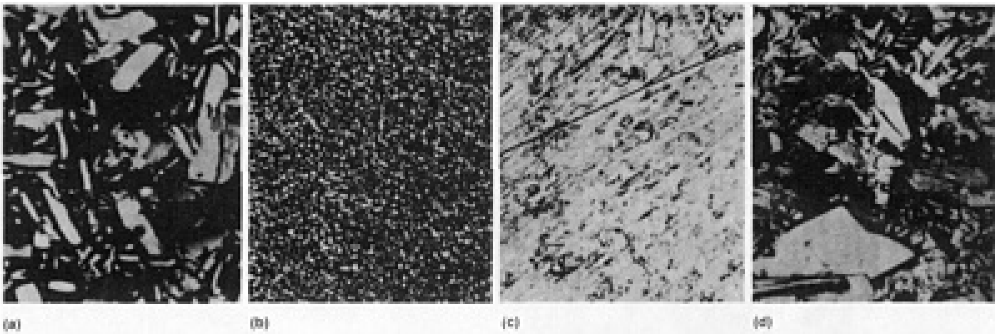


Fig. 11 Photomicrographs of microstructures for principal phosphate coatings. (a) Heavy zinc phosphate. (b) Microcrystalline zinc phosphate. (c) Iron phosphate (primarily iron oxide). (d) Manganese phosphate. 125×

Zinc phosphate coatings (Fig. 11a and b) are widely used as bases for paint or oil. A fine uniform crystal is necessary when gloss is desired for the paint film. Coarse crystals promote dullness and often require higher paint thickness to gain uniform and acceptable coverage. However, when coating is applied to provide lubricity, a coarse crystal may be preferable. With few exceptions, zinc phosphating concentrates are proprietary materials designed to produce, within a specified time and with available equipment, coatings that are within a specific range of weight and have a desired crystal size and texture.

Usually, strongly acid baths build coating at a slow rate but deposit large crystals. This is due to the longer time needed to develop neutralization at the coating interface. A bath that has been activated by an accelerator deposits coating more quickly and with a smaller crystal. Up to a point, as long as the part stays in the bath, solution continues depositing crystals by building up thinner sections of coating and filling interstices with more crystals. Because the coating gradually insulates metal from fresh solution, no crystals are deposited beyond a certain point. These characteristics are inherent in proprietary solutions, and little control can be exerted other than to maintain the bath as prescribed.

The surface condition of the parts being coated is a factor that influences the coating characteristics that can be controlled. Certain oils, residues from solvent cleaning or vapor degreasing, or solvent emulsions, when retained on the surface in very thin films, function as crystal refiners. An example is the film left on parts that are cleaned using a kerosene-based emulsion cleaner. Although this cleaning operation is usually followed by a hot water rinse, enough oil is retained on the surface to have a beneficial influence, if a fine crystal is desired. Conversely, if a strong alkaline cleaner is used and completely rinsed away, or if blast cleaning is used, a coarser crystal is obtained. Another method of refining or decreasing crystal size is the use of a proprietary titanium phosphating conditioner. These titanium phosphate salts can be used either in the water rinse that precedes phosphating or with certain alkaline-based cleaners.

Iron phosphate coatings (Fig. 11c) are generally of a very fine structure and are amorphous in appearance. Because these coatings are used primarily as bases for paint or to assist in bonding of metal to a nonmetallic surface, fine structure is desirable. With iron phosphate coatings, the problem is one of adherence and powdery coatings rather than crystal size or coating weight. Attention must be directed to surface cleanliness, maintenance of the bath within the prescribed limits, and proper processing.

Manganese phosphate coatings (Fig. 11d) are usually heavy and coarse. Because these coatings are generally used for their lubricating qualities and often incorporate a supplementary oil film, a continuous coating may not be mandatory. The length of time in bath may be varied, within limits, to vary the film thickness to meet the functional requirements of the coating. Crystal size and coating thickness are controlled by the condition of the surface to be coated. Oils, and residues from alkaline cleaning, solvent cleaning, vapor degreasing, and emulsion cleaners, serve as crystal refiners and reduce coating thickness. Proprietary crystal refiners are available and usually contain a heavy metal phosphate. They are used in the water rinse just before phosphating.

To meet severe requirements, manganese phosphate coatings may be produced to extremely heavy weights. It is difficult, however, to obtain uniformity in such coatings. Pretreatment, including cleaning, rinsing, and etching, as well as the equilibrium of the phosphating solution, is critical.

In one plant, carburized and hardened differential gears had been failing through localized surface seizure caused by extremely high unit loading. Extreme-pressure gear lubricants, zinc and manganese phosphate coatings of conventional weight, and various other surface treatments proved ineffective in preventing metal-to-metal contact. Manganese phosphate coatings that were extremely thick and heavy, 25 to 75 μm (1 to 3 mil) thick and 110 to 325 g/m^2 (0.36 to 1.07 oz/ft^2), prevented seizure under the most adverse conditions. The cycles for the application of a heavy manganese phosphate coating for lubrication of carburized and hardened differential gears are given in Table 14.

Table 14 Parameters for applying a heavy manganese phosphate coating that provides lubrication for carburized and hardened differential gears

Solution	Time, min	Temperature		Concentration	
		°C	°F	g/L	oz/gal
Alkaline immersion clean	15	99	210	30-45	4-6
Cold water rinses					
Sulfuric acid etch	5	(a)	(a)	(b)	(b)

(a) Ambient.

(b) 10 to 20% H_2SO_4.

(c) Total acid (total ions in solution), 55 to 85 points; free acid (hydrogen ions in solution), 8-17 points; ferrous iron concentration, 0.05-0.04 g/L (0.007-0.05 oz/gal). Points are the minimum milliliters of the titrating solution required to cause a reaction with a definite quantity of the solution being tested. Reaction is indicated by a color change of the solution.

Low-Temperature Coatings

Both iron and zinc phosphate coatings can be applied at much lower temperatures than have been traditional, thus reducing heat energy costs significantly. Manganese phosphate coatings still require solution temperatures around 95 °C (200 °F). Solutions are available to apply iron phosphate by either dip or spray at 24 °C (75 °F), producing coating weights from 0.44 to 0.66 g/m^2 (1.4 × 10^{-3} oz/ft^2). Zinc phosphate baths can be compounded to produce 3.3 to 5.5 g/m^2 (1.1 × 10^{-2} to 1.8 × 10^{-2} oz/ft^2) coatings at 40 °C (100 °F).

The energy demands of hot spray systems are determined primarily by their temperature and recirculation rate. In one plant, a paint preparation line using iron phosphate sprayed at 71 °C (160 °F) was found to be using 35.8 × 10^6 kJ/day (33.9 × 10^6 Btu/day). The iron phosphating stage is part of the pretreatment of an electrocoat prime paint line for castings and forgings. The energy requirements for the spray iron phosphate are:

Requirement	**Value**
Tank capacity, L (gal)	8.0 × 10^3 (2.1 × 10^3)
Pump rate, L/min (gal/min)	2.3 × 10^3 (6.0 × 10^2)
Temperature, °C (°F)	70 (160)
Operating time, h/day	16
Heat-up energy, kJ (Btu)	2.34 × 10^6 (2.22 × 10^6)
Temperature maintenance energy, kJ/h (Btu/h)	2.09 × 10^6 (1.98 × 10^6)
Total energy requirements per day,kJ (Btu)	35.8 × 10^6 (33.9 × 10^6)

Changing to a product operating at 24 °C (75 °F) allowed the system to operate with no heat required beyond the pump energy, which maintained the required 24 °C (75 °F). With no requirement for heating coils or heat exchangers, new installations saved those capital expenditures. Both systems produced coating weights of 0.44 to 0.55 g/m^2(1.44 × 10^{-3} to 1.80 × 10^{-3} oz/ft^2).

Although immersion baths have much lower heat losses than spray applications, worthwhile heat savings still can be realized. In general, heat losses rapidly increase at about 60 °C (140 °F).

A system producing fine-grain immersion zinc phosphate coatings on miscellaneous formed and machined parts was investigated, and the actual steam usage required to maintain temperature was measured at two operating temperatures (Table 15). Energy demands did not include heating the parts but can be calculated from their mass. Less energy was required to maintain the tank at temperature than to shut down for 8 h and reheat. The energy saved by operating the system at 55 °C (130 °F) instead of 88 °C (190 °F) amounted to 3.70 × 10^6 kJ/day (3.51 × 10^6 Btu/day) or 0.888 × 10^9 kJ/yr (0.842 × 10^9 Btu/yr).

Table 15 Energy demands of a system producing fine-grain immersion zinc phosphate coatings

Operating temperature	**Heat-up energy**	**Temperature maintenance energy**	**Total energy required per day**

°C	°F	kJ	Btu	kJ/h	Btu/h	kJ	Btu
88	190	1.28×10^6	1.21×10^6	0.17×10^6	0.16×10^6	3.98×10^6	3.77×10^6
55	130	9.3×10^4	8.8×10^4	1.2×10^4	1.1×10^4	0.27×10^6	0.26×10^6

Note: Tank capacity 4200 L (1100 gal). Tank surface area 2.8 m^2 (30 ft^2). Operating time 16 h/day

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Inspection Methods

The majority of phosphate coating quality control methods are based on visual inspections. For zinc and manganese phosphate, the coating must be continuous, adhere well to the surface, and be of uniform crystalline texture suitable for the intended use. Color should range from gray to black. Causes for rejection include loose smut or white powder (because of inclusion of ferric phosphate by-product into the phosphate coating or dried phosphate solution), blotchiness, excessive coarseness, and poor adhesion. Crystal size may be observed by using micrographs at magnifications of 10 to 500×, depending on the coating. Iron phosphate coatings have no apparent crystalline texture. Instead they appear to be amorphous. Their color varies from iridescent yellow to blue to brown. Loose or patchy coatings are cause for rejection.

Determination of coating weight on ferrous surfaces can be made by a stripping procedure, such as follows:

1. Phosphate a part of known surface area.
2. Thoroughly clean the part to remove all oil.
3. Weigh the part to the nearest tenth of a milligram.
4. Strip the phosphate-coated part in a $2\frac{1}{2}$% H_2CrO_4solution at 71 °C (160 °F), immersing for 10 min (zinc phosphate coating), 15 min (manganese phosphate coating), or 5 min (iron phosphate coating). Time and concentration of the chromic acid solution may require adjustment for specific coatings.
5. Rinse in clean water.
6. Dry.
7. Reweigh the stripped part to the nearest tenth of a milligram. The difference in weight from that in step 3 equals the total coating weight.
8. Calculate weight of coating per unit of area. Standard units are grams per square meter.

If the size or shape of items being coated preclude the performance of the above procedure, test specimens of identical material, heat treatment, and surface finish may be substituted. An accurate measurement of coating weight cannot be obtained by weighing the part, applying the phosphate coating, and then reweighing the part. Because the phosphating solution attacks steel, a measurable, but not always predictable, amount of steel is removed. This condition can vary with the acidity of the bath as well as with the type of metal being coated.

Coating voids or spots not covered may be checked by using a clean, dry phosphated specimen. Next, soak a piece of filter paper, 4.0×10^4 to 5.0×10^4 mm^2 (6.2 to 7.7 $in.^2$) in area, in a solution containing 7.5 g/L (1.0 oz/gal) $K_3Fe(CN)_6$ and 20 g/L (3 oz/gal) NaCl. Allow excess solution to drain off. Apply wet filter paper to the phosphated sample for 5 min. Remove and observe blue spots, which indicate noncoated areas. The method of rating may vary with different processes and requirements. One general method is as follows:

- *Excellent*: none to three fine spots up to 1 mm (0.04 in.)
- *Good*: not more than 10 fine spots
- *Satisfactory*: not more than 20 fine spots or up to 3 large spots

Repair of Phosphate Coatings

Small parts that do not accept a satisfactory phosphate coating can easily be stripped, cleaned, and rephosphated. Large parts with a faulty coating or with a coating that is damaged in processing are less easily handled, and repair of the phosphated surface may be preferable to stripping and rephosphating. The simplest method is to sand the phosphate film until all defective coating is removed and clean, bare metal is exposed. A proprietary phosphating solution compounded for this application is brushed or wiped on the area to be rephosphated and is allowed to remain for a prescribed length of time (usually measured in seconds). Surplus solution is then removed by thoroughly water rinsing and wiping dry with clean rags. These solutions range from simple systems (phosphoric acid, butyl cellosolve, and a suitable wetting agent, plus 50 to 70% water) to accelerated systems that produce a crystalline zinc phosphate coating. If the volume of repairs is considerable, a portable steam spray unit can be used. This will spray hot phosphating solution, water, and chromic acid rinsing solution through a hose and nozzle.

Limitations of Phosphating

Limitations Imposed by Shape. It is seldom impossible to phosphate a part because of its shape. However, shapes can restrict production or limit the choice of process. Parts with complex passages must be immersion coated, because spray phosphating cannot reach all areas of the passages. Cup-shape parts, phosphate coated by either method, present problems of handling to achieve complete drainage. Blind holes or cavities may entrap air, preventing phosphating solution in the immersion process from contacting all areas to be coated.

At one company, hydraulic pump components, such as gears, vanes, and valves, and hydraulic valve bodies were manganese phosphated to provide break-in lubrication. Many of these parts had blind tapped holes on several surfaces. Although all critical wearing surfaces of these components were adequately coated, investigation showed that many of the blind holes were only partially phosphated because of air entrapment. Similar parts, with holes or cavities that did require phosphate coating, would require special handling to ensure coating of these areas.

In another instance, large cylinder heads weighing approximately 120 kg (265 lb) as cast were coated with a microcrystalline zinc phosphate coating to prevent rusting during storage. These parts were placed in baskets in such a way that no air was entrapped. All internal surfaces were permitted to come in contact with the phosphating solution.

Tanks that require a phosphate coating on the inside after fabrication, and that have few drain holes or openings of any size, must be phosphated by immersion. However, if these tanks require phosphate coating on the outside only, spray coating is more appropriate.

Limitations Imposed by Size. The size of parts that can be phosphated is limited only by the size and type of equipment available. However, part size does generally determine the method of application. Very small parts, such as springs, clips, nuts, bolts, and washers, are almost always coated by immersion. Spray phosphating of these parts on a volume basis would be impractical. Conversely, for extremely large parts, such as transformer housings, that may be as much as 6 m (20 ft) high, spray phosphating is the only practical method for volume production. On extremely large parts produced in low volume, however, coatings are usually applied by brushing or wiping. Parts in between these extremes of sizes are coated by either spray or immersion, depending on the equipment available, quantity to be coated, and complexity of parts. Examples of parts satisfactorily coated by either method include automobile bodies, castings, panels, and machined parts.

Supplemental Oil Coatings

Unless they are to be painted, parts usually receive a supplemental coating of oil after being phosphated. This coating is applied to increase corrosion resistance, and it also neutralizes any residual acid that might remain on parts from the phosphating bath. The type of oil used depends on the degree of corrosion protection desired, subsequent operations to be performed on phosphated parts and the handling involved in these operations, appearance requirements, and compatibility of the oil with other lubricants in assemblies. Materials commonly used are water-soluble oils, nondrying oils, non-hard-drying greaselike materials, and oils that are dry to the touch.

Water-soluble oils provide both short-term and long-term protection against corrosion, depending on their composition. Water-soluble oils offer the advantage of allowing parts to go into water-soluble oil in a wet state. An additional advantage of the water-soluble oil is that it eliminates a fire hazard from the operation.

Figure 12 shows an immersion tank used in the coating of lightweight parts with soluble oil for applications in which subsequent handling or assembly requirements require a virtually dry part.

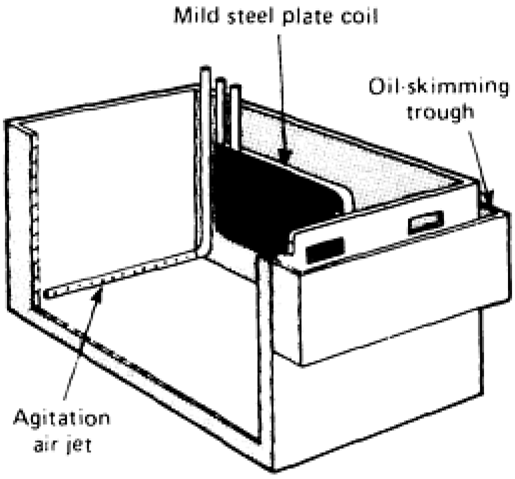

Fig. 12 Immersion tank for coating lightweight phosphated components with a soluble oil. Skimming trough removes floating globules of oil that might cling to parts.

Flash points of water-soluble oils are sometimes lower than those of petroleum-based oils or synthetic organic oils. However, after water-soluble oils are mixed with water to the 5 to 25% concentration range, little fire hazard attends their use.

Nondrying oils vary in type and viscosity and are selected on the basis of requirements of in-process handling or ultimate service. An advantage of this type of material is its ability to self-heal any scratches that may occur in bulk handling. Corrosion protection may be increased by adding a commercially available rust inhibitor that is compatible with the oil. Petroleum-based oils can be reduced with petroleum solvents to form a thinner film, if desired. If parts are not completely dry before the application of oil, water-displacing additives may be used.

Non-hard-drying materials are greaselike substances that have melting points above room temperature. These materials may be applied by dipping, spraying, or brushing. When necessary, these materials are readily removed by petroleum solvents. Figure 13 shows a tank for dip application of greaselike materials. The tank is provided with facilities for heating and cooling to maintain temperature control of the coating material.

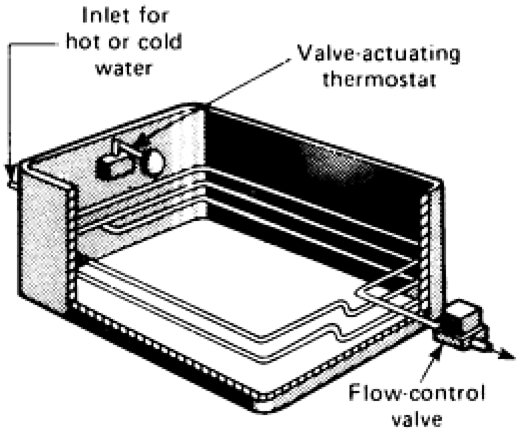

Fig. 13 Tank used for dip coating of phosphated parts with greaselike materials that require temperature monitoring

Decorative Stains (Ref 7)

Depending on the process and the substrate used, heavy phosphate coatings on steel vary from near-black to medium-gray. Manganese phosphate coatings are generally the darkest.

Many applications require a definitive, reproducible color, most often black, for decoration or identification purposes. This can be achieved by applying an alcohol-based stain, usually with a shellac or manila resin binder, and an original dye of the color desired. Because the stain has limited protective value, a light oil can subsequently be applied to help prevent corrosion and enhance appearance (see the section "Supplemental Oil Coatings" in this article). In heavy-duty applications, pigmented finishes can be used, but they produce thicker coatings that can cause problems with dimensional buildup on threaded components.

Figure 14 shows the corrosion resistance of black stain, corrosion-preventing oil, and black stain plus oil, relative to the type of phosphate coating applied.

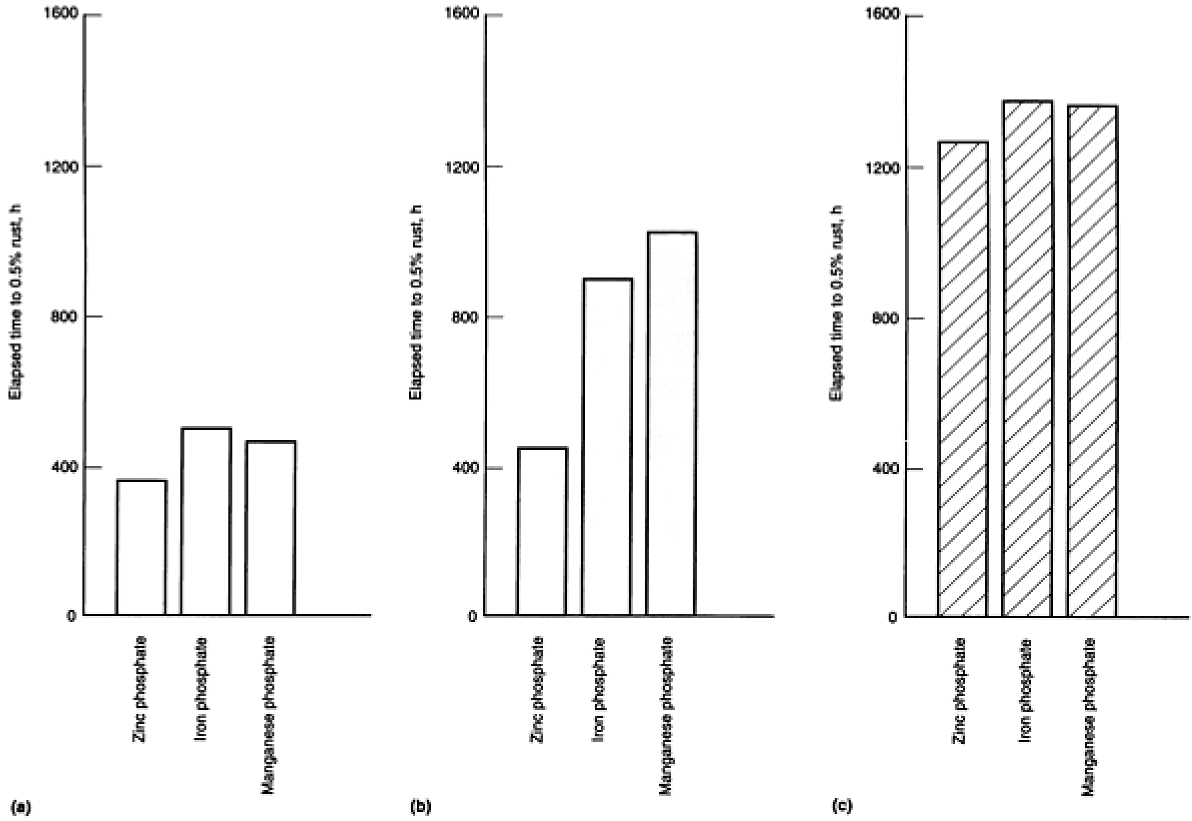

Fig. 14 Corrosion resistance of selected metal finishes relative to type of phosphate coating applied. (a) Black stain. (b) Corrosion-preventing oil. (c) Black stain and oil. Source: Ref 7

Reference cited in this section

7. D.B. Freeman, *Phosphating and Metal Pre-Treatment,* Industrial Press, Inc., 1986, p 76-77

Phosphate Coating Selection

Table 16 provides guidelines for choosing phosphate coatings based on application, coating weight requirements, and recommended process parameters.

Table 16 Process parameters for selected phosphate coatings

Coating type	Accelerator	Process type	Tank material	Coating weight		Operating conditions							
						Immersion				Spray			
						Time		Temperature		Time		Temperature	
				g/m^2	oz/ft^2 × 10^{-2}	s	min	°C	°F	s	min	°C	°F
Paint bonding applications													
Iron phosphate	Chlorate	Stripline alkaline phosphate	Mild steel	0.2-0.5	0.07-0.16	8-20	. . .	66-77	151-171	8-20	. . .	66-77	151-171
	Molybdate	Multimetal lightweight alkali metal phosphate	Mild steel	0.3-0.5	0.10-0.16	. . .	2-5	40-70	104-158	. . .	1-2	40-60	104-140
	Chlorate	Lightweight iron phosphate	Mild steel	0.3-1.0	0.10-0.33	. . .	. . .	. . .	. . .	. . .	1	70-75	158-167
	Nitrate (molybdate)	Combined cleaner/coater	Mild steel	0.2-0.5	0.07-0.16	. . .	. . .	. . .	. . .	. . .	1-2	35-70	95-158
	Molybdate	Low-temperature liquid cleaner/coater	Mild steel	0.2-0.5	0.07-0.16	. . .	. . .	. . .	. . .	. . .	1.5-3.0	25-35	77-95
	Molybdate	Multimetal lightweight alkali metal phosphate	Mild steel	0.2-0.5	0.07-0.16	. . .	2-5	40-60	104-140	. . .	. . .	. . .	. . .
						. . .	. . .	. . .	. . .	. . .	1-2	40-60	104-140

Zinc phosphate	Chlorate	Low-temperature immersion zinc phosphate	Mild steel	1.5-2.0	0.49-0.66	. . .	5-10	25-30	77-86	. . .	. . .	. . .	. . .
		Spray zinc phosphate	Mild steel(d)	1.4-2.0	0.46-0.66	. . .	. . .	. . .	. . .	. . .	1-2	50-60	122-140
	Chlorate/metanitro-benzene sulphonate	Spray zinc phosphate	Mild steel(d)	1.4-2.0	0.46-0.66	. . .	. . .	. . .	. . .	45-120	. . .	45-50	113-122
		Low-temperature spray zinc phosphate	Mild steel(d)	1.4-2.0	0.46-0.66	. . .	. . .	. . .	. . .	80-180	. . .	25-35	77-95
	Hydrogen peroxide	Spray zinc phosphate for closed-loop operation	Mild steel(d)	1.4-2.0	0.46-0.66	. . .	. . .	. . .	. . .	. . .	1-2	55-60	131-140
	Nitrite	Zinc phosphate	Mild steel	3-7	0.98-2.3	. . .	5-15	60-70	140-158	. . .	. . .	. . .	. . .
		Spray zinc phosphate	Mild steel	1.6-2.4	0.52-0.79	. . .	. . .	. . .	. . .	. . .	1-2	45-60	113-140
		Multimetal spray zinc phosphate	Mild steel(d)	2.0-3.5	0.66-1.1	. . .	. . .	. . .	. . .	. . .	1-3	55-70	131-158
		Multimetal zinc phosphate	Mild steel(d)	2-3	0.66-0.98	. . .	1-3	55-80	131-176	. . .	1-3	55-80	131-176
	Nitrite/chlorate	Spray zinc phosphate (low zinc)	Mild steel	1.6-2.0	0.52-0.66	. . .	. . .	. . .	. . .	. . .	1.5-2.0	50-55	122-131
	Nitrite	Calcium modified zinc phosphate	Mild steel	2.0-4.5	0.66-1.5	. . .	2-5	60-70	140-158	. . .	. . .	. . .	. . .

Zinc manganese phosphate	Nitrite	Low-temperature zinc phosphate	Mild steel	1.8-2.4	0.59-0.79	. . .	. . .	. . .	. . .	. . .	1-2	25-35	77-95
	Chlorate/metanitro-benzene sulphonate	Low-temperature spray/dip zinc phosphate[j]	Mild steel[d]	1.4-2.0	0.46-0.66	. . .	1.5-3.0	25-30	77-86	15-30	. . .	25-30	77-86
Zinc iron phosphate	Nitrite	Immersion zinc phosphate (low zinc)	Mild steel[d]	2.8-3.4	0.92-1.1	. . .	2-4	55-60	131-140	. . .	. . .	. . .	. . .
	Chlorate/metanitro-benzene sulphonate	Spray/dip zinc phosphate[j]	Mild steel	2.0-2.5	0.66-0.82	. . .	2-4	50-53	122-127	20-30	. . .	50-53	122-127
Rustproofing applications													
Iron phosphate	. . .	Heavy iron phosphate	Mild steel[d]	7.5-15+	2.5-4.9+	. . .	15-30	96-99	205-210	. . .	. . .	. . .	. . .
Manganese iron phosphate	. . .	Manganese phosphate (unaccelerated)	Mild steel[d]	10-30	3.3-9.8	. . .	30-90	95-100	203-212	. . .	. . .	. . .	. . .
	Nitrate	Manganese phosphate	Stainless steel or rubber-lined	7.5-15+	2.5-4.9+	. . .	5-30	96-99	205-210	. . .	. . .	. . .	. . .
	Nitroguanidine	Manganese phosphate	Mild steel[d]	7.5-15	2.5-4.9	. . .	15-30	85-95	185-203	. . .	. . .	. . .	. . .
Zinc iron phosphate	Nitrate	Zinc phosphate	Mild steel[d]	7.5+	2.5+	. . .	10-30	80-90	176-194	. . .	. . .	. . .	. . .
Antifriction applications													

Manganese iron phosphate	Nitrate	Manganese phosphate	Mild steel[d]	7.5	2.5	. . .	5-15	96-99	205-210	. . .	. . .	. . .	. . .	
Wire drawing applications														
Zinc phosphate	Nitrite	Zinc phosphate (in-line operation)	Mild steel[d]	4-8	1.3-2.6	10-30	. . .	90-95	194-203	. . .	. . .	. . .	. . .	
Tube and wire drawing applications														
Zinc phosphate	Chlorate	Zinc phosphate	Mild steel	6-12	2.0-3.9	. . .	2-15	55-70	131-158	. . .	. . .	. . .	. . .	
	Nitrite	Zinc phosphate	Mild steel	10-20	3.3-6.6	. . .	$\leq$ 20	55-95	131-203	. . .	. . .	. . .	. . .	
	Nitrate	Low-temperature zinc phosphate	Mild steel	4-10	1.3-3.3	. . .	5-15	40-50	104-122	. . .	. . .	. . .	. . .	
	Zinc calcium phosphate	Chlorate	Zinc calcium phosphate (batch)	Mild steel[d]	8-10	2.6-3.3	. . .	3-10	70-75	158-167	. . .	. . .	. . .	. . .
Zinc calcium phosphate (in-line)			Mild steel[d]	8-10	2.6-3.3	20-30	. . .	75-80	158-176	. . .	. . .	. . .	. . .	
Nitrate		Zinc phosphate (low sludge)	Mild steel	6-10	2.0-3.3	. . .	4-10	65-75	149-167	. . .	. . .	. . .	. . .	
Tube drawing lubricant applications														
Iron	. . .	Combined phosphate	Stainless steel	2-5[p] 10-	0.66-1.6[p]	. . .	5-15	65-	149-	. . .	. . .	. . .	. . .	

phosphate/lubricant		lubricant		15[q]	3.3-4.9[q]			80	176				
				Cold extrusion applications									
Zinc phosphate	Nitrite	Zinc phosphate	Mild steel[d]	10-20+	3.3-6.6+	. . .	2-10	55-95	131-203	. . .	. . .	. . .	. . .
Cold-forming aluminum applications													
Zinc phosphate	Nitrate	Zinc phosphate	Mild steel[d]	4-12	1.3-3.9	. . .	7-10	52-57	126-135	. . .	. . .	. . .	. . .
Galvanized steel applications													
Zinc phosphate	. . .	Stripline zinc phosphate	Mild steel[d]	1.6-2.0	0.52-0.66	5-15	. . .	62-69	143-156	5-15	. . .	62-69	143-156
Chromate/phosphate for aluminum applications													
Chromium phosphate	. . .	Chromate/phosphate	Stainless steel or PVC-lined mild steel	0.15-5.00	0.05-1.6	. . .	1-3	40	104	30-60	. . .	25	77

Coating type	**Control parameters**				**Other**	**Comments**	**Total acid**		**Free acid**	
	mL	**gal × 10^{-3}**	**mL**	**gal × 10^{-3}**						
	Paint bonding applications									

Iron phosphate	9-10	2.4-2.6	. . .	. . .	(a)	. . .						
	14-16	3.7-4.2	0.5-3.0	0.13-0.79	. . .	Requires precleaning. Superior performance to cleaner/coaters						
	9-10	2.4-2.6	. . .	. . .	(b)	Requires precleaning. Superior performance to cleaner/coaters						
	4.5-5.0	1.2-1.3	. . .	. . .	. . .	No precleaning necessary. Gives iridescent to gray coatings, blue when molybdate-accelerated						
	4.5-5.0	1.2-1.3	. . .	. . .	(c)	Single liquid chemical. Low operating temperature. Suitable for use with automatic control equipment						
	10-12	2.6-3.2	. . .	. . .	. . .	May be formulated as cleaner/coater for spray application	Zinc phosphate	28-30	7.4-7.9	1.3-1.5	0.34-0.40	. . .	Additions of neutralizer needed to control free acid
16-17	4.2-4.5	2.0-2.8	0.53-0.74	. . .	. . .							
10-12	2.6-3.2	0.8-1.0	0.21-0.26	. . .	. . .							
24-26	6.3-6.9	0.7-1.0	0.18-0.26	. . .	May contain fluoride and nickel for treatment of galvanized steel and limited quantities of aluminum							

14-16	3.7-4.2	0.7-1.2	0.18-0.32	. . .	Can be incorporated in closed-loop system to give total recycling of rinse water and no liquid effluent								
15-20	4.0-5.3	6-10	1.6-2.6	(e)	Tends to give coarse coatings after strong alkali cleaning or acid pickle without refining pre dip. Requires regular nitrite additions								
10-12	2.6-3.2	0.4-0.6	0.11-0.16	. . .	. . .								
15-20	4.0-5.3	. . .	. . .	(f)	Treats steel and galvanized steel in any proportion, together with maximum 15% aluminum								
14-16	3.7-4.2	0.5-2.5	0.13-0.66	. . .	Treats steel, galvanized steel and limited quantities of aluminum								
20-24	5.3-6.3	. . .	. . .	(g)	Control of zinc content may be necessary								
18-22	4.8-5.8	. . .	. . .	(h)	Refined coatings after alkali or acid cleaning without refining prerinse. Particularly suitable for one-coat finishes. Requires regular nitrite additions								
Zinc manganese phosphate	15-25	4.0-6.6	0.2-1.0	0.05-0.26	(i)	Low-temperature, low-stain. May have multimetal processing ability when fluoride-containing							
	24-26	6.3-6.9	0.7-1.0	0.18-0.26	. . .	May contain fluoride and nickel for treatment of galvanized steel and limited quantities of							

						aluminum							
Zinc iron phosphate	19-21	5.0-5.5	0.8-1.1	0.21-0.29	. . .	Submerged agitation and activating predip required							
	23-25	6.1-6.6	1.2-1.4	0.32-0.37	. . .	. . .							
Rustproofing applications													
Iron phosphate	28-32	7.4-8.4	. . .	. . .	. . .	"Working-in" of solution required. Will remove light rust. Minimum rinsing satisfactory. Not ideally suited for intermittent working							
Manganese iron phosphate	28-32	7.4-8.4	. . .	. . .	. . .	. . .							
	28-32	7.4-8.4	. . .	. . .	. . .	Coating weight and crystal structure dependent on cleaning method. Activating pre dip may be required for smooth coatings.							
	38-40	10.0-10.6	. . .	. . .	. . .	May be used without subsequent rinsing							
Zinc iron phosphate	38-42	10.0-11.1	. . .	. . .	[k]	Separate makeup and replenishment concentrates							
Antifriction applications													
Manganese iron phosphate	28-32[l]	7.4-8.4[l]	4.7-5.1[l]	1.2-1.3[l]	[k]	Coating weight and dimensional build-up dependent on pre-cleaning. Activating pre dip may							

						be required for smooth coatings.						
Wire drawing applications												
Zinc phosphate	60-70	15.8-18.5	. . .	. . .	(m)	Mild steel, stainless steel for longer life. Normally self-generating in nitrite						
Tube and wire drawing applications												
Zinc phosphate	18-22	4.8-5.8	. . .	. . .	. . .	Single chemical process. Has a higher consumption than more modern processes						
	18-22	4.8-5.8	. . .	. . .	(m)	Autogeneration of nitrite when used at 40+ points.						
	38-42	10.0-11.1	. . .	. . .	(m)	Total acid						
	40-50	10.6-13.2	. . .	. . .	(n)	Low sludge. Activating pre dip required						
Zinc calcium phosphate	18-22	4.8-5.8	. . .	. . .	. . .	Single chemical replenishment. Stable accelerator						
	65-75	17.2-19.8	. . .	. . .	. . .	Single chemical replenishment. Stable accelerator						
	20-24	5.3-6.3	. . .	. . .	(o)	. . .						
Tube drawing applications												

Iron phosphate/lubricant	. . .	. . .	. . .	. . .	(r)	No rinsing. Tubes drained at 5-15° slope for 30 min after treatment	**Cold extrusion applications**						
Zinc phosphate	18-22	. . .	. . .	. . .	(m)	Wide range of operating conditions to produce wide range of coating weights. Multichemical process							
Cold-forming aluminum applications													
Zinc phosphate	45-50	. . .	2-4	. . .	. . .	Regular fluoride additions required							
Galvanized steel applications													
Zinc phosphate	. . .	27-29	. . .	. . .	. . .	. . .							
Chromate/phosphate for aluminum applications													
Chromium phosphate	. . .	. . .	. . .	. . .	(s)	Coating weight controlled by fluoride level. Lighter coatings for paint bonding, heavier coatings for bare corrosion resistance							

Source: Ref 8

(a) 0.5-1.5 mL (1.3×10^{-4} to 4.0×10^{-4} gal) acid consumed.

(b) 1.5-3.5 mL (4.0×10^{-4} to 9.2×10^{-4} gal) acid consumed.

(c) 0.5-2.0 mL (1.3×10^{-4} to 5.3×10^{-4} gal) acid consumed.

(d) Stainless steel for longer life.

(e) 2-3 mL (5.3×10^{-4} to 7.9×10^{-4} gal) accelerator.

(f) 0.5-2.5 mL (1.3×10^{-4} to 6.6×10^{-4} gal) accelerator.

(g) Gas points (saccharometer, 0.5-2.0 mL (1.3×10^{-4} to 5.3×10^{-4} gal).

(h) 1.0-2.5 mL (2.6×10^{-4} to 6.6×10^{-4} gal) accelerator.

(i) 3-4 mL (7.9×10^{-4} to 1.1×10^{-4} gal) accelerator.

(j) Combinations of spray and dip.

(k) 0.2-0.4% Fe^{2+}.

(l) 0.2 M NaOH.

(m) Accelerator starch/iodide paper.

(n) 0.13% max Fe^{2+}.

(o) 0.2% max Fe^{2+}.

(p) Phosphate contribution.

(q) Lubricant contribution.

(r) H_2O content, 1.5-2.0%.

(s) Chromate pointage, 4-5 mL (1.1×10^{-3} to 1.3×10^{-3} gal).

Reference cited in this section

8. D.B. Freeman, *Phosphating and Metal Treatment,* Industrial Press, Inc., 1986, p 199-217

Product Standards for Phosphating (Ref 9)

In most industrialized countries, there exist published standards and specifications relating to phosphating. These standards describe various processes used in the phosphating (process standards) of iron and steel, zinc and its alloys (including both electrolytic and hot-dipped zinc) as well as cadmium and, to some extent, aluminum. Some of these standards relate specifically to the composition of the concentrates (chemical standards) used for making up the phosphating solutions. In addition, some countries provide standards for specific types of products, for which the phosphate coatings must possess certain properties.

Most standards and process specifications prescribe how the phosphate coatings should be prepared and how they enhance the properties of the substrate metal, with or without post-treatment. In several standards, a requirement exists for the presence of a phosphate coating on the base metal in question or for a qualitative test of its composition. Many standards relate to the coating weight required. In addition, these standards specify minimum coating weight or coating weight ranges for a given type of service. These specifications describe in detail the tests that can be used to determine the properties of phosphate coatings, both in their untreated state and also after post-treatment with corrosion-inhibiting oils, greases, or waxes, as well as paint and other coatings.

The extent to which standards and specifications are legally binding differs widely. Those carrying the greatest weight are issued by governmental bodies or military agencies, and regulatory bodies, both federal and military, exist not only in the United States but also in a number of European countries. An international standard relating to phosphating is in course of preparation (in collaboration with the International Standards Organization, or ISO) while in many countries, standards relating to phosphating have been published, in most cases after extensive collaboration with industry. Most of these standards provide a framework within which supplier and customer may draw up an agreement. In such national standards, care has been taken that the interests of both these parties are safe-guarded. However, it should be recognized that a number of firms and trade organizations impose their own modifications on national standards.

Phosphating standards and specifications for selected Western countries are listed in Table 17. Only rarely are phosphate coatings specified in terms of actual thickness. Most of these specifications detail methods used for analytical control and for testing of the phosphate coating itself.

Table 17 Industrial standards and process specifications for phosphating of metals in selected Western countries

Country	Standard	Section	Date of original adoption or last revision	Description
Federal Republic of Germany	DIN 50017 KK	. . .	. . .	Phosphate coating performance in condensed water at constant temperature
	DIN 50021 SS	. . .	. . .	Phosphate coating performance in salt spray
	DIN 50942	. . .	May 1987	Phosphating of metals: process fundamentals and test methods
Italy	UNI 4195	. . .	. . .	Magnetic method used to measure thickness of phosphate coatings

Country	Standard	Section	Date of original adoption or last revision	Description
	UNI 4236	4, 5	. . .	Qualitative testing for phosphate in coatings
		6, 7	. . .	Qualitative testing for zinc or manganese in phosphate coatings
	UNI 4239	. . .	. . .	Test for corrosion resistance of phosphate coating based on effect of acetic acid salt spray on coating porosity
	UNI 4527	. . .	. . .	Test for corrosion resistance of phosphate coating based on effect of aerated boiling water on coating porosity
	UNI 4528	. . .	June 1960	Surface treatment of metals; determination of phosphate coating weight
	UNI 4716	. . .	April 1961	Surface treatment of metals; properties of and tests for phosphate coatings to reduce seizing and to protect against wear
	UNI 4722	. . .	April 1961	Surface treatment of metals; testing efficacy of phosphate coatings to reduce fretting
	UNI 5343-64	. . .	Feb 1964	Chemical and electrochemical surface treatment; phosphate coatings for corrosion protection (types of coating, properties, testing)
Japan	JIS 3151	. . .	1987	Phosphate coatings as base for paint application
	JIS K 5400	. . .	. . .	General testing methods for coatings
		6.11	. . .	Impact test (uses 300 g, or 0.7 lb, weight dropped from 1000 mm, or 40 in., height)
		6.12	. . .	Flexibility test (bending over a 3 mm, or 0.12 in., diameter mandrel)
	JIS Z 0228	. . .	. . .	Wetting test method for rust-preventing oil
	JIS Z 2371	. . .	. . .	Corrosion testing with exposure to continuous salt spray (5% NaCl, with pH of 6.5 to 7.2, at temperature of 35 ± 2 °C, or 95 ± 4 °F)

Country	Standard	Section	Date of original adoption or last revision	Description
Sweden	FSD 6104	. . .	. . .	Corrosion resistance of phosphated surfaces exposed to salt spray for 240 h
	FSD 6238	. . .	10 Oct 1982	Phosphating and oiling of steel components
	FSD 6240	. . .	1 Jan 1985	Phosphating as an undercoat for painting of aluminum, zinc, and alloys of those metals
	FSD 7701	. . .	. . .	Immersion of workpiece components in corrosion-preventing oil
	K 242	. . .	. . .	Theoretical principles of surface treatment of metals
	K 3430	. . .	1968	Overview of surface treatment of metals
	K 3431	. . .	1968	Manganese phosphating of steel
	K 3432	. . .	1970	Zinc phosphating of steel
	K 3433	. . .	1970	Alkali phosphating of steel
	K 4531	. . .	1957	Bath control for surface treatment of metals
	YB 1303	. . .	. . .	Surface treatment guidelines for phosphating of zinc (or zinc-coated steel) with manganese or zinc phosphates prior to application of oils or paint coatings
	YB 5301	. . .	. . .	Nondrying oils for phosphate coatings
	YB 5302	. . .	. . .	Drying oils for phosphate coatings
	YB 7102	. . .	. . .	Testing corrosion resistance of phosphate coatings exposed to salt spray
United Kingdom	BS 1391	. . .	. . .	Salt-drop testing of phosphated and post-treated iron and steel components
	BS 3189	. . .	Sept 1973	Properties and applications of phosphate-coated irons and steels

Country	**Standard**	**Section**	**Date of original adoption or last revision**	**Description**
		Appendix B	. . .	Reduction of stress in the substrate of phosphate-coated components through the use of heat treatment
		Appendix D	. . .	Drop test to identify typical phosphate coatings
	BS 3900	. . .	. . .	Methods of testing paints
		Part 2	. . .	Resistance to humidity under condensation conditions
		Part 7	. . .	Determination of resistance to water
	BS AU148	. . .	. . .	Testing methods for motor vehicle paints
	DEF STAN 03-11/12	. . .	26 May 1986	Phosphating of iron and steel for corrosion protection and reduction of friction
United States	ASTM B 633	. . .	1985	Electrolytically coated zinc on iron and steel components
	ASTM D 2092	. . .	1986	Preparation of zinc-coated galvanized steel surfaces for painting
	DOD-P-16232 F	. . .	7 Nov 1978	Heavy-duty zinc or manganese phosphate coatings for steel
	Federal Test Method Standard 141, Method 6061	. . .	. . .	Corrosion resistance of coating exposed to 5% salt spray
	MIL-C-10578 D	. . .	28 Feb 1982	Phosphoric acid-based treatments for metal surfaces and for rust removal
	MIL-P-15328	. . .	. . .	Organic pretreatment coatings
	MIL-P-50002 B	. . .	5 Aug 1981	Phosphating chemicals for coating steels
	MIL-T-12879	. . .	21 Feb 1986	Chemical pretreatment of zinc surfaces for paint application and corrosion protection
	MIL-HDBK-205 A	. . .	15 July 1985	Phosphating and brown-colored coatings on ferrous metals

Country	Standard	Section	Date of original adoption or last revision	Description
	Federal specification TT-C-490 C	. . .	18 March 1985	Cleaning and pretreatment of steel surfaces (including cases where some surfaces are of zinc or aluminum) prior to the application of paint or other organic coatings

Source: Ref 9

Reference cited in this section

9. W. Rausch, *The Phosphating of Metals,* ASM International and Finishing Publications Ltd., 1990, p 355-374

Safety Precautions

Safety precautions on a phosphating line must begin with the basic design of the equipment involved.

Immersion Phosphating. Proper ventilation of immersion tanks is necessary to eliminate concentration of vapors from the tanks in buildings or work areas. Local regulations in some areas, however, may prohibit exhausting directly to the outside, and special filtering equipment may be required. Tanks containing acid must be resistant to the acid they hold to eliminate the possibility of the acid corroding through the tanks and spilling on to the floor. Curbing should surround tanks to retain spilled or leaked solutions.

Spray Phosphating. Equipment used in spray phosphating must be properly vented for removing vapors. A heavy grating should surmount each of the various tanks for protecting the personnel cleaning and repairing tanks, risers, and spray nozzles. These gratings also prevent workpieces from falling into tanks from conveyors. Access doors in drain areas, which are used for checking carryover and condition of work, and for access during breakdown, should be easily opened from the inside.

Handling of Alkalis and Acids. All alkaline cleaners should be handled with care. Rubber gloves and face or eye shields should be worn when these materials are added to cleaning tanks. Should these materials contact the skin, it should be flushed with water as soon as possible. Repeated or prolonged contact can cause skin irritation.

These precautions apply also to handling the phosphoric acid and chromic acid used in phosphating. Although chromic acid is oxidizing, it does not burn the skin immediately, as do common mineral acids, but severe irritation results from prolonged exposure to the skin. Goggles or face shields should be worn at all times during handling of chromic acid, because contact with the eyes can cause serious damage. All contaminated clothing should be removed and washed before reuse.

To transfer liquid from a carboy, a carboy-tilter, commercial siphon, or bulb siphon should be used. Liquid should never be drawn from a carboy by using air pressure to force it out, even when using the so-called air pressure reducers. Danger is always present that the carboy will break, or even explode, and spray or splash acid on the operator. This also holds true for drums. All drums should be specified to be plugged with one-way breather plugs. If this is not possible, the solid plug must be removed carefully to avoid acid spray, and only enough to permit the compressed gases to escape slowly. Once the inside and outside pressures are equalized, the plug may be removed.

Cyanide (Ref 10, 11) is a highly toxic chemical that can kill almost instantly. Nevertheless, despite the constant and widespread use of cyanide, deaths and illnesses associated with its use are rare. There is little danger if certain guidelines are followed closely:

- All containers for cyanide, full or empty, should have airtight lids, be stored in a well-ventilated area, and be clearly labeled as containing poison. No unauthorized person should have access to them.
- Cyanide should be handled only with gloved hands or tongs, in a well-ventilated area.

- Keep work areas meticulously clean. Spills of acid and cyanide that combine on the shop floor, or in floor drains, can generate hydrogen cyanide gas. The gas is extremely lethal if inhaled; it is the primary cause of cyanide-related deaths.
- Be prepared to provide immediate first aid in case of contact with cyanide salts. Wash the affected area in water, then with dilute sodium hypochlorite or bleaching powder solution, when with water again.

References cited in this section

10. L.J. Durney, Ed., *Electroplating Engineering Handbook,* 4th ed., Van Nostrand Reinhold Company, 1984, p 342-343
11. N.V. Parthasaradhy, *Practical Electroplating Handbook,* Prentice Hall, 1989, p 409

Treatment of Effluents from Phosphating Plants

Because aqueous effluents from phosphating plants contain both organic and inorganic residues which can damage the environment, they must be treated before they can be discharged into a public drainage system or other watercourse. Legal requirements and local laws and regulations determine how extensively the by-products of the phosphating process must be treated for proper disposal.

U.S. Regulations (Ref 12)

In the United States, industrial waste discharges are regulated by the federal government under the Clean Water Act of 1977, revised by the Water Quality Act of 1987, and are subject to additional regulation by state and local governments. Federal environmental regulations are administered by the EPA and appear in the Code of Federal Regulations (CFR), Volume 40. Some overall requirements exist that are designed to protect U.S. waters from polluting contaminants and that establish prohibitions against pollution in a broad sense.

More specific requirements are found in what are referred to as categorical standards (for example, industry-specific regulations setting numerical limitations on specific effluent parameters). These regulations are managed under the National Pollutant Discharge Elimination System (NPDES) for direct discharge to surface waters and the Pretreatment Program for discharge to sewer systems. A permit is required to discharge wastewater to any surface water, and it sets forth conditions under which wastewaters must be managed, allowable contaminants in the discharge, and permitted effluent flows.

Federal regulations covering phosphating are primarily found under the electroplating (Volume 40, Part 413) and metal finishing categories (Volume 40, Part 433) in the CFR. Table 18 summarizes effluent limitations for these industry segments. Table 18 is an oversimplification of actual regulations; the specific categorical regulations are complicated by several qualifying statements and requirements. It does provide a good indication, however, of the prevailing limitations on effluents discharged from metal finishing and electroplating operations. Individual permit requirements may vary and will include limitations on pH, suspended solids, and oil and grease.

Table 18 Effluent limits for phosphate coating processes per U.S. Code of Federal Regulations

Component	Electroplating (40 CFR 413)				Metal finishing (40 CFR 433)			
	1-day max		4-day avg		1-day max		Monthly avg	
	mg/L	lb/gal × 10^{-5}	mg/L	lb/gal × 10^{-5}	mg/L	lb/gal × 10^{-5}	mg/L	lb/gal × 10^{-5}
Cadmium	1.2	1.0	0.7	0.6	0.69	0.58	0.26	0.22

Chromium	7.0	5.8	4.0	3.3	2.77	2.31	1.71	1.43
Copper	4.5	3.8	2.7	2.3	3.38	2.82	2.07	1.73
Cyanide (total)	1.9	1.6	1.0	0.8	1.2	1.0	0.65	0.54
Lead	0.6	0.5	0.4	0.3	0.69	0.58	0.43	0.35
Nickel	4.1	3.4	2.6	2.2	3.98	3.32	2.38	1.99
Silver	1.2	1.0	0.7	0.6	0.43	0.36	0.24	0.20
Zinc	4.2	3.5	2.6	2.2	2.61	2.18	1.48	1.24
Total toxic organics[(a)]	2.13	1.78	. . .	. . .	2.13	1.78	. . .	. . .

Source: Ref 12

(a) Summed concentration of a list of 110 specific organic compounds.

Groundwater protection is accomplished primarily through the Resource Conservation and Recovery Act (RCRA) of 1976, as revised by the Hazardous and Solid Waste Amendments of 1984, which regulate waste management. The significant effect of this legislation on the phosphating industry is through regulation of treatment, storage, transportation, and disposal practices for waste treatment sludges and spent baths. Requirements include a "cradle to grave" accountability for those wastes defined as "hazardous" by regulations, strict controls and permitting of waste management facilities, and prohibitions against land disposal without treatment by approved procedures or to meet specified standards.

Environmental impairment from past disposal practices and from accidental releases or spills is covered by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), commonly known as Superfund due to the provision for government funding of cleanups when no responsible parties can be identified. Both RCRA and CERCLA regulations specifically prohibit contamination of groundwater. Enforcement occurs at both the state and federal levels, as for effluent discharge violations. Fines and criminal penalties are assessed for both corporations and individuals. The liability issues arising out of these regulations and the increasing cost of waste treatment and disposal have dramatically altered the approach to waste management and are driving industry toward recovery, recycling, and waste minimization.

State or local regulations may be more stringent than federal regulations, but they may not be less stringent. For example, the following limits were imposed on an ordnance manufacturer in Gadsden, Alabama, by the Alabama Water Improvement Commission (Ref 13):

Contaminant	Concentration limit (6.0 < pH <9.5), ppm
Cr	0.5

Cr^{6+}	0.1
PO^{3-}_4(as P)	1.0
Ni	0.5
Zn	0.8

Most states have applied for and obtained authority to implement the federal NPDES program, and many have additional regulations governing discharges. Enforcement is accomplished at the state and federal levels. Violations can carry both civil and criminal penalties.

Solid and Liquid Waste Disposal

The phosphating process generates both solid and liquid wastes that require proper disposal procedures to minimize any negative impact on the environment. Figure 15 shows typical techniques for collecting the sludge produced by the phosphating process. Typical sludge removal methods are described in Fig. 16.

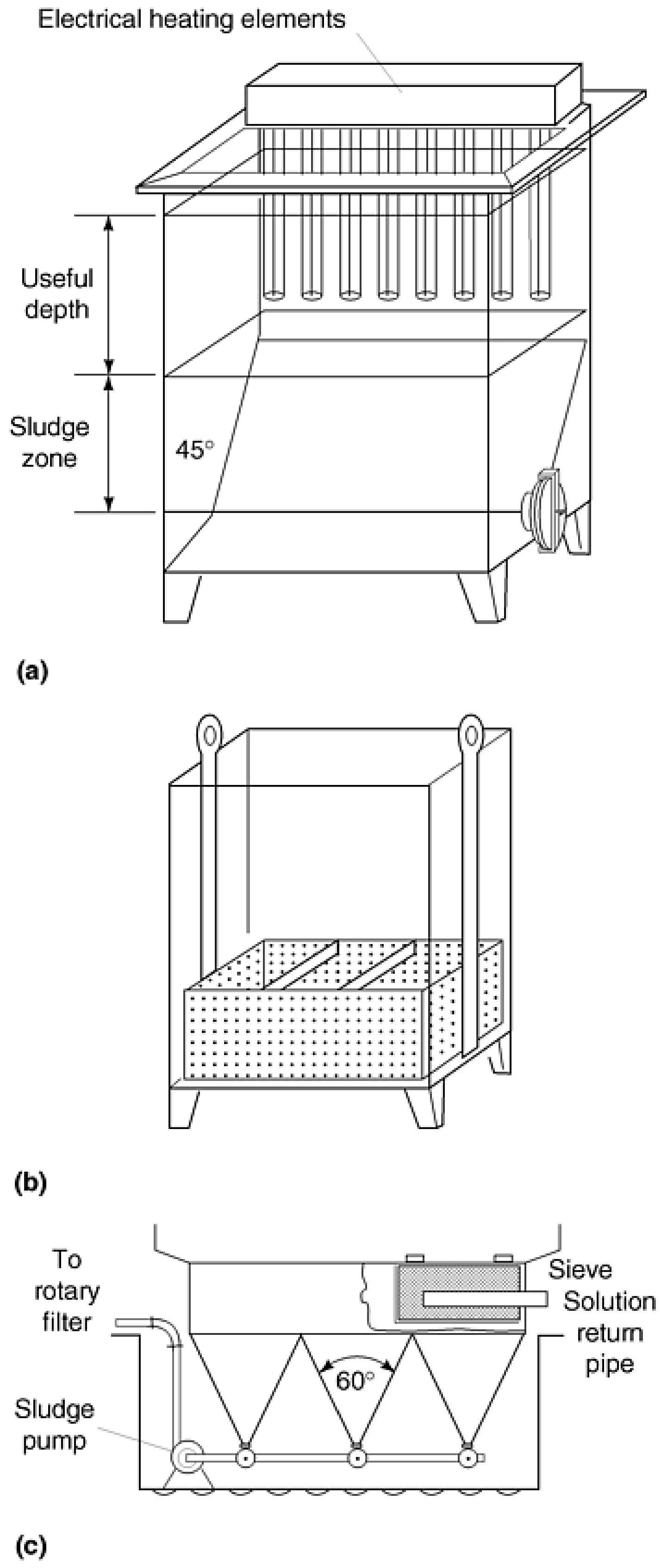

Fig. 15 Sludge-settling methods for immersion phosphate tanks. (a) Sloping bottom. (b) Removable settling box. (c) Conical-formed floor. Source: Ref 14

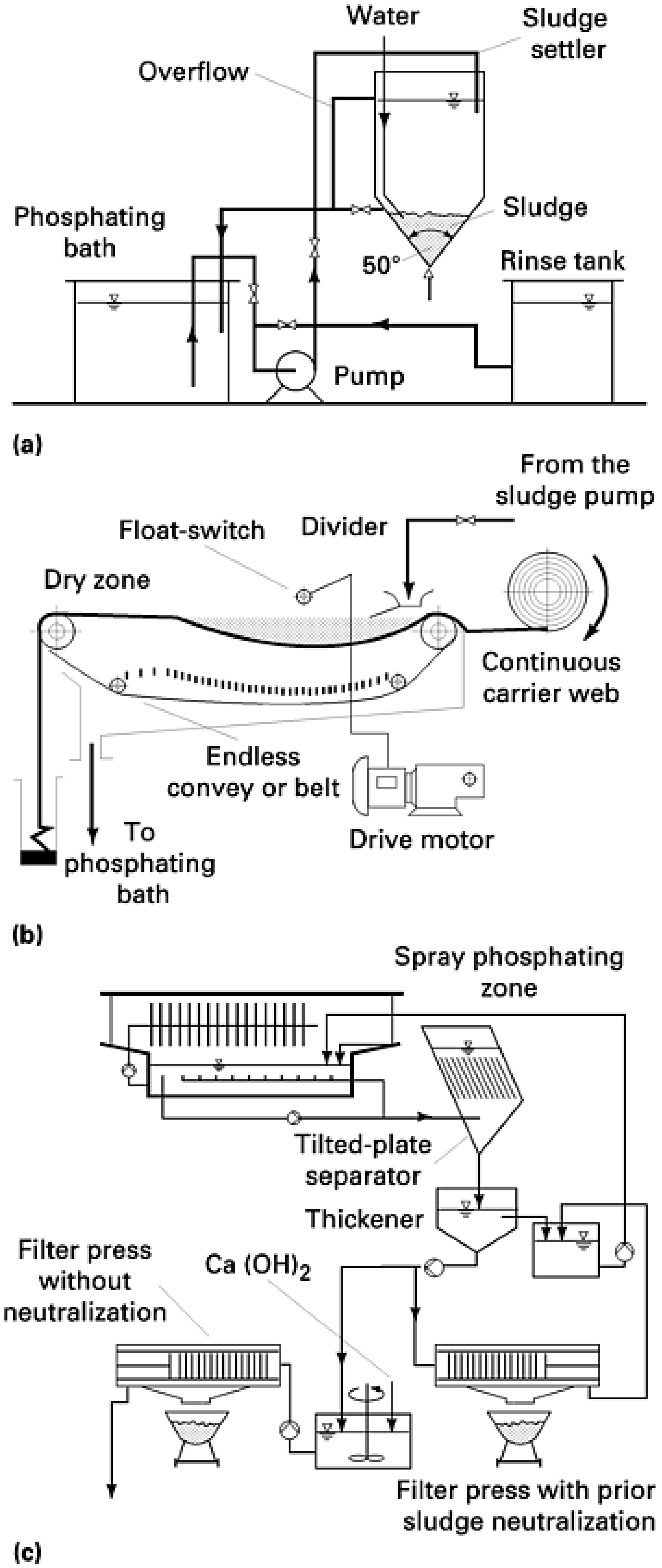

Fig. 16 Methods for removing sludge from a phosphating tank. (a) Settling tank. (b) Continuously operating cloth belt filter. (c) Tilting plate separator, thickener, and filter press. Source: Ref 15

Sludge Regulation (Ref 16). Under the RCRA, there are two types of hazardous waste: *categorical* (the waste comes from a certain industry or operation) and *characteristic* (the waste possesses certain hazardous characteristics: ignitability,

toxicity, corrosivity, and/or reactivity). The EPA and the states are authorized to make these classifications. For example, according to the EPA, all wastewater treatment sludges from electroplating operations are categorically hazardous. The prepaint cleaner, phosphating and chromating sludges, spent baths, and rinsewaters used in electroplating operations are not considered categorically hazardous, but if they show hazardous characteristics upon testing, they would be subject to the RCRA.

Sludges in Prepaint Phosphating Lines (Ref 16). In the automotive industry, and other industries that use large zinc and iron phosphating lines, it has long been general practice to routinely filter sludge from phosphate baths. Today, the ever-higher cost of phosphating chemicals and the ever-tighter regulation of sludge disposal make it economically worthwhile for small operations to investigate filtering.

In the typical prepaint finishing line, there are several types of sludge: (*a*) sludge from the cleaner rinse and ultrafilter reject, which is not hazardous; (*b*) sludge from the phosphating rinse, which is hazardous if the nickel content is high; and (*c*) sludge from the chromating rinse, which is hazardous because of the presence of hexavalent chromium or because trivalent chromium wastes are mixed with other wastes that may oxidize the trivalent chromium to hexavalent. Although these sludges are initially separate, they usually become commingled because the wastewaters generating them are treated in a centralized system. Thus, the sludge is hazardous, from the chromium content alone if not from chromium plus nickel.

When zinc phosphating sludge is fed into a wastewater treatment system, a number of costs are incurred: the cost of process chemicals, the cost of lime (used to precipitate zinc and to neutralize residual phosphoric acid), and the cost of disposing large quantities of hazardous sludge. Moreover, precipitating the sludge by lime increases the volume of the sludge (Fig. 17). A filter press system can reduce this volume by dewatering phosphate sludges, changing them from 5% solids to 30% solids. It also saves phosphating chemicals.

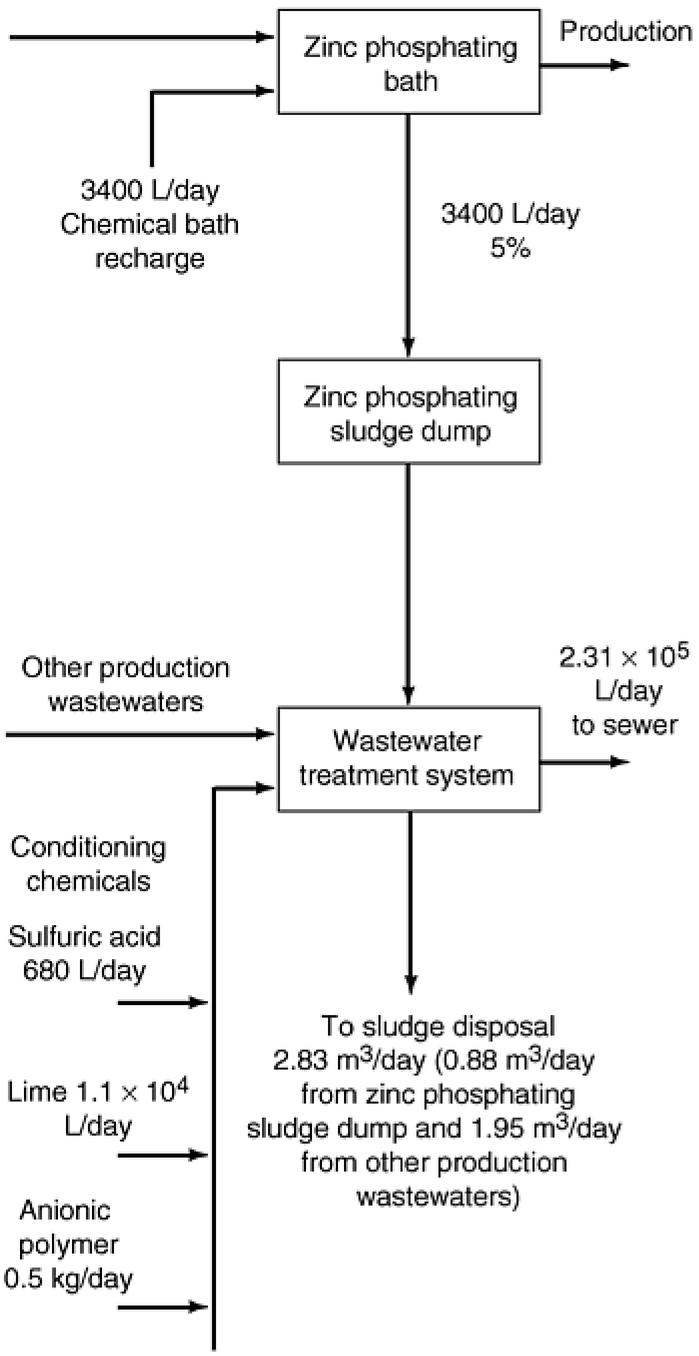

Fig. 17 Flowchart showing typical sludge output produced by zinc phosphate coil coating line. Source: Ref 17

If the flow of sludge to the wastewater treatment system is 190 L/min (50 gal/min), and the sludge consistency is 30% solids, the projected quantity of wet sludge, including zinc phosphating sludge, is 2.83 m^3/day (100 ft^3/day). The quantity produced by the wastewater treatment system after segregating the zinc phosphating sludge is 1.95 m^3/day (69 ft^3/day), but the projected quantity produced from the zinc phosphating bath after dewatering is 0.57 m^3/day (20 ft^3/day), resulting in a total net reduction of 0.31 m^3/day (11 ft^3/day).

Table 19 summarizes treatment options for sludges generated by prepaint phosphating lines.

Table 19 Treatment options for sludges generated by prepaint lines

Option	Treatment concept	Treatment technology

No.		
1	Dispose cleaner and phosphating rinsewater sludges and cleaner ultrafilter reject at Subtitle D facility. Segregate and treat separately the chromating wastewaters.	Batch tank for chromating wastewaters where hexavalent chromium is reduced to trivalent and precipitated. The sludge is sent to a Subtitle C facility (that is, a hazardous waste landfill).
2	Segregate the cleaner rinsewater and ultrafilter reject wastes. Treat and discharge separately.	Neutralization and oil recovery/destruction if effluent limits would be exceeded
3	Treat the phosphate rinsewaters in order to eliminate their hazardous contribution to the sludges, in combination with option 1.	Use reverse osmosis to recover the phosphating bath (that is, in the rinse plus technology listed above for option 1).
4	Leave sludges as they are and dewater as much as possible.	High-pressure filter press

Source: Ref 16

Equipment Selection and Operation (Ref 17). One plant chose as a dewatering device a filter press that is rated at 0.57 m^3/day (20 ft^3/day). A filter press system was chosen over continuous on-line filters and settling towers because these would have produced a liquid slurry that would have required drum disposal or further dewatering.

The components of the filter press system are a sludge holding tank, filter press feed pump, filter press, and filtrate return tank with transfer pump (Fig. 18). After the sludge in the zinc phosphating tank settles, it is pumped to the sludge holding tank for further compaction. Any solids-free bath is decanted back to the filtrate return tank. The filtered zinc phosphating bath solution is transferred to the process tank at the rate of 2860 L/day (750 gal/day), compared to the original 3430 L/day (900 gal/day), a makeup rate of 570 L/day (150 gal/day). This procedure is performed daily during the four hours of downtime for the zinc phosphating bath.

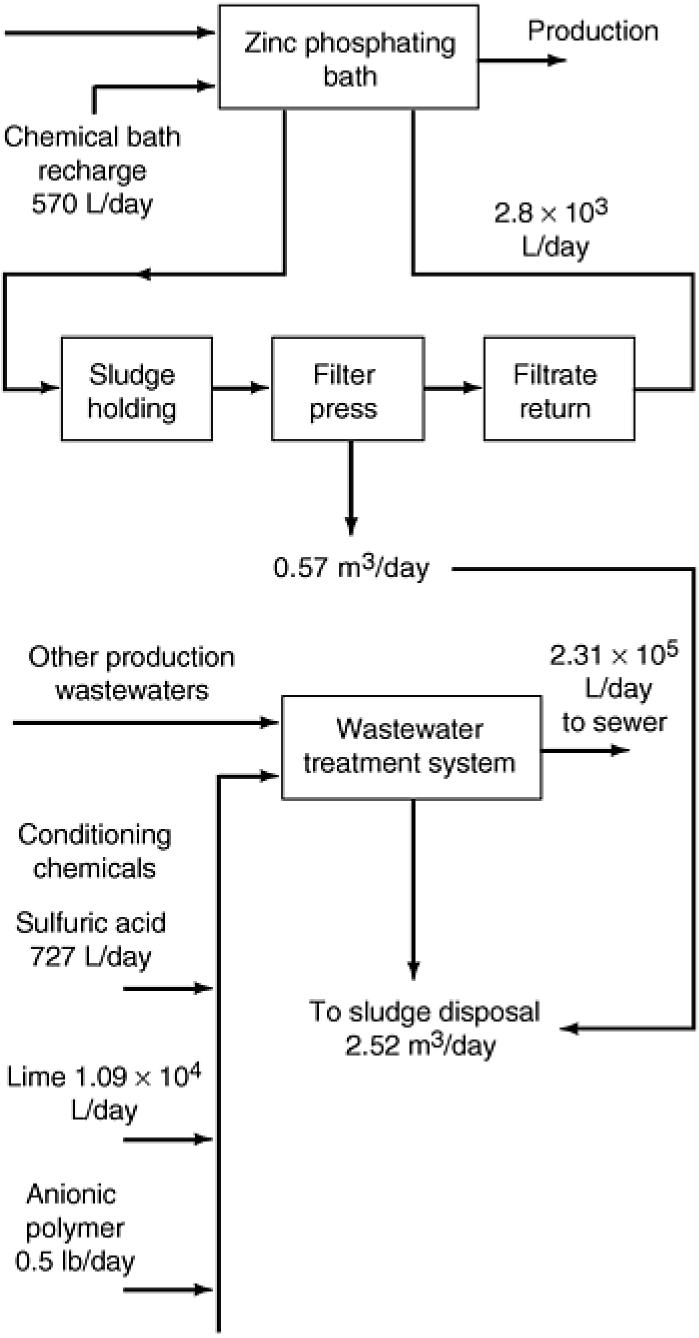

Fig. 18 Flowchart showing sludge output produced by zinc phosphate coil coating line retrofitted with a filter press. Source: Ref 17

Disposal of Solutions. Nearly all municipalities have maximum limitations on the acids, solids, chromium, zinc, nickel, iron, and oil that may be drained to a stream or sewer system. Because these limits vary widely, local governmental authorities should be consulted for specific restrictions on each toxic or nontoxic material in a phosphating system so that proper waste treatment plans can be made. The trend is toward stricter controls, and waste treatment programs should include a margin of safety to accommodate future changes. Limits and suggested treatments for the more serious contaminants from a phosphating system are indicated in Table 20. The waste treatment methods described are widely used, but other methods also are available.

Table 20 Limits and treatments of contaminants from a phosphating system

Containment	Direct discharge,	Publicly owned treatment

	ppm	works, ppm[a]
Chromium		
Hexavalent	0.05	0.05-5.0
Total	0.10-0.5	1.0-10.0
Zinc	0.1-0.5	1.0-5.0
Nickel	0.1-0.5	1.0-5.0
Oil	1.0-10.0	10.0-100

(a) Environmental protection laws are subject to change. Suppliers of the metal pretreatment should be contacted to determine needs in terms of treatments of these chemicals.

Two sets of limits need to be considered: direct discharge to streams, lakes, and rivers; and discharge to publicly owned treatment works. Table 20 lists the limits of contaminants.

Soda ash is not the best neutralizing agent. In order of preference, lime, caustic, and soda ash are suggested. Recommended neutralization pH values are:

Chemical	**pH range**
Zinc	7.0-9.0
Nickel	8.5-9.5
Chromium	8.0-9.0

Limits and Treatments of Contaminants. It is inevitable that contaminants such as metals, acids, and oils build up and must be removed from the phosphate bath when excess amounts interfere with the coating process.

Acidity is influenced by cleaning stage (alkaline), phosphating stage (acid), and final rinse (acid).

Chromium. Of all the materials used in metal pretreatment, those containing hexavalent chromium probably require the most stringent treatment, as the amount of hexavalent chromium allowed in discharges by most authorities varies from 0 to less than 1 ppm (Ref 18). Most of the chromium in final rinse stage is in the more toxic hexavalent form. However, it can be readily reduced to the less toxic trivalent form (reduction of Cr^{6+} to Cr^{3+} yields a product 100 times less toxic)(Ref 19) with sodium bisulfite or sodium metabisulfite in a pH range of 3.5 to 5.0. To remove the trivalent chromium, add an alkaline material such as soda ash, mixing thoroughly, to a pH of 8.5 to 10.0, allow to settle for 1 h, and draw off the

liquid, leaving the chromium in the sludge. The drawn-off liquid is essentially water and may be discharged into a sewer or stream in the normal manner, in compliance with local regulations.

Zinc. Usually, it is economically desirable to avoid any loss of zinc phosphating solution, and therefore a problem exists only in disposal of the rinse solution (contaminated water) following the phosphating stage and disposal of the sludge periodically removed from the phosphating tank. The sludge should be hauled to a suitable dump, rather than discharged into a sewer or stream. If it is necessary to dispose of a zinc phosphating solution, or if the rinse water, following the phosphating stage, contains enough zinc phosphating solution from carryover to create a disposal problem, first precipitate the zinc by raising the pH to 8.5 to 10.0 with any available alkaline material, such as soda ash. Then, after thorough mixing, allow to settle for 1 h and draw off the liquid, leaving the zinc to be handled as a sludge. This drawn-off liquid also is essentially water and may be discharged into a sewer or stream in the normal manner, in compliance with local regulations.

Nickel. Some of the newer zinc phosphating compounds that coat both bare and galvanized steel contain appreciable quantities of nickel. This presents no in-plant problems of disposal because nickel is precipitated along with zinc when disposal of contaminated rinse water or phosphating solution is required. However, because nickel may be more harmful in a sewage disposal plant, some municipalities that have accepted small quantities of zinc in the drain water demand almost complete freedom from nickel. More complete processing of solutions is required in these situations.

Oil. Most phosphating systems do not present a serious problem in treatment of oil waste, but some manganese of zinc phosphating systems contain a final oil or soluble-oil dip. A few systems have sufficient oil removed from parts in the cleaning stage to require treatment. Most soluble-oil and water solutions can be broken with calcium chloride, often assisted by small additions of aluminum sulfate or flocculating agents. The separated oil layer is floated off for removal in a tank truck or in drums, and the water, if sufficiently clear, is metered to a sewer system. Oils must be physically removed for such nonharmful uses as dust-laying treatments of dirt or gravel roads or parking lots.

Cyanide (Ref 20). Users of cyanide incur perpetual liability as generators of hazardous sludge. For example, aluminum finishers remove cyanide from waste water by precipitation, and the sludge may contain a total cyanide concentration of 1 to 10% (10^4 to 10^5 ppm). The EPA has ruled that such a sludge cannot be landfilled, so aluminum finishers must either stop using cyanide or destroy it in the sludge. However, ferricyanide, the forum of cyanide in aluminum pretreatments, is extremely stable and cannot be destroyed by chlorination, the relatively simple process that destroys free cyanide. Commercial methods are under development for destroying ferricyanide, but they are complex and expensive.

U.K. Regulations (Ref 21)

Consent limits for discharge to public drains in the United Kingdom are set by the eight regional water companies. In general these limits are established on a case-by-case basis rather than by the imposition of overall national or local standards. In determining the limits in individual cases, consideration is given not only to the concentration of individual pollutants but also to factors such as location, total volume of discharge, and the capacity of, and methods used by, local treatment works.

Discharge to streams, rivers, and coastal waters is controlled by the National Rivers Authority.

It should be borne in mind that the transport and labeling of solid and liquid wastes is also regulated. Solid and semisolid waste arises from the neutralization and precipitation of effluent in in-house treatment facilities and also from the sludge generated as a by-product of heavy metal phosphating processes. This sludge is removed on a continuous or batch basis and is usually disposed of to landfill sites. However, before this is done, under the Control of Pollution Act of 1974, a disposal license must be obtained from the local disposal authority, which will require detailed data on the nature of the waste.

The conveyance and labeling of hazardous wastes is covered by:

- Dangerous Substances (Conveyed by Road in Tanks and Tank Containers) Regulations, 1981
- Road Traffic (Carriage of Dangerous Substances in Packages) Regulations, 1986
- Classification, Packaging, and Labeling of Dangerous Substances Regulations, 1984

Federal Republic of Germany Regulations (Ref 22)

Legislation covering water management (water management law WHG, amended as of 23 Sept 1984) relates to surface waters, coastal waters, and groundwater. It makes the use of water (for example, by its abstraction, as well as by introduction, into discharged water, of dissolved or suspended matter) a measure requiring official consent. In addition, it requires reservoirs or lagoons for the storage and/or settling of toxic substances (for example, acids, alkalis, and pickling salts) to be constructed and operated so that impurities cannot reach the water table. Consent for discharge will only be given where the burden of toxic materials is kept as low as possible, concentrations of specific species complying with legislative requirements (Table 21).

Table 21 Effluent levels for phosphate coating process discharges in the Federal Republic of Germany

Discharge type	Temperature[a]		pH value	Suspended solids[a]		Chemical oxygen demand[a]		Toxicity to finishes as a dilution factor (G_F)[a]	Composition, mg/L(lb/gal × 10^{-5})[a]												
	°C	°F		mL/L	mL/gal	mg/L	lb/gal × 10^{-3}		Saponifiable oils and fats	Hydrocarbons	Cd	Cr[b]	Cr^{6+}	Fe	Cu	Ni	Zn	NH_4	F	NO_3	NO
Discharge into watercourse[c]																					
Electroplating	. . .	. . .	. . .	0.3	1.1	600	5.0	8	. . .	10 (8.3)	0.5 (0.4)	2 (1.7)	0.5 (0.4)	3 (2.5)	2 (1.7)	3 (2.5)	5 (4.2)	100 (80)	50 (42)	. . .	. . .
Organic coating	. . .	. . .	. . .	0.3	1.1	800	6.7	10	. . .	10 (8.3)	0.5 (0.4)	1 (0.8)	0.5 (0.4)	3 (2.5)	2 (1.7)	1 (0.8)	3 (2.5)	. . .	. . .	. . .	. . .
Discharge into main drainage systems																					
ATV A115 Jan 83	35		6.5-10	1	4	. . .	. . .	. . .	250 (210)	20 (17)	0.5 (0.4)	3 (2.5)	0.5 (0.4)	10 (8.3)	2 (1.7)	3 (2.5)	5 (4.2)	165 (138)	60 (50)	. . .	20 (17
State of Bad Wuerttemburg	35		6.0-9.5	1	4	. . .	. . .	. . .	. . .	20 (17)	1 (0.8)	2 (1.7)	0.5 (0.4)	. . .	2 (1.7)	3 (2.5)	5 (4.2)	50 (42)	50 (42)	. . .	10 (8.3
City of Mannheim	35		6.0-9.0	1	4	. . .	. . .	. . .	100 (84)	20 (17)	1 (0.8)	3 (2.5)	0.1 (0.08)	20 (17)	1 (0.8)	3 (2.5)	3 (2.5)	20 (17)	. . .	50 (42)	30 (25

Note: As specified by local, state, and federal government regulations.

Source: Ref 22

(a) Prescribed maximum values.

(b) Total chromium.

(c) Per standard. WHG 40, effluent VwV of 5 Sept 1984.

Discharge of effluent into main drains is governed by local authority legislation. These may specify the levels of toxic species discharged or the levels may be dealt with by consent at a case-by-case level. The basis, in all cases, will be guidelines as in Ruling ATVA 115, published by the Technical Effluent Group (ATV), which collaborates with the national association of urban environmental authorities (VKS)(Table 21).

According to effluent discharge legislation (AbwAG, most recent amendment 14 Dec 1984), those responsible for effluent discharge are liable to pay the local authority a sum based on the volume and nature of the effluent.

Under the terms of refuse legislation (AbfG, dated 11 Sept 1986), restrictions are imposed on the dumping of trade waste and other industrial materials that pose a potential threat to air or water quality. Such effluents can be handled, stored, processed, or shipped only at locations for which permission has been given. In the listing of types of noxious species published as an appendix to this legislation, the following categories of chemicals from the surface finishing industries are listed: acids, alkalis, oil emulsions, and residues from cleaning and degreasing baths.

References cited in this section

12. W. Rausch, *The Phosphating of Metals,* ASM International and Finishing Publications Ltd., 1990, p 296-298
13. Treating Rinses from Zinc Phosphatizing, *Prod. Finish.,* Nov 1978, p 56-59
14. W. Rausch, *The Phosphating of Metals,* ASM International and Finishing Publications Ltd., 1990, p 267-268
15. W. Rausch, *The Phosphating of Metals,* ASM International and Finishing Publications Ltd., 1990, p 280
16. C.R. Marshall and T. Daily, Getting a Payback from Waste Treatment, Part III: Pretreatment Sludges, *Prod. Finish.,* 1990, p 75-80
17. T. Daily and T. Henley, Getting a Payback from Waste Treatment, Part II: Phosphating Chemicals, *Prod. Finish.,* Dec 1989, p 65-71
18. D.B. Freeman, *Phosphating and Metal Treatment,* Industrial Press, Inc., 1986, p 182
19. B.R.W. Hinton, Corrosion Prevention and Chromates, the End of an Era, *Met. Finish.,* Sept 1991, p 55-61
20. J.R. Favilla, No-Rinse Treatment for Aluminum, *Prod. Finish.,* Nov 1990, p 45-55
21. W. Rausch, *The Phosphating of Metals,* ASM International and Finishing Publications Ltd., 1990, p 296
22. W. Rausch, *The Phosphating of Metals,* ASM International and Finishing Publications Ltd., 1990, p 294-296

Chromate Conversion Coatings

Patrick L. Hagans, Naval Research Laboratory; Christina M. Haas, Henkel Corporation

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Introduction

CHROMATE CONVERSION COATINGS are formed on metal surfaces as a result of the chemical attack that occurs when a metal is immersed in or sprayed with an aqueous solution of chromic acid, chromium salts such as sodium or potassium chromate or dichromate, hydrofluoric acid or hydrofluoric acid salts, phosphoric acid, or other mineral acids. The chemical attack facilitates the dissolution of some surface metal and the formation of a protective film containing complex chromium compounds.

A variety of metals and electrodeposited metal coatings, including zinc, cadmium, magnesium, and aluminum, can be chromate conversion coated. Several articles in this Volume contain details about the procedures used to apply chromate coatings to specific metals and metal coatings. The conversion coating of cadmium electrodeposits is discussed in the article "Cadmium Plating"; the articles "Surface Engineering of Aluminum and Aluminum Alloys" and "Surface Engineering of Magnesium Alloys" contain information relating to the application of chromate conversion coatings to these metals; and procedures for applying conversion coatings to electrodeposited zinc are described in the article "Zinc Plating." A comprehensive summary of literature sources related to chromate conversion coatings is available in a detailed review of surface treatments for aluminum alloys (Ref 1). In addition, processing and testing details for

application of chromium conversion coatings to aluminum, magnesium, cadmium, copper, silver, and zinc are continuously updated and presented in concise form (Ref 2).

Chromate conversion coatings are generally used to increase the corrosion resistance of the metal to which they are applied. Most conversion coatings slowly dissolve in water and provide limited protection in this medium; however, they furnish excellent protection in marine atmospheres and in high-humidity environments. The protection provided by chromate coatings increases directly with thickness up to a certain point, after which the protective nature is sacrificed due to the formation of a porous, nonadherent film. Chromate conversion coatings are also used for a variety of decorative and functional applications. They can be produced in a variety of colors, ranging from the very bright coatings obtained on zinc and cadmium, which simulate the appearance of bright nickel and chromium, to the olive drab frequently applied to military equipment. Chromate coatings provide an excellent nonporous bonding surface for all paints that have good molecular adhesion. A summary of general uses for chromate conversion coatings is given in Table 1; more detailed information is provided in the section "Chromating Processes and Applications" in this article.

Table 1 Common uses of chromate conversion coatings

Metal	General use				Remarks
	Corrosion resistance	Paint base	Chemical polish	Metal coloring	
Aluminum	X	X	. . .	X	Economical replacement for anodizing if abrasion resistance is not required Used to "touch-up" damaged areas on anodized surfaces
Cadmium	X	X	X	X	. . .
Copper	X	X	X	X	Thin coatings prevent "spotting out" of brass and copper electrodeposits. No fumes generated during chemical polishing
Magnesium	X	X	. . .	. . .	. . .
Silver	X	. . .	. . .	. . .	. . .
Zinc	X	X	X	X	. . .

Source: Ref 2

Most of the formulations used in chromating today are of a proprietary nature, and many of the patents in this area expired long ago. Some specific formulations are given in Ref 1, but details about solution control are difficult to find. This is unfortunate, because understanding solution replenishment chemistry is key to extending the life of chromating solutions and enhancing their versatility. This article briefly describes the basic attributes of chromate conversion and the processes for applying them. It also provides information about the influence of substrate microstructure on the performance of coating deposits, the mechanism of substrate protection supplied by chromate coatings, and the development of new replacement technologies in response to the environmental constraints that have developed around the use of chromium-base compounds. (Information related to this last item is also available in the article "Chromium Elimination" in this Volume.) Most of the information provided in this article relates specifically to the chromating of aluminum and aluminum alloys, for these metals are by far the chief recipients of chromated films. However, most of the information is generally applicable to chromating of other metals as well.

References

1. S. Wernick, R. Pinner, and P.G. Sheasby, in *The Surface Treatment and Finishing of Aluminum and Its Alloys*, Vol 1, 5th ed., ASM International and Finishing Publications Ltd., 1987, Chap 5
2. F.W. Eppensteiner and M.R. Jenkins, Chromate Conversion Coatings, *Metal Finishing--Guidebook and Directory Issue '92*, Vol 90 (No. 1A), 1992, p 413-425

Characteristics of a Chromate Conversion Coating

Conversion coating does not simply involve the deposition of a thin layer of, for example, hydrated metal oxide that "converts" a surface to a corrosion resistant state (Ref 3). As illustrated in Fig. 1, an Auger electron spectroscopy (AES) depth profile for a typical chromated layer on aluminum alloy 2024-T3, the film contains not only chromium and oxygen, but also part of the substrate (in this case aluminum) and the principal alloying element (copper). The profile was taken on the solid solution matrix, off any of the intermetallic second-phase particulates that typically form in the aluminum-copper alloy system. In the case of chromate coatings, the amorphous hydrated oxide mixture that is formed on the surface must involve oxidation of the substrate, followed by precipitation of the dissolved metal ions. Precipitation arises from an increase in pH at the surface due to reaction with excess hydroxyl ions produced as a result of the cathodic (i.e., reduction) half reaction. Either reduction of dissolved oxygen or reduction of water itself will cause such an increase in pH at the surface. A similar mechanism is postulated for the formation of crystalline phosphate conversion coatings on steel, in which two principal crystalline phases have been identified: hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$, and phosphophillite, $Zn_2Fe(PO_4)_2 \cdot 4H_2O$ (Ref 5). The latter compound involves incorporation of the main element in the substrate (i.e., iron) through oxidation of the surface in the presence of acidic zinc phosphate.

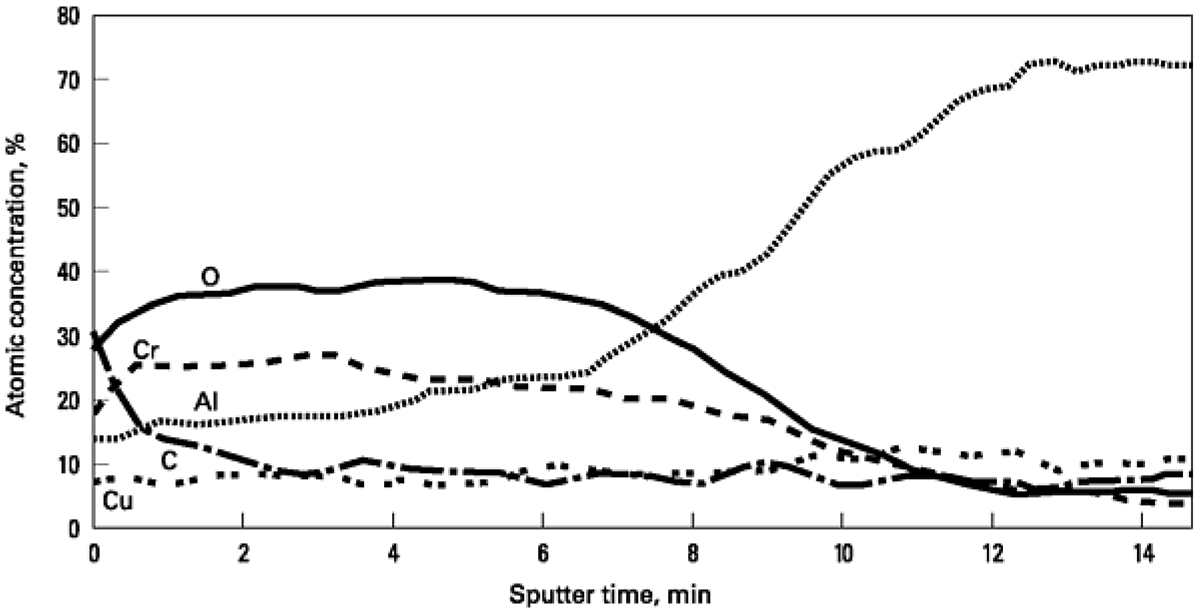


Fig. 1 Auger electron spectroscopy depth profile of polished aluminum alloy 2024-T3 solid solution matrix exposed to Alodine 1200S conversion coating solution for 5 min. Sputter rate approximately 300 Å/min (vs. SiO_2). Experiment details in Ref 7. Source: Ref 4

As evidenced by the above discussion, a conversion coating is simply a film that contains a mixture of the corrosion-resistant species and the major elements found in the substrate. The mixture promotes strong adhesion of the conversion coating to the substrate. This is unlike a film formed by physical vapor deposition, where there is a very clear interface between the film and the substrate and where essentially none of the substrate is distributed through the deposited film. Poor film adhesion can result at such an interface, and if water and/or oxygen reach the interface region, corrosion can readily occur and cause delamination of the film. Because no clear interface exists in conversion coating films, a certain amount of oxygen and water can be tolerated; the substrate concentration gradient is observed through the protective film.

References cited in this section

3. N.J. Newhard, Jr., in *Metal Finishing,* No. 7, 1972, p 49; No. 8, 1972, p 66
4. P.L. Hagans, Naval Research Laboratory, and C.M. Haas, Henkel Corp., unpublished data
5. S. Maeda, in *Progress in Organic Coatings,* Vol 11, 1983, p 1
7. P.L. Hagans and C.M. Haas, in *Surf. Interface Anal.,* Vol 21, 1994, p 65

Chromate Conversion Coating Processes and Applications

Although the beginning of chromium-based conversion coatings can be traced back to 1915 (Ref 6), the advent of modern-day chromating treatments is dated from 1945 to the early 1950s, when tradenames such as Alodine (American Chemical Paint Co., later Amchem Products Co.), Alocrom (ICI Ltd.), Bonderite (Parker Rust Proof Co.), and Iridite (Allied Chemical Co.) were synonymous with the formation of highly corrosion-resistant conversion coatings. Unlike their predecessors, these coatings could be applied at or near room temperature for short times (a few seconds to several minutes, depending on the thickness and degree of corrosion resistance desired), and good results could be obtained on difficult-to-treat alloys such as aluminum-copper alloys and magnesium alloys. The use and solution control of surface activators (most notably fluoride ion) allowed chromating reactions to proceed at a very rapid rate. In addition, when maximum corrosion resistance was required, accelerators such as the ferricyanide ion were used, especially on difficult-to-treat alloys (Ref 3).

The importance of having fluoride present in the chromium-containing bath is illustrated in the AES depth profile of a conversion coating applied in the absence of fluoride (Fig. 2). Comparison of this profile with Fig. 1 indicates that, all other conditions being constant, the presence of fluoride increases film thickness by a factor of at least 30. With fluoride present (Fig. 1), the surface was found to contain 18 at.% Cr, whereas only 5 at.% Cr was observed without fluoride in solution (Fig. 2). Without fluoride present, very little chromium is deposited, and the enriched copper interface observed on the cleaned but untreated sample remains intact (data not shown; see Ref 7 for details).

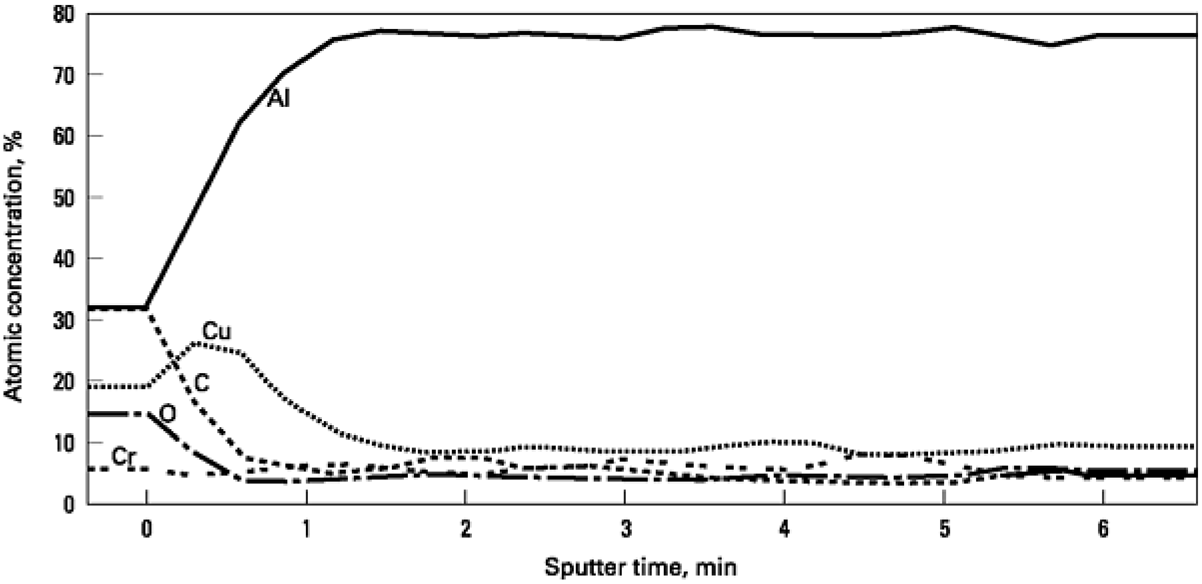


Fig. 2 Auger electron spectroscopy depth profile of polished aluminum alloy 2024-T3 solid solution matrix exposed for 5 min to the same solution as in Fig. 1 without fluoride ion present. Sputter rate approximately 300 Å/min (vs. SiO_2). Experiment details in Ref 7. Source: Ref 4

The fluoride-based treatments can be divided into two principal classes whose names reflect the predominant color of the conversion coating: "green" or amorphous phosphate treatment and "gold" or amorphous chromate treatment. The green treatments are obtained from solutions containing mixtures of chromic, phosphoric, and hydrofluoric acids; coatings ranging in weight from 5 to 10 mg/ft^2 (colorless) to 200 to 500 mg/ft^2 (deep green) can be produced. Monitoring of cation concentration in chromium phosphate baths is critical to maintaining bath life and coating performance since sludging can occur very easily due to precipitation of NaK_2AlF_6 and Na_3AlF_6. The gold treatments are obtained from solutions containing only chromic acid and a fluoride ion source; coating weights of 5 to 80 mg/ft^2 ranging in color from a light iridescence to a golden tan can easily be obtained.

In general, these treatments provide better unpainted corrosion resistance than the phosphate-based treatments and are much easier to control. The critical parameter for replenishment chemistry is control of the ratio of free-to-complexed fluoride ion. Many different fluoride ion sources have been used to affect this control. In addition to improving corrosion performance, these treatments serve as desirable substrates for promoting good paint adhesion and preventing underpaint corrosion. Corrosion performance can be enhanced by addition of accelerators such as the ferricyanide ion, which increases coating weight and also serves to complex copper in aluminum-copper alloys (see the section "Chromating Mechanism," below). Aluminum-copper alloys are some of the most difficult metals to protect against corrosion but are also some of the most often used aluminum-base alloys due to of their strength. Similar fluoride-ion-based treatments are used for magnesium and its alloys, with the Dow No. 7 treatment being the most often used where maximum corrosion protection is desired (Ref 8).

Chromate conversion coating treatments are used on five principal types of aluminum parts: aircraft and aerospace structural components, coil (for construction applications such as guttering and siding), extrusions (for window and door frames), heat exchanger parts, and containers (mainly beverage cans). A considerable amount of aluminum is also used in the automotive industry, but most receives a crystalline phosphate treatment because the aluminum is treated at the same time as the steel frame. As with chromating, fluoride ion is added to the phosphating bath to promote phosphate film growth on aluminum.

The major specifications that cover the performance of chromate conversion coatings are listed in Ref 2. The type of specifications used will depend on the end use of the fabricated part, which in turn will dictate the properties of the coating being sought. For example, in order to be used on military aircraft, aluminum alloy parts (such as those made from highly corrosive copper-containing aluminum alloy 2024-T3 or 7075-T6) must pass government specifications MIL-C-5541 and MIL-C-81706, which require that the unpainted chromated alloy must survive 336 h of salt fog testing (ASTM B 117). In addition, various tests are used to ascertain paint adhesion and underpaint corrosion under salt fog conditions. Aerospace companies use specifications similar to those used by the government. A boiling water test is often used in the container industry to detect the effectiveness of the chromate treatment in preventing discoloration caused by underpaint corrosion. Because the alloys used for manufacturing containers are not nearly as active, in a corrosive sense, as those used in aerospace, and because the specifications are not as severe, thin unaccelerated treatments are often used.

References cited in this section

2. F.W. Eppensteiner and M.R. Jenkins, Chromate Conversion Coatings, *Metal Finishing--Guidebook and Directory Issue '92,* Vol 90 (No. 1A), 1992, p 413-425
3. N.J. Newhard, Jr., in *Metal Finishing,* No. 7, 1972, p 49; No. 8, 1972, p 66
4. P.L. Hagans, Naval Research Laboratory, and C.M. Haas, Henkel Corp., unpublished data
6. O. Bauer and O. Vogel, in *Mitt. a.d. Kgl. Materialsprufungsamts,* Vol 314, 1915, p 146; in *Internat. Z.f. Metallographie,* Vol 8, 1916, p 101; British Patent 226, 776, 1916
7. P.L. Hagans and C.M. Haas, in *Surf. Interface Anal.,* Vol 21, 1994, p 65
8. H.K. DeLong, in *Electroplating Engineering Handbook,* A. Kenneth, Ed., 3rd ed., Van Nostrand, 1971, p 465-474

Chromating Mechanism

Next to the alkali metals, the metals that chromate coatings must protect against corrosion (i.e., aluminum, magnesium, zinc, and cadmium) are the most active metals in the periodic table. In fact, from the large negative standard electrode reduction potentials for aluminum and magnesium dissolution, one would expect these metals to dissolve when immersed in water. This does not occur, of course; upon exposure to water or air, these metals immediately form a hydrated oxide film that is itself somewhat protective.

Chromate conversion treatments actually take advantage of this high surface activity. Through use of a strong oxidizing agent such as chromic acid, CrO_3, a redox reaction occurs at acidic pH (pH ≈ 2) where hexavalent chromium, either in the form of $CrO_2^{2-}{}_7$ or $HCrO_4^-$, is reduced to trivalent chromium while aluminum is oxidized to trivalent aluminum:

$$Al \rightarrow Al^{3+} + 3e^-$$
$$HCrO_4^- + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Probably due to of the presence of fluoride ion (see next paragraph), another reduction reaction besides that involving chromic acid can occur. This reaction involves the reduction of either water, hydronium ion, or dissolved oxygen to form hydroxyl ions at the metal surface. This surface-localized increase in pH results in the precipitation of an amorphous mixture of hydrated aluminum plus chromium oxides.

As described in the previous section, the presence of fluoride ion is important for building films of significant thickness; without its presence, film growth is extremely slow. Fluoride presumably serves two roles. First, it solubilizes the aluminum oxide initially present on the surface and allows the redox and deposition reactions to proceed. Second, it solubilizes a portion of the growing film, which allows penetration of the electrolyte to the surface and ion transport from the surface into the growing film. Fluoride has been characterized as a unique monodentate ligand that enhances the dissolution rate of aluminum oxide (Ref 9).

The high corrosion resistance offered by chromate films is attributed to the presence of both hexavalent and trivalent chromium in the coating. Analyses of coatings by wet chemical methods (Ref 10) and with surface-sensitive techniques (Ref 7, 11, 12) have shown that both Cr(VI) and Cr(III) are present in the films. The trivalent chromium is believed to be present as an insoluble hydrated oxide, whereas the hexavalent chromium imparts a "self-healing" character to the film during oxidative (corrosive) attack by species such as chloride ion. The hexavalent chromium is reduced during corrosion to form an insoluble trivalent chromium species that terminates the oxidative attack.

The enhanced corrosion resistance attributed to accelerated chromate conversion coatings has been ascribed to the increase in coating weight that is due to incorporation of the accelerator into the growing coating (Ref 3, 13, 14). Recent studies on ferricyanide-accelerated chromate coatings deposited on a high-copper-containing aluminum alloy indicate that ferricyanide is distributed throughout the film only on the high-copper-containing intermetallic phases such as $CuAl_2$ (Ref 7). Because these phases are known to accelerate greatly the corrosion rate of aluminum (Ref 15), the decrease in corrosion rate offered by the accelerator is believed to be due to the formation of copper ferricyanides on the intermetallic surface, which alters its activity with respect to the solid solution matrix. At adequate treatment times, corrosion resistance is also believed to be enhanced by the uniform surface composition of chromium and oxygen and the absence of aluminum and copper in the near-surface region.

References cited in this section

3. N.J. Newhard, Jr., in *Metal Finishing,* No. 7, 1972, p 49; No. 8, 1972, p 66
7. P.L. Hagans and C.M. Haas, in *Surf. Interface Anal.,* Vol 21, 1994, p 65
9. W. Stumm, G. Furrer, E. Wieland, and B. Zinder, in *NATO ASI Series, Series C,* Vol 149, 1985, p 55
10. T. Drozda and E. Maleczki, in *J. Radioanal. Nucl. Chem. Lett.,* Vol 95, 1985, p 339
11. K. Asami, M. Oki, G.E. Thompson, G.C. Wood, and V. Ashworth, in *Electrochim. Acta,* Vol 32, 1987, p 337
12. M.W. Kendig, A.J. Davenport, and H.S. Isaacs, in *Corros. Sci.,* Vol 34, 1993, p 41
13. J.A. Treverton and N.C. Davies, in *Met. Technol. N.Y.,* Oct 1977, p 480
14. J.A. Treverton and N.C. Davies, in *Surf. Interface Anal.,* Vol 3, 1981, p 194
15. J.R. Scully and D.E. Peebles, Extended Abstract No. 35, *Proc. National Electrochemical Society Meeting,* Spring 1991, The Electrochemical Society, 1991

Effects of Substrate Microstructure

Because of specific physical property requirements, metal fabricators rely on a "mixed substrate," such as an alloy, rather than a pure metal. An alloy is typically of higher strength than a pure component because of the synergistic effect of the alloying element (e.g., a small amount of copper greatly strengthens aluminum for aerospace applications). The disadvantage of the alloy substrate from a conversion coating standpoint is twofold:

- The conversion coating must be tolerant of all the alloying elements. Formulating a conversion coating that can simultaneously treat all the elements present in an alloy can be difficult, depending on the elements' relative reactivity.
- The alloying elements may impart an accelerated corrosion rate to the metal. For example, when exposed to identical sodium-chloride-containing solutions, high-purity (99.999%) aluminum corrodes very slowly, whereas copper-containing aluminum alloys (e.g., the 2000-series alloys) corrode extremely rapidly (Ref 4). (On the other hand, alloying elements such as magnesium and zinc have very little effect on the corrosion rate of aluminum.) Aluminum used for alloying is typically of 99+% purity, and this aluminum will corrode at a faster rate than higher-purity material due to the presence of impurities, such as iron, that form intermetallic phases (e.g., $FeAl_3$). A few parts per million of iron, copper, or nickel in magnesium and magnesium alloys can also greatly accelerate the corrosion rate (Ref 16).

One of the principal difficulties in attempting to form a uniform conversion coating on an alloy surface is that alloys are seldom of homogeneous composition (i.e., they are not perfectly solid solutions). With the base metal and with themselves, the alloying elements often form second-phase particulates or "intermetallics" within the solid solution matrix (Ref 17). The intermetallics develop during the alloying process (as is found with precipitation hardening of a supersaturated alloy solution) and render the surface inhomogeneous. These intermetallics can form galvanic couples between themselves and the alloy solid solution matrix, and depending on their relative activity with respect to the matrix, they can either cause acceleration of the matrix or their own dissolution rate.

For example, the $CuAl_2$ that is found in aluminum-copper alloys is typically less active than (i.e., lies cathodic to) the solid solution matrix, which enhances the solid solution dissolution rate. In addition to enhancing the corrosion rate, this can have a profound effect on the uniformity achieved with a particular conversion coating process. As has been noted in a previous study (Ref 7), the activity difference between $CuAl_2$ intermetallics and the solid solution results in the application of a nonuniform (in thickness) conversion coating. A much thicker layer is found on the solid solution matrix because of its enhanced activity. The thinnest layers are found on the $(Fe,Mn)_3SiAl_{12}$ intermetallics, which appear to be less active than the $CuAl_2$ phases.

Alloy temper can also affect microstructure, which in turn can influence coating performance. For example, one study found that chromate treatments that were effective in protecting aluminum alloy 7075-T6 were not effective in treating the same alloy in the T73 (overaged) temper (Ref 18).

The pretreatment process, which usually includes cleaning and deoxidizing or desmutting steps, can have a strong effect on the surface microstructure and thus on the formation of a coherent conversion coating. In the case of the copper-aluminum alloys cited above, surface pretreatments involving either acid etching (Ref 4) or final polishing in a basic silicate electrolyte (Ref 7) produce a surface that contains a relatively uniform layer of copper, as detected by spatially resolved AES. The enriched copper found on the solid solution matrix results from either selective dissolution of the aluminum and/or redeposition of the copper that was dissolved from the intermetallics and/or solid solution. The chromate solution "sees" the homogeneous surface and readily forms a chromate conversion coating over the copper-rich interface, leaving the interface intact (Ref 7). As indicated by transmission electron microscopy studies of electropolished and acid-etched samples of high-purity aluminum that were subsequently chromated, the hydrated chromium oxide coating initially deposits on the metal ridges (the cathodic sites, produced by the pretreatment process) while the anodic sites, where the aluminum oxide was continuously attacked by fluoride ion, lie between the metal ridges (Ref 19). These studies illustrate the importance of the pretreatment steps in producing a homogeneous surface layer before application of the conversion coating.

References cited in this section

4. P.L. Hagans, Naval Research Laboratory, and C.M. Haas, Henkel Corp., unpublished data
7. P.L. Hagans and C.M. Haas, in *Surf. Interface Anal.*, Vol 21, 1994, p 65
16. J. Hillis, "The Effects of Heavy Metal Contaminants on Mg Corrosion Performance," Technical Paper 830523, presented at the Society of Automotive Engineers Annual Meeting, 1983

17. J.E. Hatch, *Aluminum: Properties and Physical Metallurgy,* ASM International, 1988, Chap 5
18. L.J. Bailin, P. Fitzpatrick, and M.J. Joyce, "Evaluation of Unpainted Alodine Chromate Conversion Coatings for Corrosion Resistance and Electrical Conductivity," Report F035575, Lockheed Missiles and Space Co., 1985
19. G.M. Brown, K. Shimizu, K. Kobayashi, G.E. Thompson, and G.C. Wood, in *Corros. Sci.,* Vol 33, 1992, p 1371

Environmental Concerns

The use and disposal of chromium and chromium compounds have received much regulatory attention because of the toxicity of chromium and indications that it is a cancer-causing agent. A summary of studies on the mutational effects of chromium compounds in bacteria, mammalian cells, and human cultures was published in 1986 (Ref 20). In 1993, a listing of hazardous chemicals stated that "Chromate salts are suspected human carcinogens producing tumors of the lungs, nasal cavity and paranasal sinus" (Ref 21). This list indicates that some type of mutational data was reported for all chromium compounds. Hexavalent chromium compounds appear to be the most severe; most are designated as "confirmed carcinogens." One trivalent chromium salt, Cr(III) acetate, is now also a confirmed carcinogen. Other Cr(III) salts are classified as "questionable human carcinogens."

To quote an earlier researcher in this field, "One of the biggest needs involving the future use of conversion coatings [for aluminum] in aerospace is to find non-toxic substitutes for those chemical processing solutions which are now labeled as pollutants" (Ref 3). Only aerospace was mentioned, because restrictions were expected to be first observed with aluminum fabricators due to the role played by the federal government in setting standards for aircraft manufacture. In the years that have elapsed since this statement was made, very few chromium-base treatments have been replaced by environmentally safer technology, and restrictions continue to be imposed on the levels of chromium in waste water effluent, solid waste, and the air to which workers are exposed.

In the United States, regulations regarding hazardous waste disposal and monitoring proliferated from the mid-1970s through the 1980s. Congress passed several laws empowering the Environmental Protection Agency (EPA) to set regulations for the control of hazardous waste (see Ref 22 for a review up to 1991). Much of this legislation espouses "cradle-to-grave " management of hazardous waste. Some of the principal legislation enacted by Congress includes the Resource Conservation and Recovery Act (RCRA) of 1976, the Safe Drinking Water Act (SDWA) of 1974, the Toxic Substances Control Act (TSCA) of 1976, the Hazardous and Solid Waste Act Amendments (HSWA) of 1984, and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or Superfund) of 1980. Most of these laws have been amended (i.e., reauthorized) at least once since their initial passage. In a number of cases, considerable time passed after enactment of the law before the EPA was able to put the basic regulatory framework together (e.g., 4 years elapsed after passage of RCRA before the basic regulatory structure was in place). HSWA resulted from Congress's dissatisfaction with the EPA's progress with RCRA. All regulations are first published in the *Federal Register,* after which they become part of the Code of Federal Regulations under Title 40, which deals with protection of the environment.

As a result of these laws, chromium and its compounds became specific targets for regulatory control. In 1975 the National Institute for Occupational Safety and Health (NIOSH) recommended a standard for occupational exposure to Cr(VI) (Ref 23). The document described a number of studies that detailed medical problems observed by workers exposed to chromium. Included in this report was evidence indicating that certain Cr(VI) compounds were carcinogenic. The List of Suspect Carcinogens published by NIOSH now contains a number of chromium-containing compounds.

As a result of regulations enforcing RCRA, all facilities involved in electroplating were forced to comply by 1 July 1984 with the Electroplating Pretreatment Standards that appeared in the 28 January 1981 *Federal Register* (Ref 24, 25, 26, 27, 28). These standards were later broadened to include the anodizing and conversion coating industries; they were also made more stringent in the Metal Finishing Regulations that were printed in the 15 July 1983 *Federal Register* and enacted in 1986 (Ref 24, 25, 26, 29). Both sets of regulations were imposed by the EPA through local publicly owned treatment works. These regulations placed discharge limitations on various metals, such as chromium, and on other substances, such as those containing cyanide. Total chromium was limited to 2.77 mg/L/day, with a monthly average of 1.71 mg/L/day, and total cyanide was limited to 1.20 mg/L/day, with a monthly average of 0.65 mg/L/day.

In 1986, chromium and its compounds were put on the Community Right-to-Know List, which resulted from the Superfund Amendments and Reauthorization Act (SARA) of 1986 (Ref 21, 22). SARA established the Community Right-

to-Know Program, which requires industry to provide information on the type of chemicals being used at their facility. This was only the beginning; many other regulations governing chromium compounds have been promulgated.

As of the time of this writing, the 1994 session of Congress is expected to pass a second reauthorization of the Clean Water Act (enacted in 1972 and first reauthorized in 1986) that will reflect the "polluter pays" philosophy (Ref 30). The intent of this reauthorization is to provide funding for public water pollution control projects through taxation on discharges. Five groups of taxable pollutants, with tax rates based on toxicity, have been compiled. Chromium falls in Group 4 and cyanide is found in Group 5; these two groups carry by far the highest tax rates. A few milligrams of these substances in the waste stream can warrant a large monetary fine over a year for a high-volume metal finisher.

Agencies such as the Department of Transportation are strengthening restrictions for shipment of treatment chemicals such as hydrofluoric acid, which is found in many chromate conversion coating formulations. Individual state EPAs may also enact their own restrictions, which could further restrict the use of harmful treatment chemicals. For example, on 24 July 1989, both Massachusetts and Oregon enacted sweeping toxic waste reduction bills (Ref 31). These bills require industries to prepare plans to reduce their use of toxic substances and to recover or reuse toxic materials from their effluents. The Massachusetts Toxics Use Reduction Act sets as a goal a 50% reduction of toxic waste in the state by 1997. Although no one can predict whether the use of chromium compounds and accelerators such as potassium ferricyanide will be completely banned, the trend in legislation is obviously making the search for viable alternatives to the current technology a top priority.

Furthermore, the Environmental Protection Agency (EPA) is scheduled to be elevated to the Cabinet level, with the head administrator assuming the post of Secretary of the EPA (Ref 30). This will attach an even greater significance to the role of the government in enacting and enforcing legislation directed at maintaining a safer environment.

References cited in this section

3. N.J. Newhard, Jr., in *Metal Finishing,* No. 7, 1972, p 49; No. 8, 1972, p 66
20. G. Kazantzis and L.J. Lilly, in *Handbook on the Toxicology of Metals,* L. Friberg, G.F. Nordberg, and V.B. Vouk, Ed., Vol 1, Elsevier, 1986, Chap 14
21. R.J. Lewis, Sr., *Hazardous Chemicals Desk Reference,* 3rd ed., Van Nostrand, 1993; in *Sax's Dangerous Properties of Industrial Materials,* Vol 2, 8th ed., Van Nostrand, 1992
22. *Patty's Industrial Hygiene and Toxicology,* G.D. Clayton and F.E. Clayton, Ed., Vol 1, Part B, 4th ed., John Wiley & Sons, 1991, Chap 30 and 32
23. H.R. Garner, in *Plating and Surface Finishing,* Vol 1, 1981, p 36
24. D. Pierce, Jr. and R.S. Capaccio, in *Metal Finishing,* Vol 11, 1983, p 45
25. F. Altmayer, in *Plating and Surface Finishing,* No 1, 1984, p 44
26. R.F. Skach, in *Plating and Surface Finishing,* Vol 8, 1983, p 30
27. Current News, *Chemical Engineering,* 16 May 1983, p 22
28. P&SF Report, *Plating and Surface Finishing,* Vol 4, 1984, p 20
29. Staff of Mabbett, Capaccio & Associates, in *Metal Finishing,* Vol 11, 1986, p 13
30. R. Dhonau, in *Metal Finishing,* No. 11, 1993, p 35; No. 5, p 49
31. T.P. Driscoll, in *Metal Finishing,* No. 11, 1989, p 19

Alternative Technologies

Much research has focused on finding an alternative to chromium-base compounds for use in conversion coating formulations. In fact, the scientific and patent literature show that attempts have been made to incorporate most elements in the periodic chart (except for radioactive elements and the rare gases) into films. This article gives the rationale for various research paths, along with specific examples where appropriate. Three principal subjects are discussed: deposition of organic-based coatings from aqueous solution, deposition of multivalent metals from aqueous solution, and corrosion-resistant surface layers formed from the gas phase, with or without the use of high-energy light or particle beams (e.g., laser and ion beams).

Organic-Based Coatings. Given that a large number of water-soluble organic corrosion inhibitors are known to exist (Ref 32, 33), conversion coatings based on organic molecules are logical alternatives to chromium. For example, molecules containing the azole functional group (i.e., those having at least two ring nitrogens in a five-membered ring, such as benzotriazole) are known to be effective corrosion inhibitors for copper (Ref 34) and zinc (Ref 35) and are used commercially in cooling water applications to protect copper piping.

The difficulty in making organic-based conversion coatings of sufficient thickness is that organic species are normally poor oxidizing agents, such as chromic acid. This prevents film thickening because of aluminum oxidation and formation of insoluble oxide and hydroxide species. Typical inhibitor-formed films have thicknesses of only 100 Å or less, making their use in severely corrosive environments impractical. In addition, the time required to form such films can be hours or more (Ref 35) unless it is possible to accelerate their deposition through use of surface activators such as fluoride ion. Aqueous solubility can also be a limitation for some molecules.

Even though these films may be thin, they have application in areas such as the treatment of architectural aluminum (since this material is not usually continuously exposed to corrosive environments). In addition, organic-based conversion coatings have the potential of being excellent undercoats for organic (paint) finishes, for adhesion can be expected to be strong between similar types of molecules. Both sets of molecules contain various active functional groups that can interact (e.g., through hydrogen bonding or possibly formation of cross-linked or intertwined structures). It is likely that organic-based treatments will find some application in replacing chromium-base systems, but great difficulties exist in attempting to produce treatments that can pass the rigors of 168 and 336 h exposure to salt spray, as required by MIL-C-5541 and MIL-C-81706 on active aluminum alloys such as 7075-T6 and 2024-T3.

Multivalent Metals. The most logical method for obtaining a chromium replacement is to choose another transition, or even a rare earth metal, that has at least two stable oxidation states, is a good oxidizing agent, and has high corrosion resistance. To this end, patents and patent applications exist for using most of these metals in some type of formulation to yield a conversion coating. Not all metals are good oxidizing agents, but the ability of certain metals to oxidize can be enhanced through complexation with the appropriate species.

The fluoride-based formulations used in chromate conversion coatings cannot be used with most metals because of the insolubility of many metal fluorides. Other surface activators need to be chosen, and peroxide, nitrate, and chloride are common substitutes for fluoride (see examples below). The initial choices would be molybdenum-based and tungsten-based reagents, because these elements lie under chromium in the same group of the periodic table and both metals are well known for their corrosion resistance. These metals have been extensively researched, but formulations based on them have not been able to match, let alone surpass, the performance shown by chromate coatings (Ref 36). Molybdates and tungstates have found some application as accelerator replacements for the ferricyanides. Three multivalent metal-based systems that have recently received considerable attention in the open literature and/or have reached the trial stage in various aluminum industries are described below.

Rare Earth Metals. Treatments based on Ce(III) and other rare earth metals were examined first in Australia (Ref 37, 38, 39) and later in the United States (Ref 40, 41, 42). Coatings in excess of 1000 Å in thickness and rich in cerium + oxygen species were formed on aluminum alloy 7075 after a 20-day exposure to a 100 ppm $CeCl_3$ solution at pH 5.8 (Ref 43). X-ray photoelectron spectroscopy (XPS) indicated that the film contained both Ce(IV) and Ce(III) species, which likely existed as CeO_2, $Ce(OH)_4$, and $Ce(OH)_3$ (Ref 43). X-ray absorption near edge structure (XANES) studies likewise indicated the presence of a mixed cerium valence film (Ref 44). Coating process time was decreased to 10 min by adding hydrogen peroxide, lowering pH, and increasing the solution temperature (Ref 45). Immersion of the film in NaCl solution converted all of the Ce(III) to Ce(IV) (Ref 43). Measured corrosion rates of treated 7075 indicated that a 50% reduction in corrosion rate from that of an untreated substrate can be obtained (Ref 45). No mention of its effect on pitting corrosion was made, but excellent paint adhesion (comparable to that on chromated surfaces) was observed.

A cathodic mechanism has been proposed to account for cerium deposition: pH is increased at the cathodic sites, because of either oxygen reduction or hydrogen evolution, to form excess hydroxyl ions (Ref 37). The hydroxyl ions can attack the metal surface and react with metal ions in solution. The mixed metal oxide/hydroxide then precipitates onto the surface to form the corrosion-resistant film.

The development of "stainless aluminum" has also been claimed for cerium-treated pure aluminum and aluminum alloy 6061-T6 (less satisfactory behavior was obtained for aluminum alloy 2024-T3) (Ref 46). The treatment involves a 2 h exposure to three separate solutions: boiling 10 mM $Ce(NO_3)_3$, boiling 5 mM $CeCl_3$, and anodic polarization in the passive region in deaerated 0.1 M Na_2MoO_4. Excellent corrosion resistance was found upon immersion of treated samples

in 0.5 N NaCl. Scratched surfaces also showed excellent resistance. No mention of salt spray testing of the cerium-based treatments was made, however.

Ce(III) molybdate has shown some promise as a corrosion inhibitor in an epoxy/polyamide primer but still does not match the performance of strontium chromate pigmented primers (Ref 47).

Manganese-based treatments for aluminum and aluminum alloys have recently been patented (Ref 48, 49, 50). One of the treatment steps involves exposure of the aluminum alloy surface to permanganate ion, which contains manganese in the +7 oxidation state. Like chromate, the permanganate ion is an excellent oxidizing agent, suggesting that the mechanism of film formation is similar to that of chromate. Although no information on film thickness or composition is given in the patents, one would expect that the manganese found in the film is in some reduced oxidation state (probably either +4 or, more likely, +2). This is a multistep treatment in which many of the steps require elevated temperatures. The last step, which involves a "seal" with alkali metal silicate, is probably necessary to block the pores created in the film during deposition. Good corrosion resistance, as evidenced from salt spray exposure, has been observed for high-copper-containing aluminum alloys.

Trivalent Cobalt. The final system is based on the use of basic solutions containing complexes of trivalent cobalt, for example, $Co(NH_4)_6^{3+}$ (Ref 51). $CoCl_2$ has shown some promise as an inhibitor for aluminum alloy corrosion (Ref 52). It is likely that Co(II) compounds have been examined in the presence of fluoride, for CoF_2 does possess appreciable solubility in water. This new system deposits a corrosion-resistant cobalt-containing film on aluminum alloys. Preliminary examination of this coating with electrochemical impedance spectroscopy (EIS) indicates that the coating has corrosion-resistant properties similar to those of a chromate treatment on aluminum alloy 2024-T3 (Ref 53). Good corrosion and paint adhesion properties are also claimed (Ref 51).

Gas Phase. Although gas-phase/high-vacuum techniques will probably not replace chromating of large parts or continuous chromating of high volumes (e.g., aluminum alloy coil stock for beverage cans) in the near future, these processes should not be ignored, for they offer the possibility of forming entirely new corrosion-resistant films. Experiments have already been undertaken in Japan to produce large surface areas of galvanized steel sheet through gas phase deposition of zinc (Ref 54). A partial selection of these techniques as they apply to the formation of corrosion-resistant films on aluminum and magnesium is briefly reviewed below.

Sputter deposition and ion implantation are nonequilibrium alloying techniques that allow solid solution alloys to be formed, which are unattainable by conventional alloying techniques. Corrosion-resistant aluminum-molybdenum and aluminum-chromium alloys have been formed by cosputter deposition of aluminum with each of the two metals (for details see Ref 55 and 56). Ion implantation of silicon, chromium, zirconium, niobium, and molybdenum into pure aluminum have been found to enhance pitting resistance of the aluminum, whereas implantation of magnesium and zinc had no effect on pitting resistance or lowered pitting resistance, respectively (Ref 57, 58). Beneficial results have been observed for iron and boron implantation into magnesium and magnesium alloys (Ref 59, 60). Ion implantation can easily form layers up to several thousand angstroms thick, depending on the mass of the species being implanted and the ion beam energy. Even thicker layers can be produced by ion beam mixing, which combines ion implantation with a vapor deposition process such as evaporation or sputtering.

Corrosion-resistant oxide mixtures can be formed on aluminum and magnesium by laser irradiation of a surface that contains a thin vapor-deposited metallic film such as chromium or molybdenum (Ref 61, 62, 63, 64). Laser irradiation is performed in an air or oxygen atmosphere to enhance the formation of oxides. The rapid heating and cooling rates provided by a laser can produce an amorphous, metastable surface composition that enhances the corrosion resistance of the substrate. Laser-irradiated chromium and molybdenum films on pure aluminum have been found to be very resistant to pitting by chloride ion (Ref 64).

Metal organic chemical vapor deposition (MOCVD) can also be used to deposit corrosion-resistant oxides onto low-melting metal substrates. MOCVD involves the deposition of thin oxide films by thermal decomposition of organometallic compounds. Metal alkoxides are the most commonly used precursors and have been used to deposit metal oxides such as SiO_2, TiO_2, Cr_2O_3, and Al_2O_3 (Ref 65, 66, 67, 68). The metal alkoxides generally have high vapor pressure and readily decompose at low temperatures (as low as 150 °C, or 300 °F). For example, Al_2O_3 films have been obtained by decomposition of the aluminum alkoxides: tri-tert-butoxide, tri-sec-butoxide, tri-n-butoxide, tri-isopropoxide, and acetyl-acetonate (Ref 69). Interestingly, the introduction of water vapor to aluminum acetyl-acetonate produces an extremely ligand-free, pure Al_2O_3 with a smooth surface morphology (Ref 70).

Additional information on alternatives to chromium is available in the article "Chromium Elimination" in this Volume.

References cited in this section

32. C.C. Nathan, Ed., *Corrosion Inhibitors,* National Association of Corrosion Engineers, 1973
33. S.N. Raicheva, B.V. Aleksiev, and E.I. Sokolova, in *Corros. Sci.,* Vol 34, 1993, p 343
34. M.M. Musiani, G. Mengoli, M. Fleischmann, and R.B. Lowry, in *J. Electroanal. Chem.,* Vol 217, 1987, p 187
35. W. Wippermann, J.W. Schultze, R. Kessel, and J. Penninger, in *Corros. Sci.,* Vol 32, 1991, p 205
36. B.R.W. Hinton, in *Metal Finishing,* No. 9, 1991, p 55
37. B.R.W. Hinton, D.R. Arnott, and N.E. Ryan, in *Metals Forum,* Vol 7, 1984, p 211
38. B.R.W. Hinton, D.R. Arnott, and N.E. Ryan, in *Materials Forum,* Vol 9, 1986, p 162
39. B.R.W. Hinton and D.R. Arnott, in *Microstructural Sci.,* Vol 17, 1989, p 311
40. F. Mansfeld, S. Lin, S. Kim, and H. Shih, in *Corrosion (NACE),* Vol 45, 1989, p 615
41. F. Mansfeld, S. Lin, S. Kim, and H. Shih, in *Electrochim. Acta,* Vol 34, 1989, p 1123
42. F. Mansfeld, S. Lin, S. Kim, and H. Shih, in *Mater. Sci. Forum,* Vol 44/45, 1989, p 83
43. D.R. Arnott, N.E. Ryan, B.R.W. Hinton, B.A. Sexton, and A.E. Hughes, in *Appl. Surf. Sci.,* Vol 22/23, 1985, p 236
44. A.J. Davenport, H.S. Isaacs, and M.W. Kendig, in *Corros. Sci.,* Vol 32, 1991, p 653
45. L. Wilson and B.R.W. Hinton, International Patent Application PCT/AU/88/00060, 3 March 1988
46. F. Mansfeld, V. Wang, and H. Shih, in *J. Electrochem. Soc.,* Vol 138, 1991, p L74
47. K.R. Baldwin, M.C. Gibson, P.L. Lane, and C.J.E. Smith, The Development of Alternatives to Chromate Inhibitors for the Protection of Aerospace Aluminum Alloys, *Proceedings of the Seventh European Symposium on Corrosion Inhibitors,* Supplement 9, 1990, p 771-785
48. J.W. Bibber, U.S. Patent 4,878,963, 1989
49. J.W. Bibber, U.S. Patent 4,755,224, 1988
50. J.W. Bibber, European Patent Application 89107533.5, 3 Jan 1990
51. M.P. Schriever, European Patent Application 91103498.1, 27 Nov 1991
52. D.R. Arnott, B.R.W. Hinton, and N.E. Ryan, in *Corrosion (NACE),* Vol 45, 1989, p 12
53. C.J. Johnson and K.Y. Blohowiak, Extended Abstract 180, *Proc. National Meeting of the Electrochemical Soc.,* Fall 1991, The Electrochemical Society, 1991
54. K. Shimogoori, H. Sato, M. Toyama, H. Nishimoto, T. Ikeda, and J. Kawafuku, Japanese Patents 01 42,571 (89 42,571) and 42,572 (89 42,572), 14 Feb 1989
55. W.C. Moshier, G.D. Davis, and G.O. Cote, in *J. Electrochem. Soc.,* Vol 136, 1989, p 356
56. G.D. Davis, B.A. Shaw, B.J. Rees, A. Iyengar, and E.L. Principe, Electrochemical Behavior and Surface Chemistry of Nonequilibrium Aluminum Alloys: Passivity Mechanism and Fabrication Methods, Final Report for ONR Contract N00014-C-93-0007, 17 Jan 1994
57. P.M. Natishan, G.T. Peace, and P.F. Slebodnick, in *Metallography,* Vol 23, 1989, p 21
58. P.M. Natishan, E. McCafferty, and G.K. Hubler, in *J. Electrochem. Soc.,* Vol 135, 1988, p 321
59. S. Akavipat, C.E. Habermann, P.L. Hagans, and E.B. Hale, in *Proceedings of the Symposium on Fundamental Aspects of Corrosion Protection by Surface Modification,* E. McCafferty, C.R. Clayton, and J. Oudar, Ed., The Electrochemical Society, 1984, p 52-61
60. S. Akavipat, E.B. Hale, C.E. Habermann, and P.L. Hagans, *Mater. Sci. Eng.,* Vol 69, 1985, p 311
61. P.L. Hagans, *Proceedings of the 41st World Magnesium Conference* (Dayton, OH), International Magnesium Association, 1984, p 30-38
62. P.L. Hagans and R.L. Yates, U.S. Patent 4,613,386, 1986

63. P.L. Hagans and R.L. Yates, U.S. Patent 4,767,678, 1988
64. P.L. Hagans and R.L. Yates, in *Proceedings of the Symposium on Environmental Degradation of Ion and Laser Beam Treated Surfaces,* K. Grabowski and G. Was, Ed., The Metallurgical Society, 1989, p 215-236
65. D.C. Bradley, R.C. Mehrotra, and D.P. Gauer, *Metal Alkoxides,* Academic Press, 1978
66. D.C. Bradley, in *Chem. Rev.,* Vol 89, 1989, p 1317
67. P. Kofstad, *High Temperature Corrosion,* Elsevier, 1988
68. K. Natesan, in *Corrosion (Houston),* Vol 41, 1985, p 646
69. V.A.C. Haanappel, H.D. van Corbach, T. Fransen, and P.J. Gellings, in *Thin Solid Films,* Vol 230, 1993, p 138
70. J.S. Kim, H.A. Marzouk, P.J. Reucroft, J.D. Robertson, and C.E. Hamrin, Jr., in *Thin Solid Films,* Vol 230, 1993, p 156

Rust-Preventive Compounds

Revised by Harry D. Ferrier, Jr., Quaker Chemical Corporation

Introduction

RUST-PREVENTIVE COMPOUNDS are removable coatings that are used to protect the surfaces of iron, steel, coated or galvanized products, and other alloys. Some compounds also protect nonferrous metals, such as aluminum, brass, and copper. Coatings of these compounds should be considered temporary, because their function is to protect surfaces during storage, handling, shipping, and fabrication. An additional application may be necessary after parts are fabricated. In some instances, the coating may need to be removed before fabrication or assembly.

Rust-preventive compounds are a combination of basic materials, inhibitors, and specialty additives. They vary in physical characteristics, depending on the properties required and the amount of protection needed at corrosion sites. A corrosion cell is like a battery, which has a cathode (-), an anode (+), and an electrolyte (liquid in cells). By coating the corrosion sites (anodes and cathodes) on a surface, rust-preventive compounds prevent contact with electrolytes, such as oxygen and moisture-containing materials.

Constituent Materials

A rust-preventive compound can consist of only one or a combination of these four basic parts: a carrier, a film former, polar materials, and specialty additives. For example, the rust protection offered by film formers, such as grease, petrolatum, and low-melting-point waxes, can be enhanced by the addition of a polar material, which has an affinity for steel and attaches to steel surfaces like a magnet.

Carriers, which can be oil, water, or solvent, facilitate the application and handling of the required amount of protective film.

Oil is the most widely used material. Because it provides little protection itself, it is usually used with both polar and specialty additives to form a temporary rust-preventing film. Oil can function as both a carrier and a film former.

As a carrier, it is widely used in the steel, aluminum, and brass industries, and is used to some extent in the pipe and tube industry. Fogging oils are used on fabricated parts for the metal-working industries (for example, appliance, automotive, and metal furniture industries), where temporary storage is needed before assembly. These parts can be readily cleaned prior to the painting process.

Water is used as a carrier when short-term indoor protection is needed. It can be used with polarity-type products and other specialty additives. Water also is used as the carrier for certain drawing compounds, but the use of water-based products is predicated on the amount of time the parts need to be stored. A fogging oil over the water-based film is sometimes required if there is a need to exceed the recommended storage time period.

Solvent, which is used with both barrier and polar additives, is designed to evaporate and leave a continuous film that affords either barrier or polar protection, or a combination of both. This type of carrier is used to coat the edges and exposed outer wraps of coiled or stacked sheet metals. When its solids content is very low, a solvent leaves behind a barely perceptible film, and has therefore become known as vanishing oil. It provides effective but temporary rust prevention on hot-dip galvanized products and other alloys used in the construction industry.

Film formers include grease, petrolatum, low-melting-point waxes, and thixotropic materials.

Grease and petrolatum are considered to be barrier films, because their consistency effectively bars electrolytes from contacting the surfaces to which they are applied. These films are usually quite viscous and are essentially self-healing in that they reflow over an area that has been disturbed during shipping and handling. Although they can be applied by brush or wiped on at room temperature, they are usually applied at elevated temperatures, in either a dip tank operation or by spray, and then allowed to set until they return to room temperature. The warm dip or spray application makes it easier to control the amount of film being applied.

Waxes also provide a barrier film that can be applied in a solvent cutback, which allows control of the coating weight, based on the amount of solids present, and facilitates application. After the solvent evaporates, a barrier film of lesser quantity remains, but good corrosion protection is still provided. A wax film is not as self-healing as one of petrolatum because it is slightly harder after the solvent evaporates.

Thixotropic materials are thick and heavy, like the petrolatum-based materials, even though they are primarily dispersed in a solvent carrier. They are used with other forms of barrier protection. When agitated under shear conditions, thixotropic materials become thin, but under static conditions, they regain their original high viscosity. After the solvent evaporates, it leaves a continuous barrier against rust.

Polar additives are used as temporary rust-preventive compounds. The addition of polar material to barrier films, waxes, or thixotropic materials will increase their corrosion protection. The unique properties of polar materials include a slight electrochemical charge and a corresponding attraction to metal surfaces. As these materials attach themselves to metal, they lift water from the surface and allow it to evaporate. Even when these additives are diluted in oil, they are usually readily removable using solvent, milk alkaline cleaners, and emulsifiers.

Water-dispersed or water-soluble oil compounds containing polar additives are typically used for short-term indoor protection of the in-process type, where subsequent operations do not exceed the stipulated protection time. The polar emulsifiers that are usually in these compounds stay with the protective film, making it readily removable. Although the length of protection afforded by these compounds is considered moderate, they are widely used because they are easy to apply and to remove, and they are economical.

Specialty additives are used to enhance both corrosion protection and the adaptability of products to subsequent operations. They also can provide short-term inhibition to in-process materials. They help reduce stain on the metal surface, and they can retard the shellacking, or oxidizing, of the rust-preventive film.

Certain additives will adhere to and passivate metal surfaces, providing short-term protection. Other additives act as oxygen scavengers, preventing oxygen from reacting with a metal surface and causing corrosion. Wetting-agent additives help spread a film and act as emulsifiers, aiding in film removal. They also serve a water-displacement function. Lubricants such as esters, soaps, and extreme-pressure additives (which are effective under high pressures and temperatures) are often used.

There also are additives that facilitate fingerprint neutralization and removal. They neutralize acids, salts, and other residues that may be introduced during handling. Lubricants such as esters, soaps, and extreme-pressure additives (which are effective under high pressures and temperatures) are oftem used. In some instances, rust-preventive compounds are removed after they have performed the intended operation and prior to reapplication of a longer-term rust-preventive compound.

Types of Rust-Preventive Compounds

Many rust-preventive compounds are designed for dual purposes. For example, in the metal-forming operations of automotive, appliance, metal furniture, and bearing industries, products are used not only as rust preventives, but as lubricants. In the steel industry, a rust-preventive compound is put on the surface of steel that has been pickled after hot

rolling. This compound, which is usually compatible with the cold-rolling oil, sometimes enhances lubrication of the rolling oil. It is referred to as a pickle oil.

In situations where steel is rolled prior to shipping, temper-mill lubricants are used. These lubricants must be compatible with the slushing oils that are designed to protect surfaces during shipping and handling. The use of polar additives in these slushing oils displaces the water diluent of the temper-mill lubricants.

Prelubes, or mill-applied lubricants, have more than dual functions. They function in tandem to other operations, offering corrosion protection, water-displacing properties that aid in removing water from the previous temper-mill operation, and lubrication that is sufficient for the parts fabrication process.

Generally, rust-preventive compounds are available as either dry films or water-based films. Products in both categories are described below.

Dry films can be categorized as those that will be removed from the metal and those that will not. The two types of products that are commonly used are hot-melt dry films and those that are diluted in either water or solvent. These products differ from the usual barrier type of protection in that they are dry to the touch and essentially stay in place. If they are disturbed in the course of handling, they cannot reflow and self-heal.

Hot-melt dry films, which are applied at elevated temperatures, are widely used as lubricants. They must be cooled prior to coiling or stacking to avoid nonadherence to the surface they must contact. Specialty additives are used in some of these films to facilitate removal when it is desired, as in the case of a prelube used in metal forming, which must be removed prior to any painting operation.

Solvent-cutback dry films, as well as hot melts, are used to control the amount of material being used. This solvent dilution allows the incorporation of specialty additives, such as those used for drying purposes or cosolvents used for fingerprint neutralization.

Hard, thin dry films are formed by the evaporation of the solvent, which leaves a product that is similar to a shellac or varnish. This product offers good protection, but is difficult to remove. Once set, the film resists abrasion during handling and cannot be removed by solvent wipes. This type of product is used in the pipe industry as a final protective film in situations that do not require its removal prior to the end use. Certain films are used as undercoats or primers in selected painting operations.

Water-based dry films use specialty additives to aid in drying, curing, or removability. Polar additives, small amounts of wax and resin (mostly acrylic), and other reactive-type additives are also used in these films. Some of these films are designed to be used without first being removed, whereas others do require removal. The films that provide the shellac-type finish are used when removal is not necessary.

Other water-based dry films are specifically designed as rust preventives and lubricants. They must be readily removable in alkaline cleaners prior to prepaint and painting operations. They also can be used in metal-forming operations, which necessitates film removal prior to painting.

Tables 1 and 2 list the characteristics, applications, and properties of rust-preventive compounds covered by military specifications. These tables indicate which of these compounds can also function as lubricants or drawing and forming compounds. For example, the MIL-L-6085 product acts as a lubricant for instruments and provides corrosion protection, whereas the MIL-H-6083 product is a hydraulic fluid that also must protect against corrosion.

Table 1 Characteristics and applications of rust-preventive materials covered by military specifications

Specification number	Specification title	Description	Intended use
MIL-C-450 (Types I, II, and III)	Coating compound, bituminous, solvent type, black	Black asphalt, dry coating; solvent cutback	Protect battery racks; coat interior of projectiles

Specification number	Specification title	Description	Intended use
MIL-C-4339	Corrosion-preventive soluble oil, for water-injection systems	Mineral oil with emulsifying agents and inhibitors	Protection against corrosion by water and alcohol
MIL-C-5545	Compound, corrosion preventive, aircraft engine heavy oil type	Thixotropic preservative oil; leaves soft, greasy film that becomes fluid when engine is started	Corrosion protection of internal parts and surfaces of engines and equipment
MIL-C-6529	Corrosion preventive, aircraft engine	Concentrate intended for 1-to-3 dilution with Navy symbol oil	Preservation of turbojet and reciprocating engines
MIL-C-8188	Corrosion-preventive oil, gas turbine engine, aircraft synthetic base	Synthetic oil plus corrosion inhibitors	Preservation of turbojet and turboprop engines
MIL-C-10382	Corrosion preventive, petrolatum, spraying application for food-handling machinery and equipment	Thin film, easily removable when dry; solvent cutback	Corrosion protection of food-handling equipment
MIL-C-11796			
Classes 1 and 1 A[(a)]	Corrosion-preventive compound, petrolatum, hot application	Thick, nondrying, dark, firm, grease-like film; leaves oil slick on salt water[(a)]	Unshielded outdoor storage of gun tubes; long-term protection of highly finished parts of simple design
Class 2	Corrosion-preventive compound, petrolatum, hot application	Thick, dark, medium-firm, greasy film	Unshielded outdoor storage in moderate climates, at below flow point of compound (64 °C or 145 °F); general packaging of automotive parts
Class 3	Corrosion-preventive compound, petrolatum, hot application	Fairly thin, soft, greaselike material	Protection of highly finished, cleanable parts of complex design; preservation of antifriction bearings
MIL-C-15074	Corrosion preventive, fingerprint remover	A mixture of organic solvents, petroleum solvents, and inhibitors	Removal of fresh fingerprint residues; temporary corrosion prevention
MIL-C-16173			
Grades 1 and 1A[(b)]	Corrosion-preventive compound, solvent cutback, cold application	Hard, dark film about 50 to 100 μm (2 to 4 mils) thick; solvent cutback; dries to touch in 4 h[(b)]	On metals under outdoor conditions; general-purpose preservation, indoor or outdoor, with or without cover; domestic or overseas shipment where a dry-to-touch film is required; not for intricate assemblies

Specification number	Specification title	Description	Intended use
Grade 2	Corrosion-preventive compound, solvent cutback, cold application	Amber-colored soft film about 25 μm (1 mil) thick; solvent cutback; drying time, 4 h; 200 μm (8 mils) maximum thickness	Extended undercover protection of interior or exterior surfaces of machinery, instruments, bearings, or materials with or without overwrap
Grade 3	Corrosion-preventive compound, solvent cutback, cold application	Nondrying film about 8 to 20 μm (0.3 to 0.8 mil) thick; solvent cutback	Where water or saline solution must be displaced; protection of materials under cover for limited periods; protection of critical bare or phosphated steel surfaces for extended periods when overwrap is used
Grade 4	Corrosion-preventive compound, solvent cutback, cold application	Transparent, nontacky film; 25 μm (1 mil) maximum thickness	Shed or indoor storage where dry transparent coating is needed; permits stacking
MIL-C-22235	Corrosion-preventive oil, nonstaining	Lubricating oil with added inhibitors; pour point, -12 °C (10 °F)	Rust preventive for hot- and cold-rolled steel in storage, in stacks
MIL-C-40084	Corrosion-preventive compound, water emulsifiable, oil type	Mineral oil with corrosion inhibitors in an emulsion; soft film; fire resistant	Low-cost corrosion preventive, fire resistant, thin film
MIL-G-10924	Grease, automotive and artillery	Preservative grease	Lubricant for automotive and artillery equipment, at -54 to 51 °C (-65 to 125 °F)
MIL-G-18458	Grease, wire rope, exposed gear	Petroleum oil and soaps plus inhibitors	Lubrication and corrosion protection for running ropes and exposed gear
MIL-H-6083	Hydraulic fluid, petroleum base, preservative	Light petroleum hydraulic fluid with inhibitors	As a preservative oil in aircraft hydraulic systems and shock-absorber struts
VV-L-800	Lubricating oil, general purpose, preservative (water-displacing, low temperature)	Lubricating oil with added inhibitors; pour point, -57 °C (-70 °F) max	Lubrication and corrosion-protection of small arms; general application wherever a multipurpose, low-temperature oil is required
MIL-L-3150	Lubricating-oil preservative, medium	Lubricating oil with added inhibitors; similar to SAE 30; pour point, -7 °C (20 °F)	Corrosion protection of highly finished internal and external surfaces; not for internal-combustion engines
MIL-L-6085	Lubricating oil, instrument, aircraft, low volatility	Light, low-volatility, synthetic lubricant containing rust preventive; pour point, -57 °C (-70 °F)	Protection of bearings in instruments, electronic equipment, or wherever a low-evaporation oil is required for both high and low temperatures
MIL-L-11734	Lubricating oil, synthetic (for mechanical time fuses)	Synthetic oil with inhibitors	Lubricate and protect mechanical time fuses at normal and below-freezing temperatures

Specification number	Specification title	Description	Intended use
MIL-L-14107	Lubricating oil, for aircraft weapons	Synthetic lubricating oil with inhibitors; pour point, -59 °C (-75 °F)	Lubrication of aircraft automatic weapons; for use below -18 °C (0 °F)
MIL-L-17331	Lubricating oil, steam turbine (noncorrosive)	Petroleum oil plus inhibitors	Lubrication of main turbine gears, auxiliary turbines, air compressors, hydraulic equipment
MIL-L-19224 (Grades A, B, and C)	Lubricating oil, mineral, preservative; pour point -34 °C (-30 °F)	Lubricating oil in three grades with inhibitors	Lubricant and preservative where uninhibited oils do not afford sufficient protection
MIL-L-21006	Rust-retarding compound, flotation type, ballast tank protection	Petroleum-base fluid compound with inhibitors; pour point, -7 °C (20 °F)	Rust-retarder in tanks used for salt-water ballast
MIL-L-21260			
Grade 1	Lubricating oil, internal-combustion engine, preservative	Engine-lubricating oil (SAE 10W) with corrosion inhibitors, including hydrobromic acid neutralizers; pour point, -29 °C (-20 °F)	Lubricant in spark-ignition and compression-ignition reciprocating internal-combustion engines
Grade 2	Lubricating oil, internal-combustion engine, preservative	Same makeup as Grade 1, but SAE 30W and pour point of -18 °C (0 °F)	Same as Grade 1
Grade 3	Lubricating oil, internal-combustion engine, preservative	Same makeup as Grade 1, but SAE 50 and pour point of -9 °C (15 °F)	Same as Grade 1
MIL-L-46000	Lubricating oil, semifluid, automatic weapons	Synthetic gel-like oil plus inhibitors	Operation of M61, M39, and related types of automatic weapons
MIL-L-46002			
Grade 1	Lubricating oil, contact and volatile corrosion inhibited	Lubricating oil with added contact and volatile corrosion inhibitors, SAE 5	Preservation of enclosed systems
Grade 2	Lubricating oil, contact and volatile corrosion inhibited	Same as Grade 1, but SAE 30	Preservation of enclosed systems
MIL-P-3420	Packaging materials volatile corrosion inhibitor, treated, opaque	Barrier material, impregnated with volatile corrosion inhibitors	Protection of ferrous metal parts

Specification number	Specification title	Description	Intended use
MIL-W-3688	Wax emulsion (rest inhibiting)	Dry, hard, nontacky, flexible surface emulsion of wax in water	Dry lubricant and rust-inhibiting coating for general weatherproofing

(a) Class 1A is similar in all respects to Class 1, except that it will not leave an oil slick on salt water.

(b) Grade 1A is similar in all respects to Grade 1, except that drying time is 72 h.

Table 2 Properties of rust-preventive materials covered by military specifications

Specification number	Minimum melting point (MP) or flash point (FP), °C (°F)	Method[(a)]	Application temperature, °C (°F)	Coverage[(b)]		Method of removal	Viscosity[(c)]	Penetration
				m^2/L	ft^2/gal			
MIL-C-450 (Types I, II, and III)	. . .	B, S	Ambient	15	750	Petroleum solvent	I: 15-28 s[(d)] II: 120-190 s[(d)]	III: 150-250 at 25 °C (77 °F)
MIL-C-4339	. . .	D, S	Ambient	. . .	. . .	Petroleum solvent	100-400 SUS at 38 °C (100 °F)	. . .
MIL-C-5545	FP: 260 (500)	F[(e)]	96	10	500	Not required[(f)]	115-150 SUS at 99 °C (210 °F)	. . .
MIL-C-6529	FP: 205 (401)	B, D, S, or fill	Ambient	30	1500	Not required[(f)]	. . .	. . .
MIL-C-8188	FP: 180 (356)	B, D, S	Ambient	40	2000	Petroleum solvent	3.0 cSt at 99 °C (210 °F) 11.0 cSt at 38 °C (100 °F) 18,000 cSt at -54 °C (-65 °F)	. . . .
MIL-C-10382	FP: 38 (100) MP: 66 (151)	B, D, S	Ambient	20	1000	Petroleum solvent	. . .	. . .
MIL-C-11796								
Classes 1 and 1A[(g)]	MP: 68 (154) FP: 180 (356)	D, S	79-93[(h)] (174-199) 93-105[(i)] (199-221)	. . .	15/lb	Petroleum solvent	. . .	30-80 at 25 °C (77 °F)

Specification number	**Minimum melting point (MP) or flash point (FP), °C (°F)**	**Method**[a]	**Application temperature, °C (°F)**	**Coverage**[b]		**Method of removal**	**Viscosity**[c]	**Penetration**
				m²/L	**ft²/gal**			
Class 2	FP: 180 (356) MP: 66 (151)	D, S	71-88[h] (160-190) 85-90[i] (185-194)	. . .	15/lb	Petroleum solvent	. . .	90-150 at 25 °C (77 °F)
Class 3	FP: 180 (356) MP: 57 (135)	B, D, S	16-49[j] (61-120) 66-82[h] (151-180) 78-85[i] (172-185)	. . .	15/lb	Petroleum solvent	. . .	200-325 at 25 °C (77 °F)
MIL-C-15074	FP: 38 (100)	B, D	Ambient	. . .	. . .	Petroleum solvent	30 cSt at 38 °C (100 °F)	. . .
MIL-C-16173								
Grades 1 and 1A[k]	FP: 38 (100) MP: 66071 (151-160)	B, D, S	7-35 (45-95)	9	450	Petroleum solvent	. . .	25[l] at 25 °C (77 °F)
Grade 2	FP: 38 (100)	B, D, S	4-35 (39-95)	20	1000	Petroleum solvent	. . .	200 at 25 °C (77 °F)
Grade 3	FP: 38 (100)	B, D, S	4-32 (39-90)	20	1000	Petroleum solvent	. . .	. . .
Grade 4	FP: 38 (100)	B, D, S	4-32 (39-90)	20	1000	Petroleum solvent	. . .	. . .
MIL-C-22235	FP: 140 (284)	B, D, S	Ambient	30	1500	Petroleum solvent	100-140 SUS at 38 °C (100 °F)	. . .
MIL-C-40084	FP: 96 (205)	B, D, S	25-82 (77-180)	30	1500	Petroleum solvent	. . .	. . .
MIL-G-10924	160[m] (320)	Gun	Ambient	. . .	. . .	[f][n]	. . .	265-295 at 25 °C (77 °F)
MIL-G-18458	66[m] (151)	Gun	Ambient	. . .	. . .	[f][n]	. . .	200-300 at 25 °C (77 °F)

Specification number	Minimum melting point (MP) or flash point (FP), °C (°F)	Method[(a)]	Application temperature, °C (°F)	Coverage[(b)]		Method of removal	Viscosity[(c)]	Penetration
				m²/L	ft²/gal			
MIL-H-6083	FP: 93 (199)	Fill	16-49	. . .	. . .	Not required[(f)]	10 cSt at 54 °C (129 °F) 800 cSt at -40 °C (-40 °F)	. . .
VV-L-800	FP: 135 (275)	B, D, S	16-49	50	2500	Not required[(f)]	12 cSt at 38 °C (100 °F) 60,000 cSt at -54 °C (-65 °F)	. . .
MIL-L-3150	FP: 150 (302)	B, D, S	16-49	30	1500	Not required[(f)]	185-255 SUS at 54 °C (129 °F)	. . .
MIL-L-6085	FP: 185 (365)	D, S	Ambient	50	2500	Not required[(f)]	8 cSt at 54 °C (129 °F) 2,000 cSt at -40 °C (-40 °F) 12,000 cSt at -54 °C (-65 °F)	. . .
MIL-L-11734	. . .	B, D, S	Ambient	40	2000	Not required[(f)]	12.5 cSt at -38 °C (-36 °F) 15,000 cSt at -57 °C (-71 °F)	. . .
MIL-L-14107	FP: 160 (320)	B, D, S	Ambient	50	2500	Not required[(f)]	5.8 cSt at 38 °C (100 °F) 900 cSt at -59 °C (-74 °F)	. . .
MIL-L-17331	FP: 180 (356)	B, D, S	Ambient	. . .	. . .	Not required[(f)]	8.2 cSt at 99 °C (210 °F) 82-110 cSt at 38 °C (100 °F)	. . .
MIL-L-19224 (Grades A, B, and C)	(A)FP: 160 (320) (B)FP: 200 (392) (C)FP: 210 (410)	B, D	-30 to 74	30	1500	Not required[(f)]	Grade A: 90-120 SUS at 54 °C (129 °F); Grade B: 45-55 SUS at 99 °C (210 °F); Grade C: 60-70 SUS at 99 °C (210 °F)	. . .
MIL-L-21006	FP: 160 (320)	. . .	Ambient	24	1200	Not required[(f)]	. . .	. . .
Grade 1	PF: 180 (356)	F, S[(o)]	Ambient	30	1500	Not required[(f)]	44-50 SUS at 99 °C (210 °F) 12,000 SUS at -18 °C (-0.4 °F)	. . .
Grade 2	PF: 200 (392)	F, S[(o)]	Ambient	30	1500	Not required[(f)]	58-70 SUS at 99 °C (210 °F) 200,000 SUS at -18 °C (-	. . .

Specification number	Minimum melting point (MP) or flash point (FP), °C (°F)	Method[(a)]	Application temperature, °C (°F)	Coverage[(b)]		Method of removal	Viscosity[(c)]	Penetration
				m^2/L	ft^2/gal			
							0.4 °F)	
Grade 3	PF: 205 (401)	F, S[(o)]	Ambient	30	1500	Not required[(f)]	85-110 SUS at 99 °C (210 °F)	. . .
MIL-L-46000	. . .	B, D	Ambient	15	750	Not required[(f)]	. . .	350-385 at 25 °C (77 °F)
MIL-L-46002								
Grade 1	FP: 115 (239)	B, D, S	Ambient	40	2000	Not required[(f)]	12 cSt at 38 °C (100 °F) 10,000 cSt at -40 °C (-40 °F)	. . .
Grade 2	FP: 120 (248)	B, D, S	Ambient	30	1500	Not required[(f)]	9.65-12.98 cSt at 99 °C (210 °F) 95-125 cSt at -38 °C (100 °F)	. . .
MIL-P-3420	. . .	. . .	Ambient	. . .	. . .	[(p)]	. . .	. . .
MIL-W-3688	74[(m)] (165)	D, S, or wipe	Room temperature	. . .	. . .	Petroleum solvent	. . .	. . .

(a) B, brush; D, dip; F, fog; S, spray.

(b) Average anticipated coverage; subject to wide variation.

(c) Viscosity conversions: 100 SUS (20.55 cSt); 115 SUS (23.85 cSt); 150 SUS (31.70 cSt); 400 SUS (86.2 cSt). According to ASTM D 217, penetration is recorded in tenths of a millimeter. Penetration values for greases are frequently reported without the units.

(d) No. 4 Ford cup reading.

(e) For cylinders. For crankcase, dilute 1-to-1 with grade 1100 Navy symbol oil, fill, run engine until hot, then drain.

(f) Removal, if desired, may be effected with petroleum solvent.

(g) Class 1A is similar in all respects to Class 1, except that it will not leave an oil slick on salt water.

(h) For dip application.

(i) For spray application.

(j) For brush application.

(k) Grade 1A is similar in all respects to Grade 1, except that drying time is 72 h.

(l) On solids; needle penetration.

(m) Dropping point, minimum.

(n) Flush with fresh grease.

(o) Into cylinders or crank case.

(p) Remove powderlike residues with methyl alcohol rinse.

In the metal-stamping and -forming industry, the properties that are usually specified include corrosion protection, ease of removability, compatibility with prepaint operations and paint systems, and lubrication when a mill-applied product is used (usually performed as an on-line forming test).

Methods of Application

Rust-preventive compounds are applied by:

- Spraying or fogging electrostatically
- Dipping
- Flowing or slushing
- Brushing or wiping

The type of rust preventive and the quantity, size, complexity, and surface finish of the articles to be coated will determine which method should be used. The equipment and methods of application are similar to those used in painting.

Petrolatum compounds can be applied either hot or cold. Generally, cold application is restricted to parts that are either too large and bulky for practical tank immersion or require only localized protection, such as the ways for a lathe bed. When these compounds are applied cold, their consistency requires the use of brushing or wiping. When brushing is used, the bristles of the brush should be stiff enough to permit brush-out of the material, but not so stiff as to leave deep brush marks in the preservative. With these materials, it is often advantageous to build up coatings to the desired final thickness by the successive application of thin layers.

When petrolatum rust-preventive compounds are applied hot, dipping is the most practical method. Parts that are too large to be dipped can be coated by brushing, wiping, or spraying. Small parts to be dipped are placed in baskets, whereas larger parts are individually dipped. Dipping can be manual, when the volume of parts is low; conveyors can be used when parts are produced in large quantities.

Most dipping tanks for petrolatum compounds are heated by steam coils, hot-water jackets, electrical immersion heaters, or plate coils using either hot water or steam. Although precise temperature control is not usually required, the compound in the dipping tank must not become overheated. Overheating can cause decomposition of the preservative, and the resulting products may act as corrosion agents. Some petrolatum products have been applied at elevated temperatures electrostatically, which can afford better control of the amount of coating being applied.

Oil compounds can be applied electrostatically or by dipping, spraying, flowing, brushing, or wiping. The thickness of the coating depends on the viscosity, fluid characteristics (whether the fluid is Newtonian or non-Newtonian), and surface tension of the oil compound. Oils of high viscosity usually are heated before being applied. Parts or assemblies coated by immersion in oil preservatives should be turned or agitated to permit all trapped air to escape. When the material is applied at room temperature, the parts will require immersion only long enough to ensure complete coverage.

For spray or electrostatic application, oil-based rust-preventive compounds usually do not require dilution and are applied as received. Moderate air pressure or an airless spray is used to avoid misting and overspraying of the material. A wetting spray is usually sufficient. It is more difficult to control coating weight and uniformity by spray application than by dipping or by electrostatic application in coil or sheet stock. To ensure an adequate coat, the material should be applied according to the specifications supplied by the end user. Oil-based compounds used on coil or sheet stock are applied by using the roll-coater spray and electrostatic methods, which allow some control of the coating weight. After a spray application, squeegee rolls are used. Changing the pressure on the squeegee can help control the amount of film on the surface.

Emulsion compounds are oil-in-water emulsions that contain from 8 to 12% solids. These compounds, which are available as concentrates, are diluted with water at ratios of 4 to 10 parts water to 1 part concentrate, as specified in MIL-C-40084.

These compounds, which are widely used for small parts, are applied by dipping or spraying. The effectiveness of the application can be increased by heating either the parts or the compound. For example, the unheated compound can be applied in the third stage of a power washer in which the parts retain residual heat produced during the first two stages. If dipping is used, then the compound can be heated to a gentle boil before immersion of the unheated parts.

Oil-in-water emulsions are fire resistant during application. However, after the water has been removed by drying, the residual film has flammability characteristics that are comparable to those of petroleum oils or waxes.

Solvent-cutback compounds are essentially waxes modified with high-melting-point polar additives, such as soaps. Compounds that use organic solvents as the diluent are applied at room temperature. Small parts usually are batch coated in wire baskets, which are immersed, withdrawn, and centrifuged to remove excess material. Commercial equipment is available for this method of application. The parts are then removed from the basket and are either spread out to dry or conveyed through an air-drying stage, which may be mildly heated.

Because some solvent-cutback compounds develop dry, hard films, parts may become bonded together by the film. Separating these parts often results in tears in the coating. Large parts can be spray or dip coated, but all solutions are not necessarily applied equally well by both methods. Parts that are too large for dipping can be coated by spraying or brushing.

When this type of product includes polar materials, it can be used on coil and sheet stock to protect edges and other exposed portions during shipping and handling. Spray, brush, or paint-roller-type applicators can be used. High-flash-point vanishing oils (solvent cutback) have also been applied electrostatically. However, extreme caution should be taken to ensure against arcing. The equipment manufacturer should be consulted prior to testing or use.

Water-displacing compounds are most effective when they are applied by dipping, although spraying also can be used. These materials actually remove films or droplets of water from metal surfaces by preferential wetting, that is, the attraction of the rust-preventive compound to the metal surface is greater than that of water and, thus, the preservative displaces the water. Complete immersion of the part makes the coverage more positive.

A suitable dip tank for automatic water removal from a water-displacing preservative system is shown in Fig. 1. Because the specific gravity of the preservative is less than that of water, the height of the column of water is somewhat less than the height of the column of preservative. Parts that are too large to coat by immersion and too impractical to spray can be

coated by wiping. Wiping is also used when only certain areas of parts need to be coated. Coiled and sheet stock can be electrostatically coated.

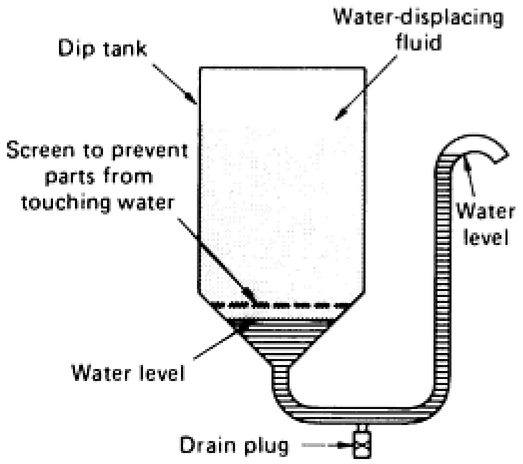


Fig. 1 Tank for dip application of water-displacing rust-preventive compounds

Fingerprint removers and neutralizers can be applied by spraying, dipping, or brushing, the latter of which is usually used only when a section of a part needs to be coated. These materials are applied at room temperature. Sufficient fluid should be present in the system to prevent gross contamination or preferential depletion of the active ingredients that dissolve or neutralize the corrosive materials.

Rust-Preventive Material Selection

The occurrence of rust on the surfaces of steel or other iron-base alloys is dependent on contact with moisture and oxygen. The extent of rusting is a function of the duration of this contact and of temperature. Temperature also affects the rate of rusting, which can be accelerated by the presence of chloride salts, oxides of sulfur, and other electrolytes that enter into or modify the chemical reactions involved.

The composition and metallurgical characteristics of the alloy also influence the extent and rate of rusting, and they frequently determine whether the rusting reaction affects the surface in a general and uniform way or by localized pitting. There are two important factors that determine the extent to which a surface must be protected from rusting. One is the degree of finish, that is, whether the surface is ground, rough machined, or as-forged. The other is the extent to which rust impairs function. The selection of rust-preventive compounds is primarily influenced by the:

- Environment, in terms of climatic conditions, geographic location, and type of storage facilities, as well as the anticipated amount of time a part must spend in storage
- Type of material to be protected and the need for removing the rust-preventive compound

These considerations are described below, whereas other selection parameters are described in the next section of this article.

Storage Environment and Duration. The severity of climatic, geographic, and storage environments varies considerably. Mild conditions are exemplified by a rural inland area with a daily temperature that ranges from -1 to 16 °C (30 to 60 °F) and a relative humidity that ranges from 25 to 70%. Severe conditions are exemplified by a southwestern seacoast or southeastern areas, where the temperature differential can exceed 33 °C (60 °F), and 100% relative humidity is reached once or twice each day. Moisture condensation results when these conditions cause the dew point to be reached. Therefore, the requirements for a successful rust-preventive compound appropriate for any specific surface stored for 6 months inside a completely enclosed building could range from a very light oil, in the rural area, to a heavy-film petrolatum, in the seacoast and southeast locations.

Because coiled stock is not fully exposed, it can be protected sufficiently for the short term by using a typical slushing oil that contains some barrier protection, along with the usual polar materials.

Outside storage in either location would require the use of a rust-preventive compound that has been designed to cope with the erosive effect of rainfall. In an industrial inland area, the corrosion-protection requirement must be extended to include resistance to the increased reactivity of the fumes present in an industrial atmosphere. For example, a very light oil might need to be replaced by a soft petrolatum. Careful determination of the environmental factors against which the rust-preventive compound must perform is of major importance in selecting the proper rust-preventive compound. Another important consideration is the duration of exposure to the environment.

The requirements of a rust-preventive compound can be affected significantly by the degree of auxiliary protection afforded by the type of enclosure used for storing coated articles. Maximum auxiliary protection is provided by storage in either a fully enclosed, humidity-controlled area in a permanent building or a container that is sealed against moisture and that holds desiccants to absorb any moisture originally present.

Types of Parts Requiring Protection. There are four general categories of parts or assemblies that require the application of rust-preventive compounds when they are being stored:

- Assembled machinery or equipment in standby storage
- Finished parts (in stock) or spare parts (for replacement)
- Tools, such as drills, taps, dies, and gages
- Mill products, such as sheet, strip, rod, and bar

Assembled machinery or equipment in standby storage requires two distinctly different types of protection. First, all exterior surfaces require protection from the atmospheric conditions to which they are exposed. The selected rust-preventive compound must be able to withstand normal handling conditions. Second, the interior surfaces of assembled machinery require the use of preservative oils that must act as temporary lubricants when the equipment is put into service. These oils must be completely compatible with the lubricating oils, hydraulic fluids, or greases that are to be used in service.

In an adequately heated, well-ventilated building, oil-film protection usually suffices for the external and internal surfaces of exposed machinery parts. In loosely constructed, inadequately heated buildings, where machinery may be subjected to extreme changes in humidity, petrolatum or solvent-cutback rust-preventive compounds are essential for all exposed surfaces. Interior surfaces must be protected with a good rust-preventive oil.

For outdoor storage or storage in open-sided or unheated sheds in a dry, clean atmosphere, petrolatum used as an outer coating and a rust-preventive oil used on interior surfaces should provide adequate protection. In marine atmospheres or environments where corrosive industrial fumes exist, hard-film corrosion preventives or heavy-duty petrolatum materials must be used on all exposed surfaces. Specially designed oil compounds are available for internal or physically shielded surfaces.

Machinery or equipment exposed to rough handling or mechanical abrasion that could damage or remove an oil or petrolatum film should be protected with a hard-film rust-preventive compound. This material should be of the type that can be removed when required.

One large manufacturer of machine tools, situated in an inland industrial location with a daily temperature differential of 11 °C (20 °F) and frequent occurrences of 100% humidity during spring and fall months, uses three basic types of rust-preventive products for in-plant preshipment protection of parts and assemblies. For in-process periods of 2 to 3 weeks, a very light fingerprint neutralizer suffices. For longer periods of in-plant storage, an oil-based compound with a viscosity of approximately 200 SUS (4.3×10^{-5} m^2/s, or 43 cST) at 38 °C (100 °F) is necessary. (SUS stands for *Saybolt Universal Seconds,* i.e., the time required for 60 cm^2 of a fluid to flow through the orifice of the Standard Saybolt Universal Viscometer at a given temperature under specified conditions.) When inventory needs to be stored for very long or indeterminate periods, or in covered storage outdoors, a solvent-cutback rust-preventive compound is used. For the shipment of assembled machine tools, products similar to those described in MIL-C-16173 (Tables 1 and 2) are used to protect exterior surfaces. Interior protection of lubricating systems and reservoirs is provided by preservative oils similar to grades 1 and 2 of MIL-L-21260 (Tables 1 and 2).

Finished machined parts and spare parts, such as gears, mill rolls, and mandrels, should be cleaned of coolants, machine oils, cutting oils, and other foreign matter before being coated with rust-preventive compounds. Highly sulfurized fatty or chlorinated cutting oils in prolonged contact with steel can cause staining. Covering these cutting oils and coolants with a rust-preventive compound does not prevent this corrosive action.

For short-term indoor protection, fingerprint-neutralizing compounds usually provide adequate protection for up to 2 weeks. Although test results for some products indicate protection for up to 6 weeks, the short-term recommendation should be followed. For long-term indoor storage, or for storage in corrosive atmospheres, fingerprint neutralizers are first applied to prevent corrosion or staining caused by body acids or salts that are deposited on the finished surfaces after finger contact. These neutralizers are then removed, and an appropriate long-term rust-preventive product is applied.

In an atmosphere that is not particularly corrosive, parts stored in a weatherproof building with no humidity control are protected with a light coating of an oil-based compound. In marine or industrial areas with corrosive atmospheres, appropriate petrolatum or solvent-cutback materials usually provide protection for 6 mo. Machined parts stored outdoors should be protected by a heavy coating of a petrolatum material.

Tools. Corrosion-protection measures may be necessary before drills, reamers, taps, cutter heads, tool holders, and other metal-cutting tools and accessories are placed in storage after use. Water-emulsion or soluble-oil cutting fluids should be completely removed before any tool is coated with a rust-preventive compound, in order to prevent moisture entrapment. One tool manufacturer suggests cleaning tools with 1,1,1,-trichloroethane before applying the protective film. Machine oils, used at the machine, may provide adequate protection for the short-term storage of tools and accessories. Surplus oil should be wiped off to minimize runoff in storage.

Although the oily, nondrying rust-preventive compounds will adequately protect tools stored in the normal crib, oil runoff or ruboff can be undesirable. Dry films circumvent this problem, and because the films are dry, normal shop dirt does not adhere to them. If the dry film is not thick, it may be unnecessary to remove it when the tools or accessories are again placed in service. If this protective material will not be removed, then it should be compatible with fluids used at the machines.

Tools such as drills, reamers, and milling cutters are sometimes protected from rust and abrasion after being coated with a strippable cellulose acetate compound. The coating is applied by dipping the tool in the compound at a temperature of approximately 120 °C (250 °F).

Hard film coatings are not recommended for use on adjustable chucks and other tool accessories, because the incomplete removal of a hard film could cause malfunction. Instead, thinner, oily films are usually recommended. If shop dirt is a problem, then a protective wrapping can be applied. In this case, it is necessary for the wrapping and the preservative to be compatible, so that accelerated corrosion of the metal is not initiated.

When a corrosive environment is not severe, molding, stamping, or forming dies may require only a light coating of rust-preventive oil, before being placed in storage. When the atmosphere is corrosive, these dies may require a petrolatum compound. It is often unnecessary to provide any additional rust-preventive coating once these dies have been used in production, because the oily film of the die lubricant that remains from the production run can provide sufficient protection. If residual die lubricants do not provide a complete film, then a thin oil is usually sprayed on the die. In extreme cases, a grease-like material is brushed on.

Dies for molding or extruding plastic parts, which are highly polished, are run in a dry condition. Consequently, a rust-preventive compound that is usually thin and oily is sprayed on the die or mold before storage. This material is then removed with a solvent before the die or mold is placed in production.

Mechanical gages require special consideration in the rust-preventive selection process. Although complete protection is required of a film, it must allow the gage to be used without the need to remove the film. Therefore, thin oil preservatives are applied in a light film. Periodic renewal of the film may be necessary.

During temporary storage, used gages often can be protected by being brushed with a soft petrolatum that can be removed easily by wiping. Specially treated papers for wrapping precision tools and gages for maximum protection are required during overseas shipment.

Mill products, as received from the mill, usually have light to medium oil coatings that protect against corrosion for short periods. It is often necessary to provide additional protection. For short-term outdoor storage, light oils usually provide adequate protection, although exposure to corrosive atmospheres may necessitate more protection. For an extended period of outdoor storage, heavy oils or petrolatums may be required.

The use of rust-preventive compounds on mill products must be considered in terms of the manufacturing operations that the products will undergo. For the protection of rod and bar stock, a rust-preventive compound must be compatible with the cutting fluids that will be used, so that there is no need to remove the compound. Sheet and strip that will go through a punch press can be coated with a compound that does not require removal and can also function as the lubricant to facilitate manufacturing. Other rust-preventive compounds, such as prelubes, are removed after the stamping process and prior to painting. Slushing oils applied to sheet and coiled stock utilize polar materials to retard corrosion. They are used primarily where they will eventually be removed, such as after drawing and forming operations. They also must be removed prior to plating operations.

Depending on either the severity of the expected storage conditions or the requirements of the user, finished tubing is usually protected by one of these products:

- Well-refined, neutral mineral oil (No. 1 or No. 2 color) with a viscosity of 100 SUS (2.05×10^{-5} m^2/s, or 20.55 cST) at 38 °C (100 °F), containing a suitable rust-preventive additive
- Rust-inhibited petrolatum of a soft, grease-like consistency, applied by dipping at 82 °C (180 °F). Its color should be amber to green; its melting point should range from 51 to 57 °C (125 to 135 °F); and its viscosity should be approximately 90 SUS (1.8×10^{-5} m^2/s, or 17.98 cST) at 100 °C (210 °F).
- Transparent, varnish-like rust-preventive compound in the form of a solvent-cutback hard-film product that is spray applied at room temperature. The coating should set in 25 min and be dry to the touch in 2 to 3 h.

Physical and Chemical Considerations. Some assemblies incorporate nonmetallic materials that can deteriorate upon contact with either hydrocarbon-based materials or preservatives containing acids and bases. Polymeric materials, for example, can swell, harden, crack, soften, or otherwise deteriorate and become unfit for service. Product storage and shipping requirements should be anticipated in the beginning stages of design, so that a proper preservative is selected to protect the metallic units of the assembly without attacking the nonmetallic components.

The physical form of a rust preventive, that is, whether it is an oil-based or petrolatum material or an aqueous emulsion, can either dictate or prevent its use for a specific application. For example, a petrolatum compound is unsuitable for the corrosion protection of internal components of high-speed business machines, because its heavy makeup could cause excessive sticking and eventual malfunction of the machine, even when the components are well protected from corrosion. The use of a solvent-cutback material also is undesirable, because minute traces of the solvent might vaporize after assembly of the components, and the resulting hard film could interfere with proper machine function. Solvent-diluted rust-preventive compounds should not be used in a confined system unless ventilation is provided to disperse the combustible solvent vapors and prevent internal degreasing. For this specific application, a rust-preventive compound based on a mineral oil of suitable viscosity should be selected.

The physical characteristics of the film left by a rust-preventive compound should be considered if the surface to which it is applied must receive additional coatings. The use of an oily material of any type is less desirable than the use of a material that forms a hard, dry film, if the surface is to be painted without an intermediate cleaning operation. Extremely viscous or semisolid rust-preventive compounds should not be used on intricate assemblies that may present a cleaning problem or on highly polished surfaces. For example, the polished surfaces of plastic molding dies must remain mirror bright. Rust-preventive compounds applied for storage or shipping purposes must be readily removed without any surface abrasion before the die can be used.

The protection of antifriction bearings with viscous or semisolid rust-preventive compounds is impractical because the removal of such materials is difficult. Antifriction bearings should be protected by a compound that does not require removal and is thin enough to permit satisfactory operation after the addition of lubricant. In one plant, antifriction bearings are coated with a rust-inhibited petrolatum that has a melting point of 40 to 43 °C (104 to 110 °F) and an application temperature of 115 °C (235 °F). The petrolatum coating produces a thin film that is compatible with any lubricant. Afterward, the bearings are wrapped with treated paper.

Chemical reactions that can occur between a rust-preventive compound and the surface to which it is applied must be considered in the selection process. Some aqueous-based rust preventives passivate the surface instead of forming a protective film. When these materials are based on alkaline solutions of organic chemicals in water, they should not be used in contact with magnesium, zinc, or other metals susceptible to alkaline attack. The corrosion inhibitor frequently used to regenerate automotive antifreeze solutions is one example of this material. Automotive radiators typically use dissimilar metals.

Rust-preventive compounds based on mineral oil, which are used on components of hydraulic systems, can be difficult to remove when preparing the system for operation, because many of the newer hydraulic fluids are incompatible with mineral oils. The U.S. Navy uses hydraulic fluids based on phosphate ester systems in various types of operating equipment. At the time of manufacture, such equipment needs to be protected by a rust-preventive compound based on a phosphate ester similar to that which will be used in operation. Because many government and industrial installations use water-glycol fluids in hydraulic equipment, any rust preventives used on this equipment should be compatible with the water-glycol fluid.

Other Selection Parameters

The film thickness of rust-preventive compounds must be controlled in order to maintain both uniform corrosion protection and a prescribed level of efficient application. Films that vary in thickness do not permit an accurate forecast of storage life or material cost.

The film thickness of oil compounds is controlled by viscosity and surface tension. However, gravitational pull causes oil to seek its own level. Thus, all oil films are reduced over time, so the viscosity effect is temporary at best. Rust-preventive compounds based on solvent cutbacks are formulated to provide a specific film thickness when the solvent evaporates. This thickness is controlled by the percentage of solids contained in the compound. For petrolatum compounds, thickness is controlled by the application technique and temperature.

Fluid types that are applied by any method will drain off to a thin film. Varying viscosity levels will initially allow varying coating weights, but both high and low levels will seek the same level of coating weight because of the pull of gravity. Roll coating and electrostatic application, as well as a spray application followed by wiping or squeegee rolls, will lay down a consistent film. Oil- and solvent-based films will migrate and puddle in low areas. On plated products, these puddled areas will appear shiny, in contrast to areas that appear dull. In the dulled area, however, oil is present at a lesser coating weight. Because coiled or sheet metals cannot be produced perfectly flat, puddling will occur over time. Usually, a sufficient amount of oil is present to provide corrosion protection.

When compounds are applied by hot dipping or hot spraying, the temperature of the coating and the temperature of the part both influence film thickness. Thick coatings will congeal on room-temperature parts that are dipped and withdrawn quickly, so that there is no appreciable increase in part temperature. However, if a part is immersed until its temperature approximates that of the heated rust-preventive compound, then a thinner coat results. In general, the greater the difference between the temperature of the compound and the temperature of the part at the time of withdrawal, the heavier the coating.

Figure 2 shows the influence of the temperature of a petrolatum rust-preventive compound and the temperature of dip-coated panels on the film thickness obtained when the panels are dipped and withdrawn rapidly (1 s for immersion, 1 s for withdrawal). The curve shown is for panels at 27 °C (80 °F). Comparisons of film thicknesses are presented for panels at temperatures of 21 and 32 °C (70 and 90 °F), dipped in rust-preventive compound with a temperature of 85 °C (185 °F).

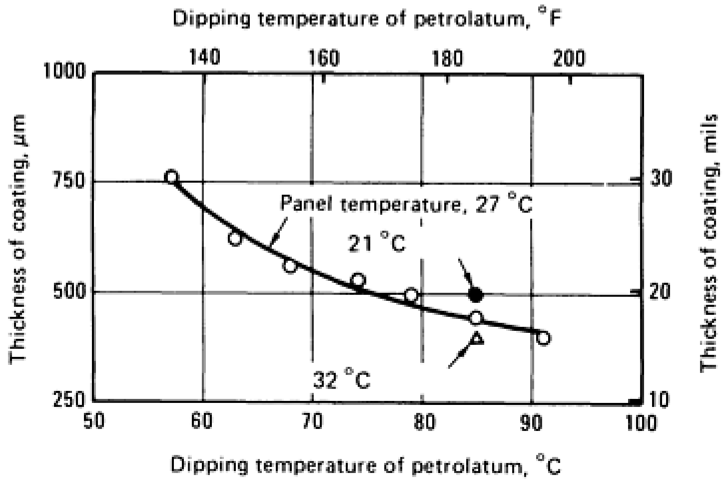


Fig. 2 Effects of panel and compound temperatures on thickness of petrolatum film applied by dipping

The specific gravity of the compound also influences coating thickness. For a specific weight of compound, the film thickness increases as the specific gravity of the compound decreases. The results of a test that determines the influence of specific gravity on film thickness are shown in Fig. 3. The panels used in this test were 75 mm (3 in.) long, 50 mm (2 in.) wide, and 3.2 mm ($\frac{1}{8}$ in.) thick. They were at an ambient temperature of approximately 24 °C (75 °F) when they were subjected to a 1 s dip into and a 1 s withdrawal from the petrolatum compound, which was heated to various temperatures to produce different film thicknesses. Five petrolatum preservatives were used, each of which had a different specific gravity.

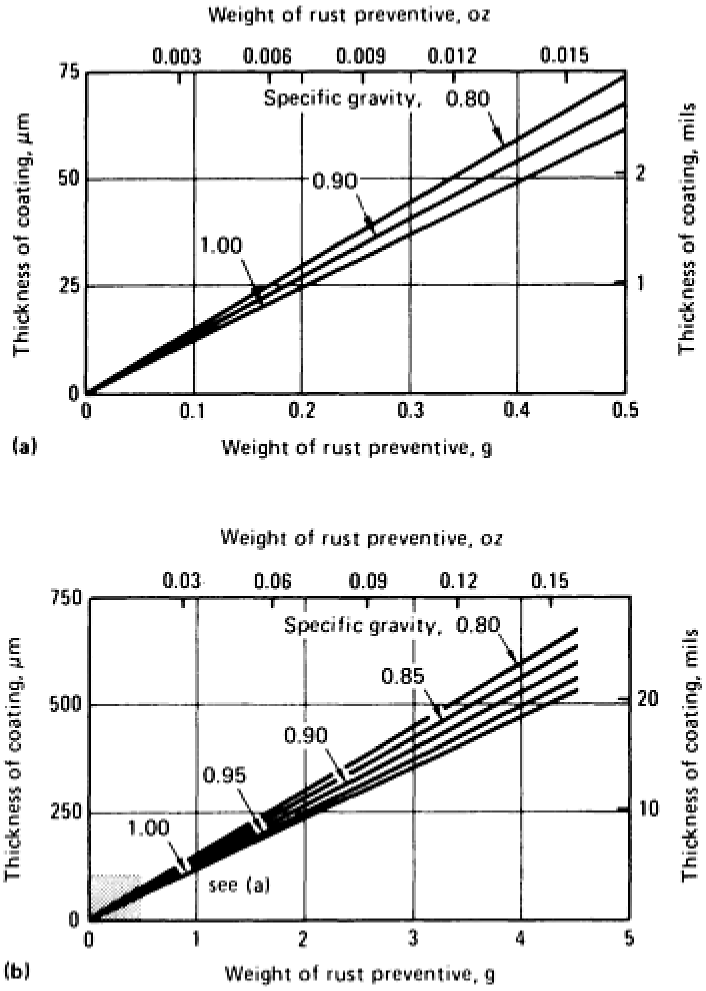


Fig. 3 Influence of specific gravity of petrolatum compound on film thickness for a specific weight of rust preventive applied to test panels. (a) Coating thicknesses up to 75 μm. (b) Coating thicknesses up to 750 μm

Tests also were conducted to determine the influence of four other variables on coating thickness obtained under laboratory conditions using a petrolatum rust-preventive compound. These variables were:

- Temperature of preservative
- Mass of metal specimen
- Duration of immersion
- Rate of withdrawal

Four conclusions were drawn from data obtained in these tests. First, as the temperature of the compound increased, its fluidity increased. Thus, progressively thinner coatings can be obtained with petrolatum rust preventives as temperature increases.

Second, the thickness of the panel (the mass of the metal specimen) influenced the thickness of the coating. With a greater metal mass, a temperature lag existed between the specimen panel and the heated preservative. The coating thickness was greatest with the greatest temperature differential. Thinner coatings developed as the temperature of the panel approached that of the compound.

Third, the duration of immersion had great influence on coating thickness. As immersion time increased, the coating first reached a maximum value, and then melted away uniformly as the panel temperature approached that of the compound.

Fourth, a slow rate of withdrawal left the surface of the coating smooth and regular, indicating uniform film thickness. Rapid withdrawal resulted in distorted, irregular surfaces with numerous small, shallow areas.

The curves in Fig. 4, which were obtained from these tests, show the influence of mass and withdrawal rate of the panel on film thickness for one petrolatum rust-preventive compound. For both curves, the immersion time was 10 s.

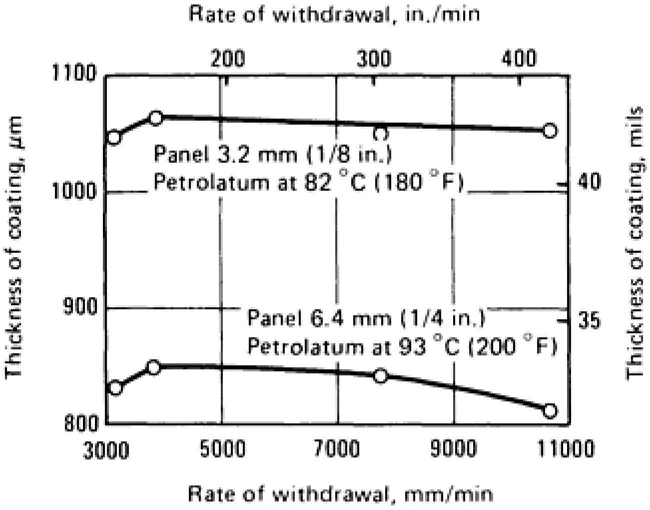


Fig. 4 Comparison of coating thicknesses obtained using the same withdrawal rate of panels from a petrolatum rust-preventive compound

The removability of rust-preventive compounds primarily depends on the thickness, hardness, and chemical characteristics of the protective film. Nondrying oil or grease compounds can be removed by simple petroleum solvents, preferably those with a flash point above 40 °C (105 °F). Vapor degreasing, hot power-spray washing with alkalies or strong detergents, and steam alkali or steam detergent blasting are also used to remove nondrying oil or grease compounds. Wiping can be used, as well, if the desired degree of removal will permit it. The solvent-cutback asphaltic or dry-film compounds usually require high-solvency organic solvents, vapor degreasing, or vigorous extended treatment with steam or hot spray cleaners.

Highly active rust-preventive compounds are difficult to remove. Therefore, when readily removable products are necessary, some corrosion protection usually must be sacrificed.

Scraping, blasting, or wire brushing may be required to remove hard-film preservatives that are completely or partially impervious to solvents, and damage to machined or polished surfaces can result. Compounds of hard film, viscous oil, or heavy grease, which are used to protect parts in either outdoor storage or highly corrosive atmospheres, will cause problems if they are not thoroughly removed, because their residues usually are incompatible with lubricating oils and greases. Examples of parts that can experience such problems are components of hydraulically actuated systems and precisionmachinetoolspindles. These rust-preventive compounds also can clog filters and screens in circulating-oil systems. Additionally, hard-wax rust preventives can cause serious problems in sliding bearing mechanisms if they are not completely removed.

Costs. Rust-preventive compounds are rarely selected on the basis of cost alone. Table 3 lists the typical duration of protection provided by four general types of compounds in three different storage conditions. In general, the cost per liter increases as the amount of protection increases.

Table 3 Duration of protection afforded by rust-preventive compounds

Type of compound	Duration of protection, method		
	Indoor	Shed	Outdoor

	storage	storage	storage
Petrolatum	Not used	12-24	6-18
Oil	2-12	1-6	1-2
Solvent	<1-3	<1	Not suitable
Solvent cutback	6-18	3-12	1-6
Emulsion	3-12	Under 3	Not suitable

The quality control of rust-preventive compounds is necessary for maintaining established levels of efficiency and performance. The extent and frequency of the quality-control program depends on the compound being used and the degree of control required. It is often advisable to start with frequent checks, in order to develop a system history, and then to adjust to safe intervals.

The checks should include the concentration level of the active ingredients; contaminant levels for dirt and water; and degree of oxidation, as determined by some means of pH and neutralization numbers. The nature of the processing operations prior to the application of the rust-preventive compound may make it necessary to run other special quality-control checks, such as those that determine viscosity, flash point, copper strip corrosion, and infrared spectra.

The viscosity and specific gravity, or both, of oil and solvent-cutback rust-preventive compounds are checked as received, at a specific temperature. Standard values, against which the result of checks are compared, either are obtained from the supplier or are established from material that has performed satisfactorily in controlled salt spray, humidity, or field tests. The viscosity is checked using effluent cups, or instruments that measure the resistance of the material to a moving circular spindle or a falling ball. Methods for testing viscosity are described in detail in the article "Painting" in this Volume.

Specific gravity, sometimes used to indicate solids content, is determined by the correct hydrometer. This measurement is usually taken at a specific temperature of the preservative. The viscosity of the compound should be checked when processing begins, and then rechecked at definite intervals in order to correct changes that result from usage conditions, such as the replacement of solvent lost by evaporation. However, because some materials have approximately the same viscosity as the material used to dilute it, periodic checking of specific gravity or other characteristics is necessary for maintaining the proper balance between solids and solvents.

The flow characteristics of petrolatum compounds can be determined empirically by methods described in ASTM D 937. The results obtained by this method are of maximum value when correlated with the flow characteristics of similar materials.

Film Characteristic. The efficiency of the film ordinarily is determined by exposing a precisely coated part to either a salt-spray test (ASTM B 117) or a humidity test (ASTM D 1748). However, the accurate projection of test results to give an expected service life requires experience. Because storage areas undergo varied and changing conditions, it is difficult to predetermine actual protection data. If the product is held under static or ideal conditions, then correlations between lab tests and storage conditions would be more reliable.

The preparation of surfaces to be protected has an important bearing on the effectiveness of a rust-preventive compound. Prior surface treatment ensures freedom from incompatible processing oils, waxes, hygroscopic or chemically reactive salts, or random dirt. These materials could either modify the adhesion or thickness of the film or counteract the inhibitors in the film.

Precleaning during routine parts processing should occur under effective process control, in order to minimize variance from acceptable limits of surface cleanliness. When a temporary setup is used, extra precautions against contamination are essential. Contamination of the compound itself from careless handling or storage procedures should be prevented.

Safety Precautions

Although rust-preventive compounds do not present abnormal or unusual hazards to personnel or equipment, their use and storage do require the observance of safety precautions. Of the oil-based, water-based, and solvent-cutback compounds, the latter type of material presents the most hazards.

Oil-based compounds generally present few health hazards and may have no more ill effects, physiologically, than household soaps. However, these materials usually owe their rust-preventing characteristics to surface-active agents, which can contain heavy metals, such as barium. If excessive quantities are allowed to remain on the skin for extended periods of time, then toxicity can result. This type of product should be kept from contacting the eyes. Some people also experience a sensitivity to oil when it contacts their skin for extended periods. Although oil-based compounds usually do not present fire or explosion hazards, they should not be exposed to intense heat.

Water-based compounds are rarely hazardous in terms of ignition or explosion. However, the additives they contain can cause dermatitis, depending on the degree of sensitivity of the individual exposed to them. These materials should be kept away from the face, especially the eyes.

Solvent-cutback compounds, if inhaled for a prolonged period, can either result in respiratory difficulties or produce the appearance of intoxication. These compounds include those materials that are diluted with low-boiling-point hydrocarbons; volatile solvents, such as the ketones and alcohols; and aromatic solvents, such as toluene and xylene. The aromatic solvents are probably the most hazardous, physiologically. When selecting a solvent, the regulations of the Occupational Safety and Health Administration should be consulted.

Solvent-cutback compounds also can present fire and explosion hazards. Solvent flash points can range from -12 to 40 °C (10 to 104 °F). Those solvents with flash points below 38 °C (100 °F) are considered hazardous, and some spraying shops do not use them. Whenever these materials are used, adequate ventilation is essential to reduce the solvent concentration below the lower explosion level and thereby eliminate explosion and fire hazards. Ventilation systems should be designed to maintain the vapor concentration at a level below explosive limits.

Painting

Revised by Jeffrey P. Gossner, PreFinish Metals Inc.; Kenneth B. Tator, KTA-Tator, Inc.

Introduction

PAINTING is a generic term for the application of a thin organic coating to the surface of a material for decorative, protective, or functional purposes. Painting offers the following advantages over other processes used for the protection or decoration of metal parts and assemblies:

- The equipment required for applying paint is usually less expensive to buy and install, is simpler to operate, and requires less control.
- Material and labor costs per unit area of surface coated often are much lower.
- Organic coatings are available in a wide range of pigments and vehicles and can meet practically any coating requirement for color, gloss, or surface texture.
- Paints have been developed that can withstand most corrosive conditions, and unlike many metallic protective coatings, organic films can simultaneously resist more than one corrosive condition, such as combinations of marine atmosphere and acid fumes.
- Conventional paint films have good dielectric properties, which enable them to inhibit galvanic action between dissimilar metals. Conversely, paints are available that contain special pigments to provide conductivity suitable for grounding induced or static electricity.
- Paints have been developed to meet newer environmental regulations.

Types of Paint

The general terms "paint" and "organic coating" are essentially interchangeable and are used to designate certain coatings having an organic base. Most organic coatings are based on a film former or binder that is dissolved or dispersed in a solvent or water. This film-forming liquid constitutes the vehicle in which pigments are dispersed to give color, opacity, and other properties to the dried film. Many other ingredients can be added to the vehicle to achieve specific film properties. These would include such things as driers to aid curing, plasticizers to impart flexibility and other properties, and stabilizers to lessen the deleterious effects of heat or sunlight. A wide variety of film-forming materials is available and includes oils, varnishes, synthetic resins and polymers such as cellulose, vinyl, epoxy, and polyester. In general, major performance characteristics depend on the binder used.

Enamels are topcoats characterized by their ability to form a smooth surface that is typically of high gloss, but may also include lower degrees of gloss such as flat enamels. Enamels may air dry or bake. Air-dry enamels are cured essentially by a combination of solvent evaporation and oxidation. Baking enamels incorporate catalysts and cross-linking agents that require heat for polymerization.

Lacquers are compositions based on natural or synthetic thermoplastic film-forming materials dissolved in organic solvent. These dry primarily by solvent evaporation. Lacquers are generally characterized by fast drying properties. Typical lacquers include those based on nitrocellulose, other cellulose derivatives, vinyl resins, and acrylic resins. A natural lacquer resin, based on secretions of the lac beetle, is called shellac.

Water-borne paints are dilutable with water. There are three principal types: solutions, colloidal dispersions, and emulsions. Solution coatings are based on water-soluble binders. Many conventional binders (alkyds, acrylics, and epoxies) can be made water soluble by chemically attracting polar groups such as carboxyl, hydroxyl, and amide, which are strongly hydrophilic. Some hydrocarbon solvents are usually necessary, up to 20% of the total, to improve solubility.

Colloidal dispersions are very small particles of binder, less than 0.1 μm in diameter, dispersed in water. Normally, these dispersions contain water-soluble polar groups to partially solubilize a portion of the resin. Emulsions, or latexes, are water dispersions that differ from colloidal dispersion by having much larger particle size on the order of 0.1 μm or larger. They are made by precipitation in water and therefore do not need to be dispersed.

Pigments must be compatible with water. Metallic particles are usually coated before being mixed into the paint to prevent chemical reaction with water, which would cause the mixture to generate gas. Water-reducible paints have a low volatile organic content (VOC) and comply with most environmental regulations. The advantages of water-borne paints include:

- Low flammability
- Reduced toxicity and odor
- Easy cleanup with water
- Good film continuity, with continuous film similar to conventional solvent systems
- Good mechanical stability; can be pumped in all types of equipment similar to conventional solvent paints
- Application by air spraying, dipping, flow coating, electrodeposition, and roller coating

The disadvantages of water-borne paints include:

- Application by electrostatic spraying requires complete electrical isolation because of the water conductivity.
- Coatings require a longer flash tunnel before curing.
- Temperature must be raised more slowly to evaporate water at a slow enough rate to prevent the coating from blistering.
- Coatings are more susceptible to dirt pickup.
- Proper temperature and humidity control are vital. If the humidity is too high or the temperature too low, coating can sag or run off the workpiece.

Electrophoretic paints are special water-reducible paints. Resin and pigment materials are shipped and stored as concentrates to be added to the production tank as needed. Electrophoretic films are always deposited from a dip tank. The operating bath consists of resin concentrate and pigment concentrate mixed with deionized water and small amounts of solubilizers and defoamers. The concentration of nonvolatile solids in the bath varies from about 10 to 20%, depending on type and composition. Paint films are deposited on the work by electrophoretic action. Immediately after the film has been deposited, the work is removed from the bath and rinsed with water to remove the excess paint bath, leaving a uniform, tightly adhering film of paint on the workpiece. The workpiece is then baked. Paints can be prepared to deposit films on either the anode or cathode. The resins used most frequently are epoxies and acrylics, including numerous modifications and hybrids. For more information on this process, see the section on electrocoating in this article.

Autophoretic paints are water-reducible paints deposited on metal surfaces by the catalytic action of the metal on the paint materials in the bath. Currently, only ferrous surfaces activate the autophoretic paints available commercially. Tubular automotive frames are coated with this method, because the entire length of the tubing can be coated inside and outside with equal ease.

High-solids paints contain 70% or more solids by volume. One method of obtaining high-solids paints is to use lower molecular weight polymers, which require less solvent to attain the desired application viscosity. Another method of reducing viscosity of high-solids paints is by heating the paint material to a temperature of about 32 to 52 °C (90 to 125 °F). Many two-component systems use a catalyst to increase the rate of the curing reaction. Fast-reacting two-component systems are usually applied with special spray guns that mix the two components at the spray nozzle. Single-component resins in high-solids paints include epoxy, acrylic, polyester, and alkyd; whereas two-component resins may be urethanes, acrylic-urethane, or epoxy-amine. The advantages and disadvantages of using high-solids paints are listed below:

Advantages

- Color control and color matching is no more difficult than with conventional solvent paints.
- These paints can be applied by higher speed (6000 to 30,000 rev/min) electrostatic bells and disks requiring minimum facility conversion from existing bell or disk systems.
- Performance properties are equivalent to those of conventional solvent paints.
- Applied cost per square foot is lower than that of conventional solvent paints.
- In many cases, these paints require less energy for curing than conventional solvent paints.
- VOC compliance is more readily attained because of reduced solvent use.

Disadvantages

- High-solids paints require specialized pumping and transport equipment.
- Cleanup of overspray is much more difficult than with conventional solvent paints.
- Toxicity of the isocyanates used with urethanes and amines used with epoxies can be a problem.
- Drying and/or curing times may be longer than those for conventional solvent paints unless the coatings are baked.

Powder paint consists of plastic resins, color pigments, and additives. In a mixing and grinding unit, the ingredients are combined in a homogeneous mixture that is heated to the melting point. The molten material is extruded into a thin sheet, which is cooled and crushed. The chips are pulverized to a fine powder of carefully controlled particle size, ensuring optimum fluidity and efficient flow through the finishing system. For more information on powder painting, see the section on methods of paint application in this article.

Selection of a Paint System

To select a paint system consistent with the production and economic requirements of the product being coated, a general knowledge of coatings is necessary, including favorable and unfavorable characteristics, available forms, relative costs, and application methods. Table 1 lists some of the major resins used and their general properties. Many of the resins listed are compatible with others, and when blended, undergo changes of properties which provide performance not available with the individual resins. From a performance standpoint, several equally good choices may be available. Many resins

are supplied as both solvent- and water-borne types. These resins can be formulated for a wide variety of application methods, including conventional air atomized, airless, and electrostatic spray; roller coating; dip coating; and flow coating. Other resins have properties that make them suitable for special application techniques such as powder or electrophoretic coating. Although a wide variety of coatings is available, the ideal coating system, one with all desired performance properties, simple application, and low cost, is difficult to find. Factors such as regulations, service environment, substrate and service condition, basic function, application limitations, and cost usually must be compromised.

Table 1 Properties and applications of coating resins

Resin	Forms available	Drying method	Favorable characteristics	Unfavorable characteristics	Cost	Uses
Acrylic	Solvent, waterborne, powder	Air dry, bake	Water white, outdoor durability, chemical, heat resistance	Poor-fair adhesion, tendency to be brittle	Moderate, high	Automotive topcoats, appliances, coil coatings, aluminum siding, general industrial use
Alkyd	Solvent, waterborne	Air dry, bake	High gloss, flexibility, good durability, versatility	Poor alkali resistance, generally not hard, tendency to yellow, depending on resin	Low, moderate	Trade sales enamels, trim paints, exterior enamels, general metal finishing
Chlorinated rubber	Solvent	Air dry	Water, alkali, acid resistance	Abrasion resistance, hardness, gloss, sensitivity to solvents	Moderate	Maintenance coatings, ship bottom paints, swimming pool paints, chemical process equipment
Epoxy	Solvent, waterborne, powder	Air dry, bake	Excellent adhesion, chemical resistance, flexibility, abrasion resistance, hardness	Rapid chalking on exterior exposure, poor resistance to oxidizing acids, yellows in clears	Moderate, high	Maintenance paints, automotive primers, appliances, metal products
Fluorocarbon	Solvent, powder	Bake	Highest exterior durability, chemical resistance	Adhesion, recoatability, high baking temperatures	High	Coil coatings, siding
Nitrocellulose[(a)]	Solvent	Air dry, bake	Extremely fast drying, good hardness, abrasion resistance	Low solids content, fair to good exterior durability, low flash point solvents	Low, moderate	Furniture finishes, touch-up lacquers, general-purpose product finishes, aerosol lacquers
Phenolic	Solvent, waterborne	Air dry, bake	Hardness, adhesion, resistance to chemicals, corrosion	Darkens, can only be used in darkcolored coatings	High	Can linings, tank linings, maintenance paint on metals
Polyester	Solvent, waterborne, powder	Air dry, bake	High gloss, hardness, chemical resistance, high film build	Fair adhesion, may hydrolize under certain conditions	High	Wood finishes, coil coatings, specialty bake coats
Polyurethane	Solvent, waterborne,	Air dry,	Chemical resistance, abrasion resistance,	Some types yellow and chalk readily on	Moderate,	Aircraft finishes, maintenance paints,

	powder	bake	hardness, exterior durability	exterior exposure	high	metal and plastic coatings
Silicone	Solvent, waterborne	Air dry, bake	High heat resistance, exterior durability, gloss and color retention	Tendency toward brittleness. Unmodified types require high baking temperatures	High	Any finish for high heat resistance, exterior metal coatings
Vinyl	Solvent, powder	Air dry, bake	Chemical resistance, flexibility, fast air dry, formability, resistance to acid, alkali, abrasion	Generally low solids, low flash points	Moderate	Can and tank linings, maintenance paints, metal decorating paints

(a) Must be modified with other resins

Service Environment. When selecting a paint system, many factors concerning service environment must be considered. Needs are different for interior and exterior coatings. The specific properties needed, such as resistance to heat, cold, sunlight, and weathering must be determined. If the coating needs to be resistant to chemicals, the specific chemical, such as acid, alkali, solvent, or water immersion should be specified. Mechanical properties required, including hardness, flexibility, impact resistance, and abrasion resistance, should also be decided.

Substrate and Surface Condition. The type of substrate must be considered. A coating capable of giving excellent performance on one metal may fail badly on another. Smoothness, porosity, dimensional stability, and corrodibility affect the choice of a proper finishing system. Smooth, clean metal surfaces that cannot be phosphate coated lack sufficient "tooth" for good adhesion of some air-dried coatings. ("Tooth" is the coarse or abrasive quality of a substrate that facilitates the application and adhesion of a coating).

No special primer coats are required on surfaces containing small quantities of tightly adhering rust, if the finished parts are intended for indoor service in a mildly corrosive atmosphere. Attractive and durable finishes can be obtained over such surfaces with a single coat of a special paint that produces a textured finish, such as wrinkle finishes and pebble finishes. These paints are relatively inexpensive and hide surface irregularities with their own irregular appearance.

On parts intended for outdoor use where tightly adhering rust is present and not economically removable, a rust-inhibiting primer with good penetrating qualities must be used to prevent, or at least substantially retard, further rusting in service. Parts with heavy rust or mill scale should not be painted unless the loose rust and mill scale are removed.

The diverse requirements of substrate and environment often necessitate a dual or multiple coating system. In these systems, a primer with one composition is used to satisfy substrate adhesion and corrosion resistance, and a coating with a different composition is used as a topcoat to withstand environmental conditions, for example, a vinyl wash primer followed by an epoxy primer with an acrylic topcoat.

Basic Function. Coatings may be applied for appearance, to meet functional requirements, or to meet combined function and appearance needs. If the basic purpose is appearance, the gloss, color, and retention of these properties in service are emphasized. In some applications, functional requirements are of equal importance to appearance. On office furniture, for example, paint films must provide attractive appearance and resist marring and abrasion. On automobiles, paint films must be attractive in appearance, easily applied, and readily repaired, but be resistant to abrasion, marring, and impact as well as capable of protecting the underlying metal from corrosion. In other applications, such as corrosion protection of tanks or chemical equipment, the functional requirements of the paint film are of prime concern. Corrosion resistance is the most important of functional requirements.

Corrosion of steel and cast iron occurs in all common environments. The rate and extent of corrosion vary from mild attack in dry, clean environments to highly accelerated attack in marine or industrial areas where corrosive fumes are present in air. Table 2 lists paints selected for service in a wide range of corrosive conditions.

Table 2 Organic coatings selected for corrosion resistance in various environments

Coatings	Applications
Outdoor exposure	
Oil paints	Buildings, vehicles, bridges; maintenance
Alkyds	Trim paints, metal finishes, product finishes
Amino resin-modified alkyds	Automotive, metal awnings, aluminum siding
Nitrocellulose lacquers	Product finishes, aerosol lacquers
Acrylics	Automotive finishes
Marine atmosphere	
Alkyds, chlorinated rubber, phenolics, epoxies, vinyls, vinyl-alkyds	Superstructures and shore installations
Urethanes	Clear marine varnishes
Water immersion	
Phenolics	Ship bottoms
Vinyls	Ship bottoms, locks
Chlorinated rubber	Ship bottoms, swimming pools
Urethanes	Clear marine varnishes
Epoxies	Ship hulls, marine structures
Chemical fumes	
Epoxies, chlorinated rubber, vinyls, urethanes	Chemical-processing equipment
Extreme sunlight	
Vinyls	Metal awnings

Acrylics	Automotive finishes
Silicone alkyds	Petroleum-industry processing equipment
High humidity	
Amino resin-modified alkyds	Refrigerators, washing machines
Epoxies	Air conditioners
Catalyzed epoxies, chlorinated rubber, phenolics	Maintenance; chemical and paper plants
High temperature	
Epoxies	Motors, piping, 120 °C (250 °F) max
Modified silicones	Stove parts, roasters, 205 °C (400 °F) max
Silicones	Stove parts, roasters, 290 °C (550 °F) max; aluminum-pigmented paints 650 °C (1200 °F) max
Inorganic zinc-rich	Structural steel, chimneys to 370 °C (700 °F)

In service, paint films are frequently required to resist exposure to highly deleterious materials. For example, decorative finishes, such as those on home laundry equipment, must resist detergents, and paint films on equipment powered by gasoline engines must withstand attack from gasoline.

Paint films also may be required to resist acids and alkalis, solvents, staining, heat, impact, marring, and abrasion. Some coatings must be able to withstand flexing without cracking or flaking. Table 3 lists paints that have proven successful in withstanding mechanical and chemical action.

Table 3 Paints selected for resistance to mechanical or chemical action

Action	**Paint**
Abrasion	Vinyls; plastisols; polyurethanes
Impact	Epoxies; vinyls; polyurethanes
Marring	Thermosetting acrylics; vinyls
Flexing	Epoxies; vinyls

Acids	Chlorinated rubber; vinyls; epoxies
Solvents	Epoxies; phenolics
Detergents	Thermosetting acrylics; epoxies
Staining	Thermosetting acrylics
Gasoline	Alkyds; epoxies
Alkalis	Phenolics
Heat	Alkyd-amines; silicone resins

Application Limitations. In selecting a coating for a given purpose, application properties in relation to available facilities and conditions in which the coating is to be applied must be considered. The most suitable application, such as spraying, dipping, roller coating, or brushing, as well as drying speed, storage stability, flammability, and toxicity should all be determined. For example, toxic and flammable materials should not be used in areas without adequate ventilation and safety equipment. Heat-convertible coatings cannot be used unless adequate baking facilities are available. Two-component coatings, such as epoxies and some polyurethanes, have limited pot life after mixing and must be used within a determined period or discarded, unless two-component spray equipment is used.

Cost must be weighed against the performance required of the coating system. A low-cost coating that fails to perform its function is a wasted expense. With the effort involved in applying protective coatings, a short service life of a low-cost, inferior material makes ultimate coating and maintenance costs far higher than if a more expensive durable coating had been used originally. Other factors must also be considered in arriving at an overall cost estimate, including: spreading rate, the area adequately covered by a unit of volume of paint; probable application time and resulting labor costs; equipment required for application; and expected service life.

Examples of Selection. Paints are seldom selected to meet only one requirement. Most organic coatings must perform several functions. The considerations that governed the selection of paint in three different applications are described in the following production examples.

Example 1: Painting of Ballast Cases for Fluorescent Light Fixtures.

One plant annually produces over a million ballast cases for fluorescent lighting fixtures. Paint applied to these cases, which are rectangular steel boxes, must provide acceptable appearance, resist mildly corrosive exposure, and withstand a certain amount of handling and abuse during assembly. Processing and material costs must also be low. These requirements are met by a water-emulsion paint, applied by conveyorized dipping and subsequently baked. This paint is low in initial cost and because the solvent is water eliminates the usual cost of solvent replacement. It has good dipping qualities, provides adequate corrosion resistance, and stands up well in assembly. The paint has good tank stability and, unlike volatile-solvent paints, is nonflammable.

Example 2: Painting of Interior and Exterior Surfaces of Electric Motor Shells.

Electric motor shells, 75 mm (3 in.) long by 90 mm ($3\frac{1}{2}$ in.) in diameter, required a thin paint film for corrosion protection. Dip painting was desired, because both the inside and the outside of each shell were to be coated. To avoid the necessity of removing paint from the portion of the shell that mated with the motor end bells, the thickness of the paint film had to be closely controlled. The maximum permissible thickness was 50 μm (2 mils) to avoid misalignment of the

bearings in the end bells and maintain a uniform air gap between stator and rotor in final assembly. No runs or beads could be tolerated.

A vinyl butyrate lacquer was selected for its good flow characteristics and hiding power. It provided the required corrosion protection and was compatible with cost limitations. By standing the parts vertically in coarse-mesh baskets and carefully controlling withdrawal from the dip tank, 36 parts at a time were successfully painted to coating thicknesses that met tolerances.

Example 3: Prime Coat and Top Coat Painting of Cold Rolled Steel Parts.

One company that had been painting cold rolled steel products with one coat of baking primer and one topcoat of baking enamel needed to expand production facilities. One method would have been to set up a duplicate finishing line. It was found, however, that an acceptable finish could be obtained by priming with an air drying, flash primer and finish painting with a topcoat of baking enamel. Rather than adding a complete painting line, only two prime booths for applying the primer and flash-off leg on the conveyor, to permit the primer to air dry, had to be added, saving a capital expenditure of several thousand dollars.

Numerous other examples could have been cited. Coating manufacturers and equipment suppliers can provide valuable assistance in the selection of an appropriate coating system for a desired product finish.

Surface Preparation

The importance of proper surface preparation to the durability of any coating system cannot be overemphasized. Without proper surface preparation, the finest paint, applied with the greatest of skill, will fall short of its maximum performance or may even fail miserably. A coating can perform its function only so long as it remains intact and firmly bonded to the substrate.

An adequately prepared surface not only provides a good anchor for the coating but also ensures a surface free of corrosion products and contaminants that might shorten the life of the film by spreading along the coating/substrate interface and destroying adhesion or by actually breaking through the coating.

Cleaning

Before being painted, metals usually are exposed to one or more fabricating processes, such as rolling, stamping, forming, forging, machining, and heat treating. In these processes, the metal surfaces pick up various contaminants that can either interfere with the adhesion of the paint film or allow corrosion to progress beneath the paint film and cause it to fail prematurely.

The principle surface contaminants that adversely affect the performance of paint films include oils, greases, dirt, rust, mill scale, water, and salts such as chlorides and sulfides. These contaminants must be removed from the surface before paint is applied.

Selection of cleaning process is governed by the soil or contaminant to be removed, the degree of cleanness required, the type of paint to be applied, and the size, shape, material and end use of the part. In addition, the speed with which the process runs will affect the cleaning characteristics.

Methods of cleaning metal surfaces can be classified as mechanical and chemical. To meet rigid requirements for surface cleanness, mechanical or chemical cleaning methods can be used in combination. For example, before structural steel intended for an application involving exposure to corrosive chemical environments is painted, oil, grease, rust, mill scale, and any other surface contaminants must be completely removed. Chemical paint strippers or solvent cleaners are often used prior to mechanical cleaning to remove oil, grease, or old paint.

Additional information is available in the article "Classification and Selection of Cleaning Processes" and in the other articles in the Section "Surface Cleaning" in this Volume.

Mechanical cleaning methods include power brushing, grinding, and abrasive blasting.

Power brushing is an abrasive cleaning operation utilizing a power-driven rotary brush. Different types of brushes, and various lengths and gages of wire or fiber provide a wide range of abrasive action. For heavy abrasion, steel wire brushes are used. Mild abrasion is obtained with fiber, horsehair, or other bristle-type brushes. Power brushing may be used to remove surface rust, dirt, and loose mill scale; it is unsuitable for removing embedded oxides or tight mill scale.

Grinding, using abrasive wheels of various shapes and grit sizes, is used for the removal of coarse irregularities, such as burrs or flash, and coarse mill scale and heavy rust. Selection of the proper grade of abrasive wheel is important: Too coarse a wheel may produce deep abrasions that are difficult to hide by paint; a wheel with grit that is too fine will clog easily and make the process inefficient.

Abrasive blast cleaning is accomplished by bombarding a surface with abrasive particles propelled at high velocity by air, water, or centrifugal force. The effects of blasting are influenced by the type, hardness, particle size, velocity, and angle of impact of the abrasive. Blasting is a rapid method of removing rust and mill scale. Virtually any degree of cleanness of the blasted surface is obtainable.

Chemical cleaning includes emulsion cleaning, solvent cleaning, vapor degreasing, alkaline cleaning, acid cleaning, pickling, and steam cleaning.

Emulsion cleaning, solvent cleaning, and vapor degreasing employ common organic solvents for the removal of oil, grease, loose metal chips, and other contaminants from metal surfaces. For a description of processing methods, see the articles "Emulsion Cleaning" and "Solvent Cold Cleaning and Vapor Degreasing" in this Volume.

Alkaline cleaning is an effective method for removing oils and greases, water-soluble residues, heat treating salts, acid deposits, and other inorganic dirt. Alkaline cleaners work by detergent action and saponification, and are usually used in soak tank, pressure spray, or electrolytic cleaning. Thorough rinsing or neutralizing of the cleaned surface is necessary after alkaline cleaning prior to painting. For a more detailed discussion of processes, see the article on "Alkaline Cleaning" in this Volume.

Acid cleaning is used for removal of light soil or rust. It is unsuitable for removing heavy coats of oil, grease, dirt, and mill scale. Acid cleaners used prior to painting usually are water solutions of phosphoric acid, organic solvents, acid-stable detergents, and wetting agents. These solutions are used either hot or cold, in soak tanks or spray cleaning systems. Cleaning is accomplished by emulsifying the oils that are on the surface and by dissolving or undercutting oxide films. For additional information on processing, see the article "Acid Cleaning" in this Volume.

Pickling also utilizes acid, for the removal of rust, mill scale, and some types of soil. Wide variations are possible in the type, strength, and temperature of the acid solutions. The acids most commonly used for pickling ferrous metals are sulfuric and hydrochloric. Inhibitors usually are added to pickling solutions to retard acid attack on the metal. Some parts are precleaned to remove films of oil, grease, or other contaminants that would prevent the pickling solution from contacting the metal surface. After pickling, thorough rinsing and neutralizing of the metal surface are necessary. For a more detailed discussion, see the article "Pickling and Descaling" in this Volume.

Steam cleaning may be used on parts too large or too heavy to be cleaned by conventional methods. In this process, a jet of live steam is directed against the metal surface. The cleaning power of the steam is enhanced by the addition of detergents or alkaline cleaners to the water being vaporized. When such additives are used, cleaning should be followed by thorough rinsing or neutralizing, and drying. Paint adhesion may be poor on steam-cleaned surfaces. If no further surface treatment is feasible, a paint such as one of the asphalt types is recommended. These paints adhere well to a wide variety of surfaces and usually have good adhesion on steam-cleaned metals.

The effectiveness of abrasive blast cleaning compared with wire brushing in removing mill scale is illustrated in the following example. A laboratory study was conducted to compare the effectiveness of abrasive blast cleaning and wire brushing in removing mill scale from hot-rolled carbon steel panels. Panel surfaces were cleaned by each method. Surfaces were then individually coated, under controlled conditions, with alkyd, vinyl, epoxy ester, or catalyzed epoxy-based paints. The panels were then exposed to an industrial atmosphere. Within 12 months, all coatings on the panels that had been wire brushed indicated failure in the form of either blistering of the paint or rusting of the steel surface. After 24 months, however, no signs of paint failure were evident on the panels that had been blast cleaned. The poor performance of the paint on the wire-brushed surfaces was the result of incomplete removal of mill scale by wire brushing.

A high degree of cleanness can be obtained by combining mechanical and chemical cleaning methods. Before being painted, steel surfaces of tank cars used to carry corrosive materials were alkaline or solvent cleaned and then abrasive blasted. This removed all contaminants. A corrosion-inhibiting primer was applied, followed by a chemical-resistant topcoat. This paint film, controlled to a minimum thickness of 75 μm (3 mils), has a life expectancy of 4 to 6 years.

Surface Smoothness

If a smooth, high-quality paint finish is desired, imperfections such as scratches, die marks, indentations, roughness, and localized porosity must be repaired before finish painting.

If the imperfections are deep (3.2 mm, or $\frac{1}{8}$ in., or more), they may be filled with wiping solders, which are lead-tin alloys prepared for this application. The metal surface is first degreased with a nonflammable solvent such as 1,1,1-trichloroethane. When dry, the surface is coated with a flux and heated using a torch. The solder is flowed into the indentation or depression and blended with the contour of the part. All traces of flux are removed with solvents or neutralizers. After the surface is dry, it is primed and sanded smooth and then given the prime and finish coats of paint.

Significant surface imperfections also can be primed and filled with a suitable putty. The putty used must be chemically compatible with both the prime coat and the finish coat and should adhere well to both. Putties are usually highly pigmented pastes, containing such materials as vinyls, epoxies, alkyds, or drying oils as binding or drying agents. Air drying or baking putties can be used, although air drying putty is most frequently used. Baking of thick putty films, either for curing the putty or for curing subsequent paint films, usually results in blisters or pinholes, because of the release of entrapped solvents during baking. Catalytically cured putties should be used when subsequent baking is required, because these putties cure with an exothermic reaction, driving the solvent from the film of putty before it is set and minimizing the formation of pits or blisters during subsequent baking of paint films.

Prepaint Treatments

In addition to cleaning and smoothing, the metal surface is often given a prepaint treatment to improve paint adhesion and reduce corrosion. Prepaint treatments include phosphate coatings and organic pretreatments known as wash primers or etch primers. The choice of a prepaint treatment depends largely on the substrate metal to be painted. Care should be taken to choose the appropriate pretreatment for the particular substrate being coated to ensure corrosion protection and paint adherence.

Phosphate coatings are formed by chemical reaction during immersion of the metal in the phosphate solution that deposits a nonmetallic and nonconducting coating. Both coating weight and crystal size can be varied to provide almost any surface condition required for the appearance or function of the paint. For a detailed discussion of coatings, equipment, and processing methods, see the article "Phosphate Coatings" in this Volume.

The advantages of a phosphate coating as a base for paint are indicated in Table 4, which outlines the results of comprehensive tests conducted on panels for a large manufacturer of home appliances. In these tests, three methods of surface preparation, including cleaning only, cleaning plus iron phosphating, and cleaning plus zinc phosphating, were evaluated by their effect on properties of subsequent paint films. Alkyd-melamine paints from various suppliers were used in the tests and prepared specifically for use following each of the prepainting surface-preparation methods. All panels were spray painted to the same film thickness and were baked and cured in the same manner to achieve polymerization.

Table 4 Effect of prepainting surface treatments on performance of paint films in tests

Alkyd-melamine paints were from various suppliers and specially prepared for each of the prepainting; after being applied, paints were baked for 30 min at 150 °C (300 °F) and cured for 72 h at 49 °C (120 °F); dry film thickness was 38 to 46μm (1.5 to 1.8 mils); gloss, as measured with 60° glossmeter was 82°.

Test	Results, for prepainting treatments		
	Cleaning only	Cleaning plus	
		Iron	Zinc

		phosphating	phosphating
Pencil hardness	HB[a]	HB-F	HB-F
Adhesion	Poor	Excellent	Excellent
Impact resistance (face and back)[b]	7.2 N · m (64 in. · lb)	7.2 N · m (64 in. · lb)	7.2 N · m (64 in. · lb)
Bend[c]	Fair to good	Excellent	Excellent
Crimp	100% failure	Excellent	Excellent
100% relative humidity at 43 °C (110 °F), h[d]	300 (max)	1000	1000
5% salt spray, h[d]	72 (max)	500(max)	750

(a) Pencil of this hardness cut through and removed paint cleanly; when cut, paint scratched cleanly with fingernail.

(b) Impacting surface 1.59 mm (0.0625 in.) in diameter tested with 0.9 kg (2 lb) weight.

(c) 180° bend over 6.4 mm ($\frac{1}{4}$ in.) mandrel.

(d) Hours to 65 mm (2.6 in.) creepage from scribe or to blistering, or both

It is important to note that phosphate coatings may not be suitable for all substrates.

Organic pretreatments, or wash primers, are materials that provide the properties of an inhibitive wash coat or metal conditioner in an organic film. The essential components of wash primers include polyvinylbutyral resin, chromate pigment, and phosphoric acid. Wash primers are described in Military Specifications DoD-P-15328 and MIL-P-8514. Organic pretreatments are formulated for spray application and should be used in the following situations: where phosphating equipment is not available, where size and shape of parts preclude use of the phosphating process, or where parts containing mixed metal components are assembled before painting.

Spraying

Spraying is adaptable to either large-volume or low-volume production. Applications may be limited because of solvent emissions, possible fire hazards, or potential damage from overspray. Spraying methods include conventional air spraying, in which the paint is atomized and propelled against the work by means of compressed air, hot spraying, hydraulic airless spraying, and air and airless electrostatic spraying.

Spraying is used for applications in which good appearance and uniformity of coating are desired, such as automobile bodies. Figure 1 shows large and medium-size metal housings that are examples of parts painted by conventional (air atomized) spraying to obtain a good appearance and uniform coating. In the application of metallic or polychromatic enamels, the spray process achieves the necessary dispersion of the particles. Also, very large objects such as bridges are usually spray painted.

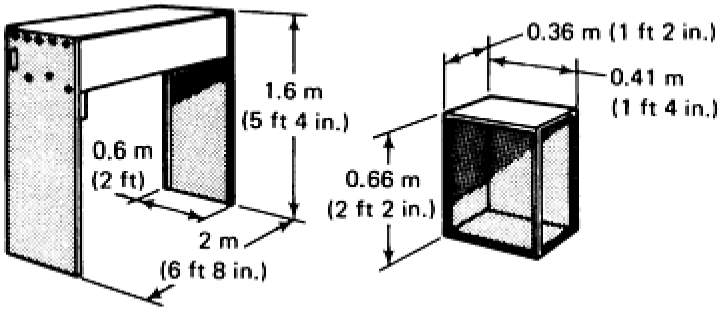


Fig. 1 Parts where conventional (air atomized) spray painting is used to meet requirements of good appearance and uniform coating

Spray painting generally consumes more paint than other painting processes, because of overspray losses. In air atomized spraying, only a small amount of the air at the nozzle is used for atomizing. The remainder of the air pushes the paint and controls the pattern and droplet size. The remainder of the air also causes overspray, as the atomized paint bounces off, or is driven past, the part being painted. The efficiency of the spray operation depends on part shape and size; operator ability; setup of spray guns; and type of equipment whether air atomized, electrostatic, or hydraulic airless spray systems are used.

Hot spraying is a method in which air atomized or airless spraying equipment is used in conjunction with a heat exchanger to heat the paint to a predetermined temperature. The temperature range for hot spraying is usually from 60 to 82 °C (140 to 180 °F). In air atomized spraying, viscosities suitable for application are obtained with the use of solvents. The hot spraying method uses heat to lower the viscosity to the optimum range for spraying, allowing the application of paint with higher solids content.

Heating units are available in two basic types, recirculating and nonrecirculating. Recirculating heating units circulate heated paint between the heater and spray gun, maintaining a constant temperature. Nonrecirculating units heat the paint only once. After the paint passes through the heater, it is subject to various degrees of cooling, depending on hose lengths and conditions of application.

When properly prepared paint materials are used, the hot spray method may have three distinct advantages over conventional spraying:

- Little or no solvent is used for thinning, reducing labor and solvent costs.
- Thicker films can be applied using fewer gun passes or fewer coats.
- Paint can be stored in unheated areas or at very low temperatures.

The principal disadvantages of hot spraying are:

- The purchase and operation of the heating unit add to the overall cost of painting.
- Spraying with paint containing a greater solids content can result in higher overspray losses if improper spraying techniques are used.

Airless spraying, with either heated or unheated paint, uses hydraulic (pumping) pressure to propel the paint through the hoses and atomizing nozzle. The main advantages of airless spray painting stem from the elimination of air as the force for atomizing and propelling the paint. Airless spraying requires the release of considerably less energy at the nozzle, and overspray is minimized. Heavier film thickness without runs or sags can be obtained when more viscous material is sprayed. As in air atomized spraying, however, airless spraying requires an increase in pressure as the paint increases in viscosity.

Elimination of air also permits the use of comparatively simple and inexpensive spray booth exhaust systems, permits full-coverage spraying into corners and recesses with a minimum of bounce-back, and reduces masking requirements. Airless systems use simpler, lighter weight guns, and fewer hoses than are required in air systems.

The chief disadvantage of airless spraying is that, unlike air spray guns, airless spray guns cannot be throttled. Because a full flow of paint comes constantly from the airless gun, greater operator skill is required for controlling coating application in difficult-to-reach areas.

Electrostatic Spraying. In electrostatic spray painting, electrically charged atomized particles of paint are attracted to the grounded part. Paint for electrostatic application can be atomized by conventional air, airless, or rotational techniques.

One of the chief advantages of electrostatic spraying is the small loss of paint from overspray. Whereas in conventional spray painting as much as 70% of the paint sprayed may be lost because of overspray, as little as 10% may be lost in electrostatic spraying. Another advantage is the ability of this method to produce a consistent paint film over a long production run.

The main disadvantage of electrostatic spraying is that the electrostatic attraction of the part for the paint draws the paint to the nearest edge or surface of the part, and it is difficult or impossible to get paint into deep recesses, corners, and shielded areas. Another disadvantage is that the necessity for grounding the surfaces to be coated makes it impossible to paint assemblies in which parts are insulated from other parts by a dielectric component.

Equipment for Air Atomized Spray Painting

Basic equipment for air atomized spray painting consists of a spray gun, a container for the paint, an air compressor, an air regulator or transformer, connecting pipes and hoses, a spray booth, and an air filter and moisture trap.

Spray guns are available commercially to fit virtually any requirement. An air cap at the front of the gun atomizes the paint and forms the desired spray pattern. Air caps may be interchanged to meet the requirements of different applications.

A fluid tip or nozzle, located directly behind the air cap, directs and meters the paint into the air stream. These tips vary in material and size according to the type and viscosity of the paint being applied and with the speed and volume requirements of the application. Larger orificed nozzles are required for heavy, coarse, or fibrous paints. Smaller orificed nozzles are used for thin paints. Because atomization of the paint improves as the nozzle size decreases, the smallest orifice that permits proper passage of the paint should be selected. Small nozzle sizes also permit more effective control of fluid pressures, a necessity when applying thin paints that have a tendency to sag. Abrasive or corrosive paints require tips made of materials with resistance to wear or corrosion.

Air compressors provide the force for air atomized spray painting. Air compressors may supply compressed air throughout the shop or only to the paint line. A fluctuating air pressure at the gun, usually caused by inadequate compressor capacity or an inadequate distribution system, can result in improper atomization of the paint and defective paint films.

Air regulators or transformers regulate air pressure as required. Air filters and the moisture trap remove oil, dirt, and moisture from the compressed air. Air regulators, filters, and the moisture trap are installed in the air-supply lines between the compressor and the paint container and between the compressor and the spray gun. The regulators and filters should be as close to the tanks and guns as possible.

Pipes and hoses that distribute the compressed air or paint must be of adequate size to handle peak loads without starving any station and must be able to withstand any abrasive or chemical effects of the paint.

Spray booths are fire-resistant enclosures that confine overspray and fumes and use ventilating systems to draw in fresh air and exhaust the contaminated air after filtering out the solids. A booth face air velocity of 0.559 to 0.635 m/s (110 to 125 ft/min) is required. Dry or water-wash filters may be used. In most installations, spray booth and exhaust stack are protected with automatic sprinklers.

In dry spray booths, fumes and overspray are forced through special filters that remove solids before exhausting the air and fumes. Dry spray booths with replaceable filters are usually less costly to install than water-wash booths, because no water or drain lines are required.

In water-wash spray booths, contaminated air is drawn through a series of water curtains and baffles to remove solids from overspray before air and fumes are exhausted. These booths also reduce fire hazards by collecting overspray in water. However, water-wash spray booths are usually more costly to install, operate, and maintain than dry booths. Some localities prohibit discharging spray booth water into sewers, and adequate recirculation systems and controls must be installed.

Spray booths exhaust large volumes of air, and to ensure a sufficient quantity of replacement air without creating drafts or heating problems in other areas of a plant, air replacement units must be installed. These units, which are placed next to the spray booths, draw in air from the outside, filter it, heat it, and deliver it to the spray booth. This permits proper functioning of spray booth exhaust systems and maintains the desired booth temperature for suitable spraying conditions. Few manufacturing operations are dust free, and air replacement units greatly reduce the possibility that airborne contaminants will be drawn into the paint area and deposited on wet paint surfaces.

Table 5 lists and describes the equipment required for air atomized spray painting of two production parts: a fire extinguisher shell 355 mm (14 in.) long by 75 mm (3 in.) in diameter, constructed from 1.0 mm (0.040 in.) thick steel; and an enclosure panel 915 mm (36 in.) long by 760 mm (30 in.) wide, produced from 0.268 mm (0.105 in.) thick sheet.

Table 5 Equipment requirements for conventional spray painting of two production parts

Procedure or equipment	**Shell for fire extinguisher[(a)]**	**Enclosure panel[(b)]**
Production requirements		
Surface preparation	Clean and phosphate[(c)]	Clean and phosphate[(c)]
Prime coating	Zinc chromate primer	Red oxide primer
Finish coating	Alkyd baking enamel	High-luster lacquer
Production per hour	500	40
Equipment requirements		
Overhead conveyor	305 mm (12 in.) hook spacing	610 mm (24 in.) hook spacing
Cleaning and phosphating[(c)]:		
Capacity and solution of rinse tanks	379 L (100 gal)	379 L (100 gal)
Solution and rinse temperature	66 °C (150 °F)	66 °C (150 °F)
Prime and finish coating:		

Spray booth[d]	2.4 × 2.1 × 1.5 m (8 × 7 × 5 ft)	3.7 × 2.4 × 1.8 m (12 × 8 × 6 ft)
Spray gun	Hand operated	Hand operated
Paint supply tank (with agitation)	95 L (25 gal), pressurized	95 L (25 gal), pressurized
Drying	Infrared oven[e]	Air dry[f]

(a) Shell, 75 mm (3 in.) in diameter and 355 mm (14 in.) long, of 1.0 mm (0.040 in.) steel.

(b) Panel 915 by 760 mm (36 by 30 in.), of 12-gage (2.657 mm, or 0.1046 in.) sheet steel.

(c) Proprietary phosphate cleaner coater used; 2-min immersion in solution and rinse tanks, followed by drying.

(d) Open-ended water-wash.

(e) Drying cycle, 10 min at 160 °C (325 °F).

(f) Drying of prime coat may be forced by brief infrared heating.

Equipment for Electrostatic Spray Painting

Basic equipment for electrostatic spray painting consists of a paint supply system, an atomizer (or gun), a source of electrical power, a spray booth with a ventilating system, a conveyor, and properly designed racks.

Paint supply systems deliver paint under pressure to one or more atomizers. In such systems, paint is prepared and stored in a central tank, from which it is distributed to the atomizers by air or variable-speed positive-displacement pumps.

Atomizers (guns) can be either air or airless. An air gun uses compressed air to atomize the paint delivered to it. In one air gun, the nozzle is insulated from the metal atomizer body by a plastic sleeve. The fluid tip and needle are charged to a high negative electrical potential that is imparted to the atomized paint particles as they leave the nozzle.

Another air electrostatic spray painting system uses ordinary air spray painting guns for atomization. Parts on the conveyor are surrounded by a grid of fine wires charged to a high negative potential. The paint is sprayed between the grid wires and the parts, where it picks up the negative charge and is repelled by the grid wires and attracted by the grounded parts on the conveyor.

Guns that are operated automatically may be mounted in a fixed, but adjustable position, or they may be attached to a mechanism that causes them to reciprocate vertically or horizontally as required by the size and shape of the part being painted.

Airless atomizers use a rotating component, either disk-shaped or bell-shaped, charged to a high negative electrical potential. Paint, forced up through the center of the rotating member, is charged with this same high negative potential. The centrifugal force of the spinning component moves the paint to the outer edge, where the combination of centrifugal and electrostatic forces atomizes the paint and disperses it. The paint is attracted electrostatically to the grounded parts on the conveyor.

Bell-shaped atomizers generally have the plane of the opening of the bell parallel to the surface being coated, and the work is carried past on a straight-line conveyor. The bell may be fixed or may reciprocate and can be used in any position. Hand-operated portable guns with bell-shaped atomizers are available.

Disk atomizers are operated as automatic or manual units. The disks operate in an essentially horizontal plane; however, in nonreciprocating installations, the disk may be positioned at up to a 35° angle to produce a greater vertical spray area. Because the paint is dispersed around the entire periphery of the disk, conveyors usually carry the part in a circular path around the atomizer. For long parts, the disk may be reciprocated up and down to facilitate coating the entire length of the parts as they are conveyed around the loop.

Power supply units must be capable of providing the high static potential required for each atomizer. These units can operate on 110, 220, or 440 V at 60 cycles. The power output is usually 90,000 to 120,000 V and 5 mA. One power supply unit can handle up to ten atomizers. Units produce a very small current to eliminate any serious hazard to the operator. Usually, an automatic cutoff control is incorporated for added safety.

Spray booths and ventilating systems are used to confine and collect the overspray and to exhaust the fumes from the vaporizing solvents. Minimum velocity of air through the booth is desired to avoid interference with deposition of paint on the part. However, velocity must be adequate to maintain the solvent concentration below its lower explosive level and toxic concentrations. Air velocities of 0.25 to 0.5 m/s (50 to 100 ft/min) are usually adequate for electrostatic spraying applications.

Racks and conveyors used in electrostatic spray painting, in addition to holding and moving the parts, must provide the electrical ground necessary to develop the electrostatic attraction. Parts should be mounted as close to one another as possible on the conveyor to minimize overspraying. Some parts require rotation as they pass the atomizer to ensure coating of all surfaces.

Dip Painting

Dip painting consists of submerging a part in paint contained in a tank, withdrawing the part, and permitting the part to drain. Parts with complex surfaces may be coated efficiently by dipping. Larger parts, produced in quantity, are racked or hung on conveyors, which carry the parts to the paint tank, automatically immerse and withdraw the parts, and carry them over drip troughs into which the excess paint runs off.

Dip painting is seldom used where uniformity of paint thickness is required. This procedure may be unsatisfactory for painting parts having machined holes or surfaces where masking is impractical. Usually, paint films applied by dipping are heavier at the bottom than at the top, because of paint runoff, and are thin at sharp edges. In addition, bubbles and bumps may be found at the bottom edges of painted pieces. Parts may be dip painted to obtain complete coverage and then spray painted to obtain a required surface appearance.

The blower wheel shown in Fig. 2(a) is an example of a part that requires coating of all surfaces, but for which a variation in the coating thickness is acceptable. Dip painting, followed by spinning to remove excess paint, is the preferred method for coating this part. If a part of this type were so large that dip painting would require a prohibitive volume of paint, flow coating could be substituted, although rotation of the part as it passes through the nozzles might be required. If the size were increased still further, spray painting might be used.

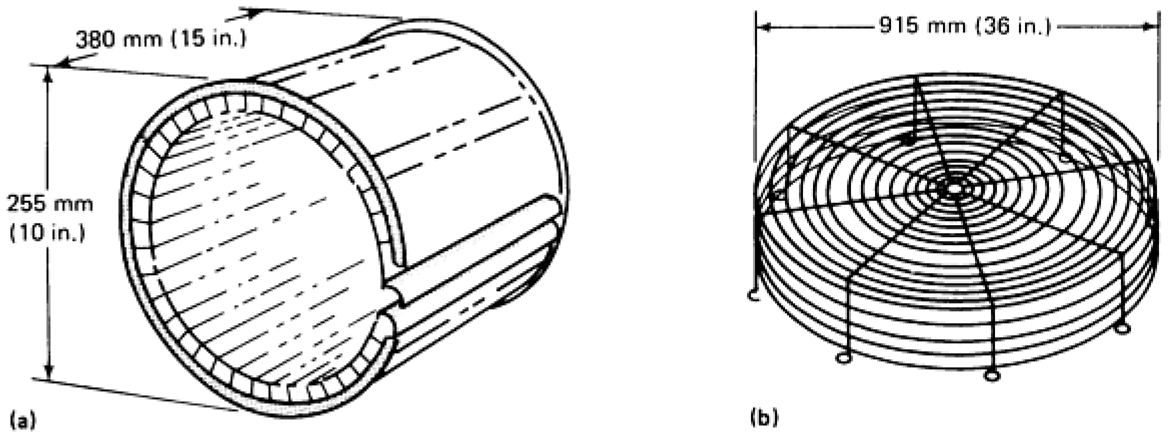


Fig. 2 Parts that can be efficiently coated by dip painting. If considerably larger, parts like these could be painted more efficiently by the flow coating process. (a) Blower wheel. (b) Wire fan guard

The wire fan guard shown in Fig. 2(b) is an example of a part that is difficult to cover efficiently by conventional spraying without considerable loss of paint by overspray, but can be efficiently coated by dipping. The part in Fig. 2(b) also could be painted by flow coating, electrostatic spraying, or electrodeposition. If the part were larger, flow coating might be preferred to dipping because of the smaller volume of paint required.

Equipment for Dip Painting

Basic equipment for dip painting consists of a tank to contain the paint, a device to agitate the paint and prevent settling or separation of ingredients, a device for lowering the parts into the paint and raising them out of it, a drip trough, and ventilators.

Dip tanks should be as small as possible, consistent with the maximum size of parts to be dipped. Smaller tanks require less paint to fill them, and the higher rate of turnover helps to maintain paint stability. Dip tanks should be designed to expose the smallest possible area of paint to prevent evaporation of paint thinner.

Dip tanks for conveyorized dipping should be designed with ends that slant according to the angle parts travel as they are conveyed into and out of the paint. This angle should be not less than 30°, measured from the horizontal, and should be 45° if possible. The sharper the angle of travel, the shorter the dip tank, and there is consequently less exposure of paint to air.

Introduction of fine air bubbles into the tank should be avoided, because these bubbles can cause pinholing in the final film. Pumps are used to dislodge trapped air bubbles from blind spots in parts. Mechanical devices, such as tipping bars that change the position of parts during immersion, are also used to dislodge bubbles.

Dip tanks should be designed with provision for paint agitation. The bottom of the tank should be just wide enough to accommodate the agitator.

Agitators in dip tanks prevent the paint from separating. Horizontal screw or horizontal paddle agitators may be used. Usually, agitators extend the full length of the tank and are no greater than 0.3 m (1 ft) in diameter. Tanks with a capacity of 7570 L (2000 gal) or more may require agitators of larger diameter.

Agitator speed is usually between 60 and 120 rev/min. Correct speed is usually determined by visual inspection of the tank surface. The entire surface of the tank should show agitation with no clear vehicle forming. Agitation should be of sufficient force to keep the paint well mixed and prevent the pigment from settling. Protective screening should be installed over the agitator to protect the blades from being damaged by parts that may fall into the tank.

A pump circulator added to an agitator system permits the use of strainers to remove lumps that may form or foreign material that may be introduced into the tank.

In tanks with a capacity of about 1135 L (300 gal) or less, complete recirculation of the paint every 20 min usually provides sufficient agitation for preventing settling or separation of ingredients. Paint should be withdrawn from the bottom of the tank and pumped back into the tank just under the minimum working level.

Ventilation. Dip tanks should have a means of ventilation to remove fumes from the tank. Hoods should not interfere with the conveyor system or the device for immersing parts.

Drip troughs catch the excess paint that drips from the parts after they have been removed from the tank. A conveyorized dip plating system usually includes a sloped drip trough to allow excess paint to flow back into the tank. Working areas around drip troughs and dip tanks must be equipped with adequate fire control equipment.

Table 6 lists equipment requirements for dip painting two production parts. One part is an angle bracket about 25 mm (1 in.) wide, produced from 3.2 mm ($\frac{1}{8}$ in.) thick stock and with each leg 75 mm (3 in.) long. The other, a spring hanger produced from 4.8 mm ($\frac{3}{16}$ in.) stock, is 100 mm (4 in.) wide with 150 mm (6 in.) and 100 mm (4 in.) legs.

Table 6 Equipment requirements for dip painting two steel production parts

Procedure or equipment	**Angle bracket[(a)]**	**Spring hanger[(b)]**
Production requirements		
Surface preparation	Clean and phosphate[(c)]	Clean and phosphate[(c)]
Prime coating	None	Red oxide primer
Finish coating	Lacquer; air dry	Lacquer; bake
Production per hour	1200	650
Equipment requirements		
Work handling	Manual; baskets[(d)]	Automatic; conveyor[(e)]
Cleaning and phosphating:		
Capacity of solution and rinse tanks	190 L (50 gal)	190 L (50 gal)
Solution and rinse temperature	66 °C (150 °F)	66 °C (150 °F)
Prime coating:		
Capacity of dip tank	. . .	190 L (50 gal)
Drying	. . .	12 m (40 ft) infrared oven[(f)]

Finish coating:		
Capacity of dip tank	190 L (50 gal)	190 L (50 gal)
Drying	Air dry	12 m (40 ft) infrared oven(f)

(a) 75 by 75 mm (3 by 3 in.) L-shaped bracket, 3.2 mm ($\frac{1}{8}$ in.) thick, 25 mm (1 in.) wide.

(b) L-shaped bracket, of 4.8 mm ($\frac{3}{16}$ in.) stock, 100 mm (4 in.) wide and with one 100 mm (4 in.) leg, one 150 mm (6 in.) leg.

(c) Proprietary phosphate cleaner coater used; 1-min immersion in solution and rinse tanks, followed by drying.

(d) 90 to 100 pieces per load.

(e) Hooks 305 mm (12 in.) apart.

(f) Parts conveyed through oven; drying cycle, 10 to 12 min at 160 °C (325 °F)

Flow Coating

In flow coating, paint is pumped from a storage tank through properly positioned nozzles, onto all surfaces of parts, as they are conveyed. Excess paint drains back to the storage tank for recirculation. Paint films applied by flow coating are wedge shaped, thinner at the top and thicker at the bottom of painted parts. In flow coating, utilization of paint approaches 95% as opposed to about 50% for atomized air spraying and 70 to 80% for dipping. Properly designed flow coat machines with vapor chamber flow-out reduce solvent losses and eliminate tears, sags, and curtains.

Flow coating is used extensively to paint panels for home appliances. Flow coating is also used to coat parts with recesses inaccessible to spraying, to coat parts (such as bedsprings) for which good appearance is desirable but is secondary to complete coverage and economical application, and to coat intricate parts that are too open in design to permit efficient spray painting and too large to be practical for dip painting.

Figure 3 shows a large assembly which, because of its size and construction, is an example of a part for which flow coating is the most efficient method of painting. Spraying would be inefficient because of overspray, and dip coating would require a large quantity of paint to fill the dip tank. However, flow coating would be impractical for a similar assembly twice as large, and spray painting would be preferred.

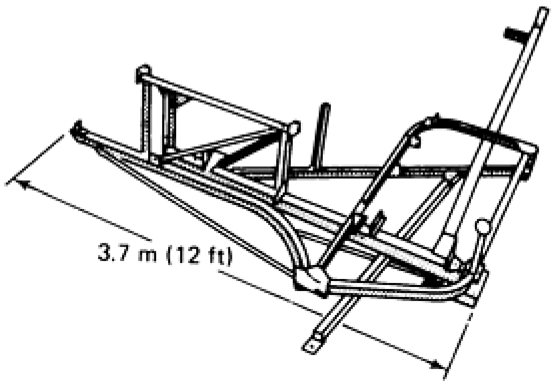


Fig. 3 Assembly for which flow coating is an efficient painting method

Equipment for Flow Coating

Basic equipment for flow coating consists of a chamber, a paint-storage tank, a pump, a drain-off section, and continuous conveyors. Because flow coating ordinarily is used only for high-volume production parts, equipment usually is set up as part of a continuous process, which may include cleaning, phosphating, drying, prime flow coating, finish flow coating, and baking. One conveyor may carry the parts through all operations. Process variables that require close control are nozzle pressure, viscosity and temperature of the paint, and hanger design and spacing of the parts.

Pressure control of paint in the circulating system is critical, particularly at the nozzle. Excessive pressure causes the paint to flow off the parts at too high a rate, resulting in high solvent losses and bubbles in the paint. Too low a pressure leaves areas on the work uncoated or improperly coated. Pressures vary from 0.02 to 0.2 MPa (3 to 30 psi). The higher pressures are used to coat difficult-to-reach or recessed areas. The lowest pressure that can be used in a particular operation is the most economical when solvent loss is considered.

Paint viscosity must be closely controlled. Viscosity that is too high causes poor flow-off of paint from the work. This results in sags, beads, blistering, and other defects associated with excessive paint thickness. Viscosity that is too low results in excessive solvent loss and inadequate film thickness. Viscosities are held within the range of 18 and 32 s (No. 2 Zahn cup), although paints with a No. 2 Zahn cup viscosity as high as 100 s have been used. Viscosity must be adjusted for each paint and each differently shaped part. Once the optimum viscosity has been determined, it should be maintained.

Temperature control of paint is essential. Too high a temperature results in excessive solvent loss and may cause instability of the paint. Too low a temperature requires increased use of solvents to maintain proper viscosity and can result in inadequate film thickness. Although temperatures as low as 16 °C (60 °F) and as high as 38 °C (100 °F) have been used, 21 to 32 °C (70 to 90 °F) is the recommended temperature range.

Drain-off chambers, enclosed tunnels immediately adjacent to the coating chamber, are incorporated in many installations. In drain-off chambers, a high concentration of solvent vapor is maintained to retard drying. This eliminates beads, bubbling, and other surface defects that result when flow-off of paint is incomplete. Some installations include an electrostatic detearing device to remove any beads or drops of paint still clinging to the edge of the part.

The equipment and production requirements for using flow coating to paint two steel production parts are discussed below. One part is a step hanger (an angle bracket) produced from 4.8 mm ($\frac{3}{16}$ in.) stock 50 mm (2 in.) wide, with two legs 355 and 125 mm (14 and 5 in.) long, respectively. The other, a bracket for holding a fire extinguisher, is produced from 1.5 mm (0.060 in.) stock and has legs 305 and 75 mm (12 and 3 in.) long; a metal clamp is attached to the 305 mm (12 in.) leg to retain the extinguisher. The production requirements are as follows:

Part A

- Step hanger, 4.8 mm ($\frac{3}{16}$ in.) thick; maximum dimensions 125 by 355 mm (5 by 14 in.)
- Production rate, 540 pieces per hour

Part B

- Bracket for holding fire extinguisher, 1.5 mm (0.060 in.) thick; maximum outside dimensions, 75 by 305 mm (3 by 12 in.)
- Production rate, 720 pieces per hour

Both parts

- Clean and phosphate, using proprietary phosphate cleaner coater with 2-min immersion in solution and rinse tanks before drying; color coat with alkyd baking enamel (no prime coat)

Equipment requirements for both parts are as follows:

Work handling	Overhead conveyor[(a)]
Cleaning and phosphating[(b)]	
Solution and rinse tanks	190 L (50 gal)
Solution and rinse temperature	66 °C (150 °F)
Flow coating	
Flow coater	Conventional; 2 nozzles
Nozzle pressure	275 kPa (40 psi)
Drying	Infrared; 7 to 8 min; 160 °C (325 °F)

(a) 305 mm (12 in.) hook spacing.

(b) Proprietary phosphate cleaner coater used; 2-min immersion in solution and rinse tanks, then drying

Roller Coating

Roller coating, or coil coating, is a high-speed machine painting process used for continuous coating of sheet and strip stock. The process consists of transferring an organic coating from a revolving applicator roller to the surface of sheet or

strip as it is passed through the machine. The top, the bottom, or both surfaces may be coated in one pass. In addition, two and sometimes three coating layers can be applied in one pass. Paint can be rolled on with excellent control of film thickness.

Roller coating is one of the most economical and environmentally safe painting processes. Steel strip can be roller coated, baked, and coiled for later fabrication into parts, such as the slats used in the manufacture of Venetian blinds, building products, automotive parts, and a host of other items.

Because this process is similar to rotary printing, designs can be reproduced and repeated in any pattern necessary. Thus, bottle caps, food cans, toys, and similar painted parts can be produced economically. The designs are roller coated on the metal strip before it is stamped or formed to shape.

Equipment for Roller Coating

Equipment for roller coating, similar in function to a rotary printing press, may vary from a relatively simple machine to an elaborate complex installation several hundred feet long. The equipment transfers an organic coating from the revolving applicator roll to sheet or strip as it travels through the machine. The thickness of the film is regulated by a metering roll that controls the amount of paint transferred to the applicator roll.

Applicator rolls must be made of material that does not swell, soften, or dissolve from contact with paint. Usually, applicator rolls are made of, or faced with, a resilient material, such as neoprene or polyurethane. Resiliency permits rolls to conform to irregularities found in commercial stock.

Almost every organic coating material can be applied by roller coating. Usually, the paints use slow-evaporating solvents and are applied at higher viscosities than in other painting methods, which permits close control of paint flow and film thickness.

Curtain Coating

Curtain coating is a method of applying finishes at high speeds with little paint loss. In curtain coating, flat or shaped strip and sheet are moved by conveyor belt beneath a pump-fed reservoir with an adjustable slot opening at its lower edge. The slot opening provides a controlled continuous wet curtain of coating flowing onto the work. Some curtain coaters have heads that function by use of gravity overflow of material over one side of the reservoir.

The pressure-fed curtain coater applies a uniform wet film to flat or shaped surfaces of practically any material. Coatings can be applied between 13 and 2540 μm ($\frac{1}{2}$ and 100 mils) thick, depending on coating characteristics, conveyor speed, and parts being coated. Deposited films are smooth and uniform with no ridges, washboarding, or similar effects that can be found with roller coating. No sagging or uneven thickness occurs as with flow coating and dipping.

Equipment for Curtain Coating

Curtain coating equipment consists of a conveyor belt that moves the items to be coated under a special coating head. This coating head may be either pump fed or gravity overflow. In the former, the reservoir has an adjustable slot opening at its lower edge that provides a controlled continuous wet curtain of coating on the work as it moves past. In the latter, the material flows over one side of the reservoir. Viscosity must be closely controlled and flow properties adjusted to form a good curtain. A collection trough is located under the head and any of the coating that does not fall on the work is returned to the pump for reuse. Figure 4 shows examples of curtain coating equipment.

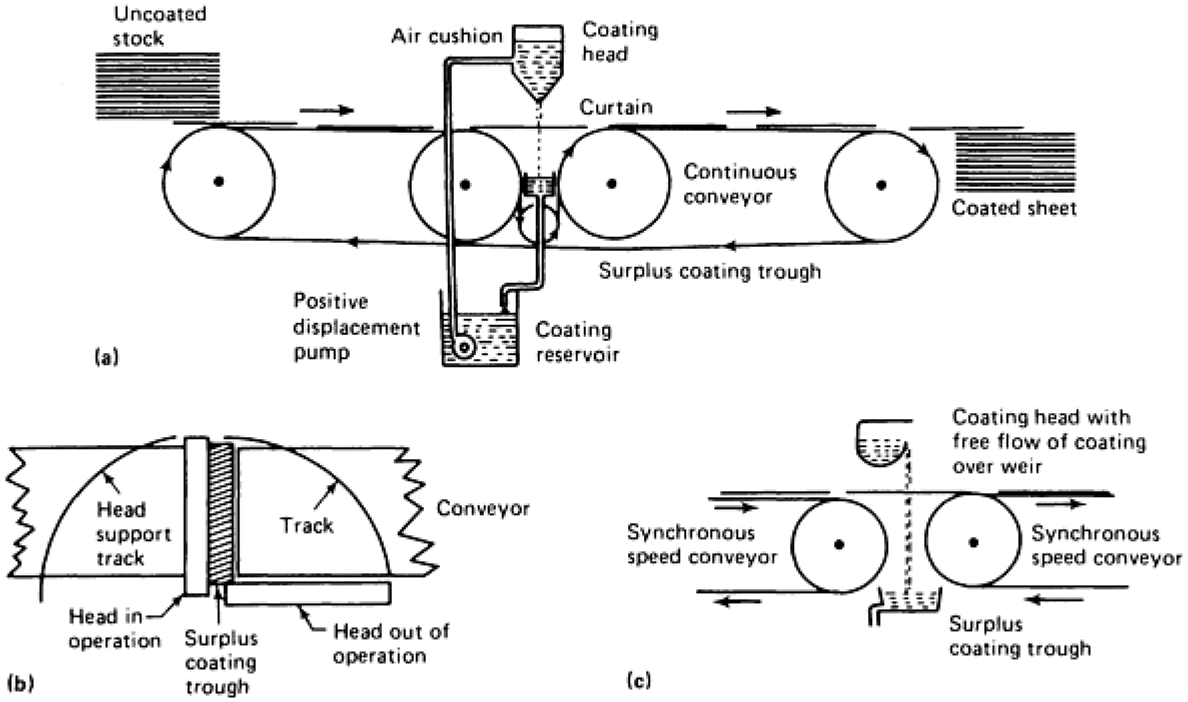


Fig. 4 Examples of curtain coating equipment. (a) Pressure head curtain coater. (b) Double head machine gives fast color changes, applies two component coatings. (c) Gravity flow coater with synchronized conveyors

Tumble Coating

Tumble or barrel coating is one of the most economical means of coating large numbers of small pieces. It is particularly useful for such articles as nails, screws, buttons, and other metal objects weighing less than 0.5 kg (1 lb). Tumble coating is also a good method for pretreating objects to be coated by other systems. In barrel coating, a predetermined weight of coating, adequate to produce a uniform finish over each item without causing drops to form, is poured over the items. The barrel is rotated to distribute the coating evenly over the parts. Drying air is then forced through the center axle and circulates through the continuously moving charge, finally escaping through the other end of the axle and removing solvent vapors. After sufficient air has passed through, parts are dry and ready for packing. In some cases, drying is not done in the barrel. Pigmented coatings are a good example, because the rubbing process during drying damages the appearance of the coatings. In this case, the parts are discharged wet onto a screen and allowed to dry by forced air or natural air circulation. The slight blemishes that occur at the points of contact are virtually invisible.

Electrocoating

Electrocoating is a process in which the object to be coated is dipped into a tank of water-borne paint, and a current is passed through to charge the paint particles electrically. The charged paint particles migrate to the object to be coated, which has an opposite charge. When the object is reached, the paint materials come out of solution and coat the surface. The article is then withdrawn from the tank, rinsed with water to remove any undeposited paint, and baked. This process is also known as electrodeposition, electrophoretic deposition, or electropainting.

Coating Thickness. Paint particles migrate to the part to be coated when a sufficient potential difference, usually between 80 and 180 V, is applied between the part and the tank or separate electrodes. Coating thickness depends on complexity of the part, time, temperature, voltage, solids content, throwing power of the paint, and its ability to penetrate recessed areas. Coating thicknesses up to 38 μm (1.5 mils) are obtainable. The applied coating has a solids content of about 95% and is essentially water insoluble. The relatively high electrical resistance of the coating drastically reduces the rate of deposition as thickness increases. The thickness on easily reached portions of a part builds up rapidly to a near-maximum value and then levels off, and the thinner coating at recessed portions continues to increase in thickness until a very uniform paint film is deposited on even the most complex parts.

Resins used for electrocoating include:

- Maleinized drying oils
- Styrenated and vinyl toluenated maleinized oil
- Phenolic modified maleinized oils
- Alkyds
- Epoxy esters
- Styrene-alkyl alcohol copolymer esters
- Acrylic copolymers
- Polyesters

Advantages and Limitations. Electrocoating offers several advantages over more conventional coating processes. These include:

- The process lends itself to total automation, reducing labor costs.
- Intermixed parts with different shapes and sizes can be coated.
- A more uniform coating thickness is obtained.
- Good edge and recess coverage without heavy buildup produces better corrosion resistance.
- Absence of runs and sags minimizes rework.
- Significant paint savings of as much as 30% are obtainable.
- Dangers of fire hazard are absent.

The disadvantages of the process should also be considered:

- Cost of equipment is high.
- Temperature, pH, and alkali content of the coating material must be controlled closely.
- Pretreatment and rinsing requirements are more stringent than with conventional coatings.
- Surface defects in the substrate are visible through the coatings.
- Only a single film can be applied.
- Changing colors is difficult and expensive.

Cathodic Systems. All early electrocoating systems were anodic. However, many have recently been converted to cathodic. The advantages of cathodic over anodic systems are as follows:

- In cathodic systems, unlike anodic, metal dissolution does not occur at the cathode. The absence of electrodissolved metal in the film results in better film properties, especially in the case of white electrodeposits over steel.
- Cathodic deposition tends to deposit over contaminants in the metal surface, and they do not appear in the film.
- Salt spray and humidity resistance is improved.
- Cathodic coatings have better color consistency over welded areas.

Equipment for Electrocoating

Electrocoating systems usually include a dip tank, power supply, heat exchanger, filters, plane replenishment tanks, and a baking oven. Dip tanks are equipped with stirrers and circulating pumps to keep the paint homogeneous. Tanks can range in size from several hundred to several thousand gallons. In an anodic system, parts may be made the anode or the cathode, and the tank the other electrode, or separate metal electrodes can be placed in an insulated tank. For cathodic systems, tanks must be insulated and kept at ground potential. A relatively large power supply is needed, with voltage ranging from 50 to 400 V and amperage from 50 to 4000 A. Heat exchangers are needed to keep the bath at optimum plating temperature, because the electrodeposition process generates heat. Ultrafilters are used for reclaiming dragout

paint. Figure 5 illustrates an electrocoating system layout. Figure 6 depicts a basic layout of a cathodic electrodeposition system.

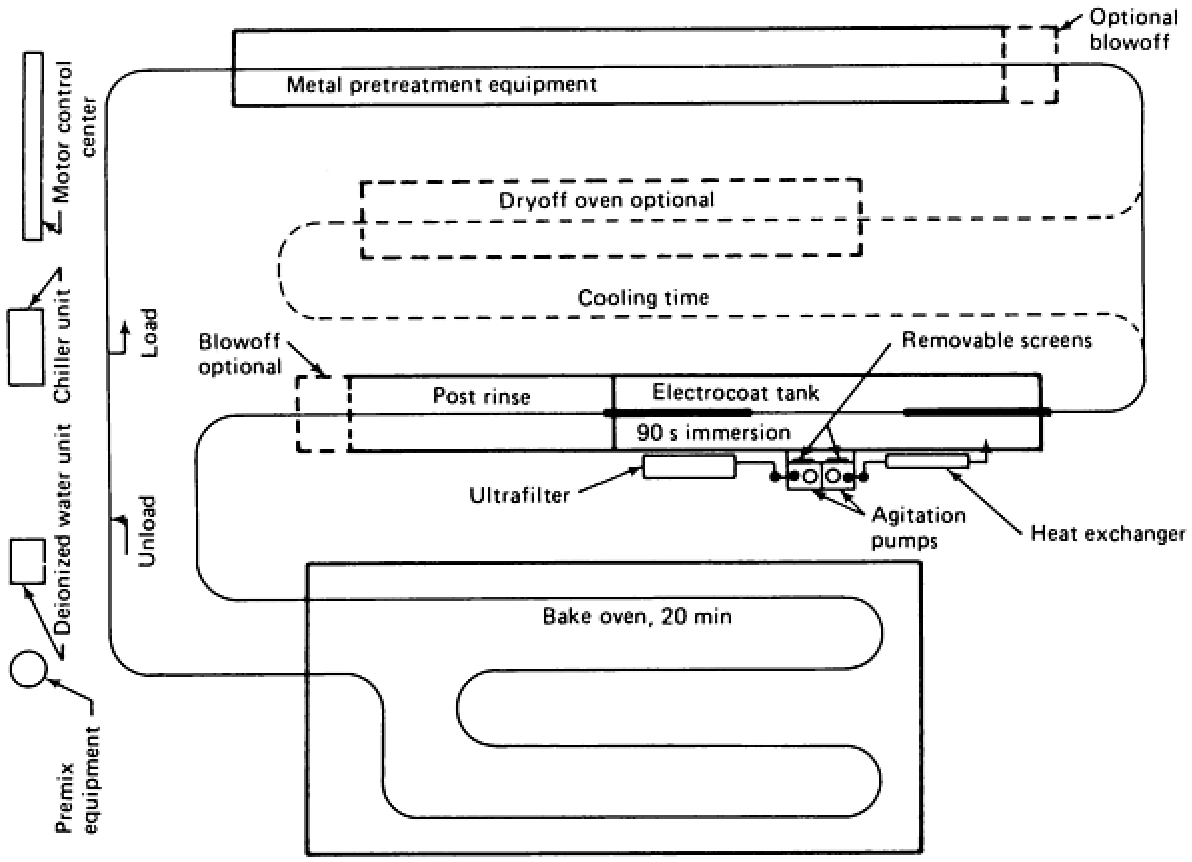


Fig. 5 Electrocoating finishing system

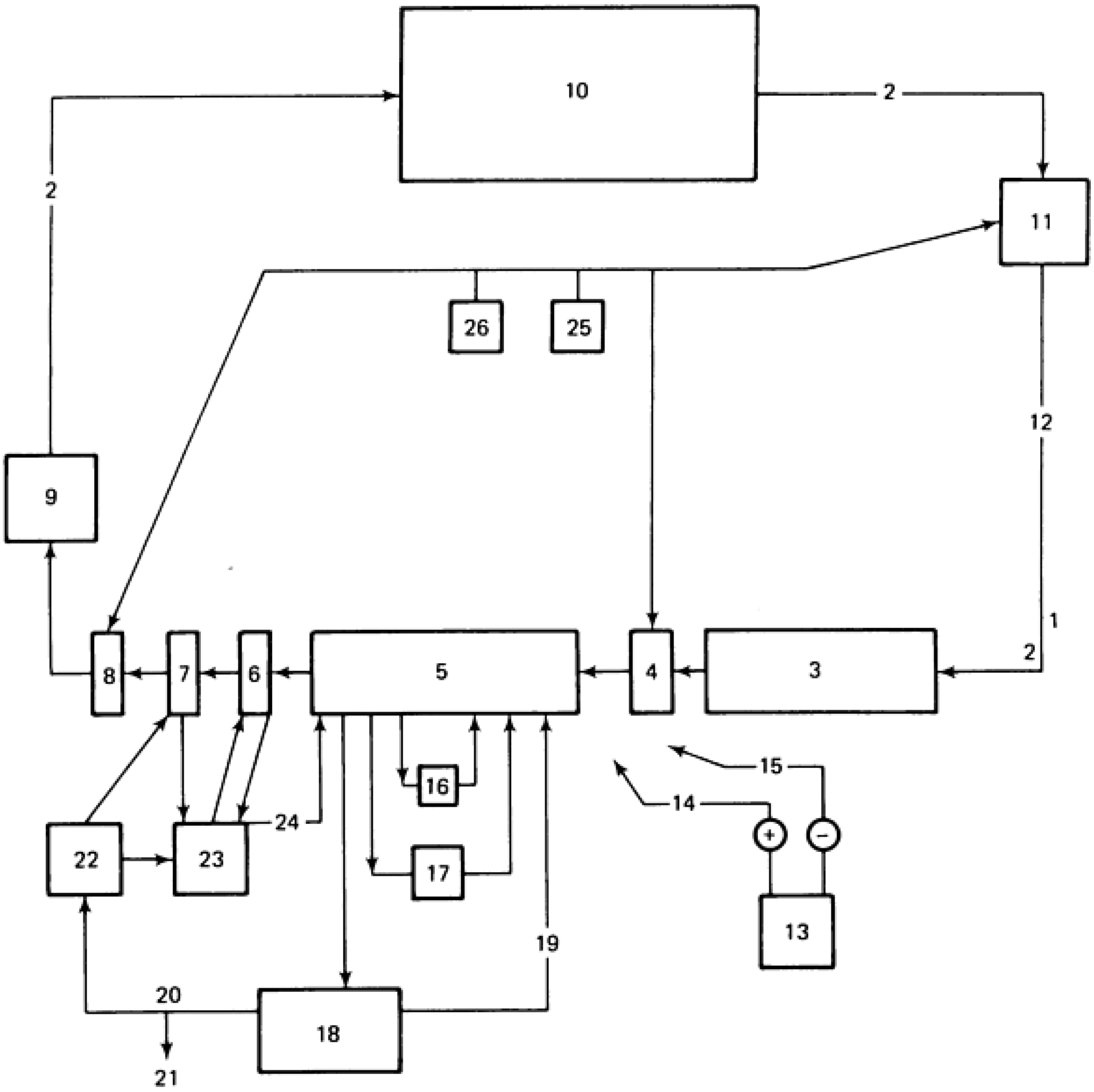


Fig. 6 Cathodic electrodeposition coating system. (1) Load area. (2) Conveyor. (3) Pretreatment. (4) Deionized water rinse. (5) Electrodeposition tank. (6) Recirculated permeate rinse. (7) Fresh permeate rinse. (8) Deionized water rinse. (9) Dryoff. (10) Curing oven. (11) Deionized quench for cooling. (12) Offload area. (13) Source for direct current. (14) To anodes in paint bath. (15) To work on conveyor. (16) Particle filter. (17) Cooler. (18) Ultrafilter. (19) Paint solids return. (20) Permeate. (21) Controlled flow to waste. (22) Permeate storage. (23) Recirculated permeate. (24) Overflow permeate. (25) Source of deionized water. (26) Deionized water storage

Powder Coating

Powder coatings are paint films that are applied to parts as a dry powder. The powders are basically the same type of polymers and resins (see Table 1) as used in liquid coatings except no solvent is used. Instead, the coating composition is ground to a fine powder. After application the film is formed by fusing the powder particles at temperatures above the melting point of the powder. Powder coatings are used on a wide range of products including metal furniture, wire goods such as baskets and racks, appliance housings, chemical and laboratory equipment, and aircraft and automotive components. The advantages and disadvantages of powder coating systems are given below:

Advantages

- The process meets all current EPA requirements for reduction in VOC emissions.

- Material use can approach 100% if powder can be collected and reused.
- Maintenance is less, because powder can be vacuumed from any unbaked surface.
- Exhaust air volume is greatly reduced from that used for solvent-borne systems.

Disadvantages

- Color change is difficult, because a separate booth is usually required for each color.
- Color matching is more difficult with powder coatings than with solvent coatings.
- Powder coating materials are discrete particles, each of which must be the same color. No tinting or blending by the user is possible.
- Applying films of 25 μm (1 mil) or less is extremely difficult, and at times, impossible.

Equipment for Powder Coating

The three primary methods of applying powder paints include: electrostatic spray, fluidized bed, and electrostatic fluidized bed. In addition, several variations can be applied to the basic electrostatic spray process. The best process for a particular application depends on such factors as: end-use of coating, coating thickness, size and shape of parts, rate of production, and material handling techniques.

Electrostatic spray is the most versatile and flexible application process. The electrostatic disk, cloud chamber, and Gourdine tunnel are variations of the basic electrostatic spray process.

The basic electrostatic spray process uses spray guns to apply powder to the parts (Fig. 7). These guns may be manual or automatic. Powder is delivered to the guns through flexible tubing from a supply hopper. At the guns, the powder is charged electrostatically. Coating parts are then carried to the oven, where the powder melts, flows, and fuses to the surface. Air exhausted from the booth serves three functions: maintains the powder-air concentration below the minimum explosive concentration (MEC), keeps powder from drifting outside the booth, and begins the powder recovery process. The dust collection equipment used may be a cyclone, a bag filter, or a cartridge filter. Air exhausted from the dust collector is returned to the plant. The moving filter belt is a modification of the basic powder recovery technique. An endless belt of porous fabric forms the floor of the spray booth. Booth exhaust air passes through the belt into a plenum beneath, and the powder is left on the belt. The belt carries the powder to the end of the booth beneath a vacuum pickup head.

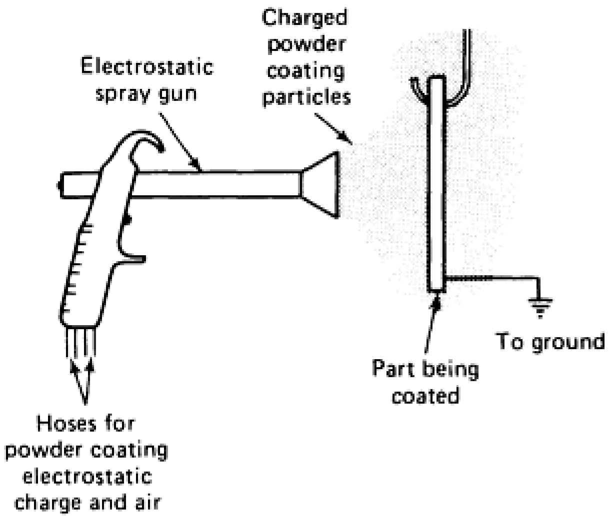


Fig. 7 Electrostatic spray system for application of powder coatings

The electrostatic disk is a variation of the electrostatic disk for liquid paint. The disk propels the charged particles outward by air force as it reciprocates. The workpiece passes around the disk in an omega booth.

In a cloud chamber, automatic electrostatic spray guns create a cloud of electrostatically charged powder in an almost totally enclosed booth. Powder not adhering to parts conveyed through the booth falls to a fluidized bed in the bottom of the booth. The powder is withdrawn from the fluidized bed and recycled to the guns. Only enough air is drawn into the booth to keep powder from drifting from the workpiece openings. Because there is the constant potential for exceeding the MEC, cloud chambers must be equipped with an explosion suppression system.

In the Gourdine tunnel, powder is sprayed in a nonconductive plastic tunnel. The tunnel is not grounded, and charged particles are not attracted to its surface. The parts themselves are grounded, and they move through the tunnel, first passing through the charging section where powder is sprayed from electrostatic guns on both sides of the workpiece. Parts then pass into a precipitation chamber, with interior walls lined with conductive plates charged at the same polarity as the powder particles. Air introduced into the tunnel carries particles not adhering to the part into the precipitation chamber. The particles are repelled by the charged plates and directed back toward the workpiece. The system is said to achieve 90% deposition efficiency, needing no recovery system. Like the cloud chamber, the Gourdine tunnel also needs explosion protection.

Conventional Fluidized Bed. In the fluidized bed process, dry air is forced through a porous plate or membrane into an open top tank that is about half filled with powder (Fig. 8). The air suspends the powder, increasing its volume, and makes the powder act like a fluid. The item to be coated is preheated above the fusion point of the powder and is dipped in the powder for a few seconds. The powder that comes in contact with the item fuses and forms a coating. The item is then removed, shaken or blown to remove any loose powder, and either recooled or reheated to obtain a more uniform film. Reheating is used if a thermoplastic powder is used or if a thermoset powder is used, and the film is to be cured. With the fluidized bed method, film thicknesses of 150 to 1525 μm (6 to 60 mils) can be obtained. Films of less than 150 μm (6 mils) are difficult to obtain with this method. This procedure does not coat recesses well and cannot coat one side of an object without the use of masking.

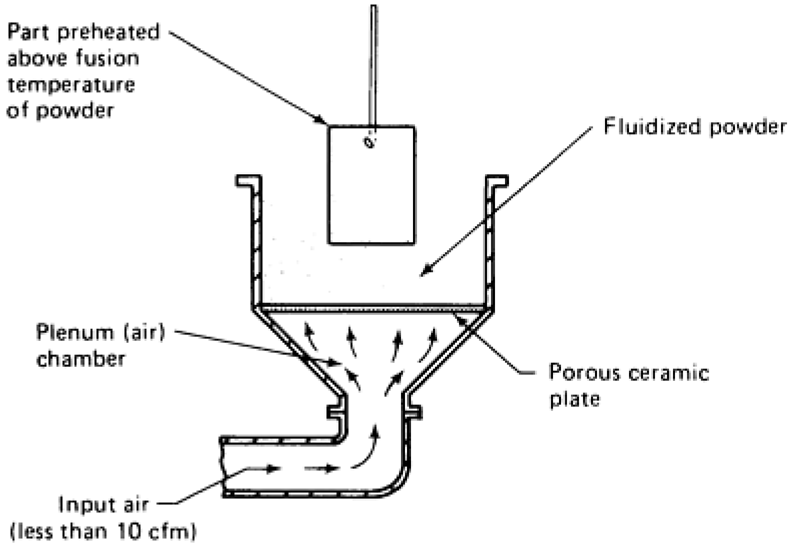


Fig. 8 Fluidized bed system for application of powder coatings

Electrostatic Fluidized Bed. In this system, an electrode is incorporated in the powder chamber (Fig. 9). The powder is fluidized as in the conventional procedure. However, high voltage is applied, and the particles receive a charge and rise in a fine cloud above the fluidized bed. When a grounded part is passed into or through the cloud, the charged particles are attracted to and adhere to the part. With this system, preheating is not necessary. A smaller amount of powder is necessary, and the less dense powder suspension permits better control of film thickness. This system also eliminates the need for dipping, because powder rises to the part. Because the part is not preheated, powder can be removed from areas that are to be left bare, eliminating the need for mechanical masking and the problems associated with it.

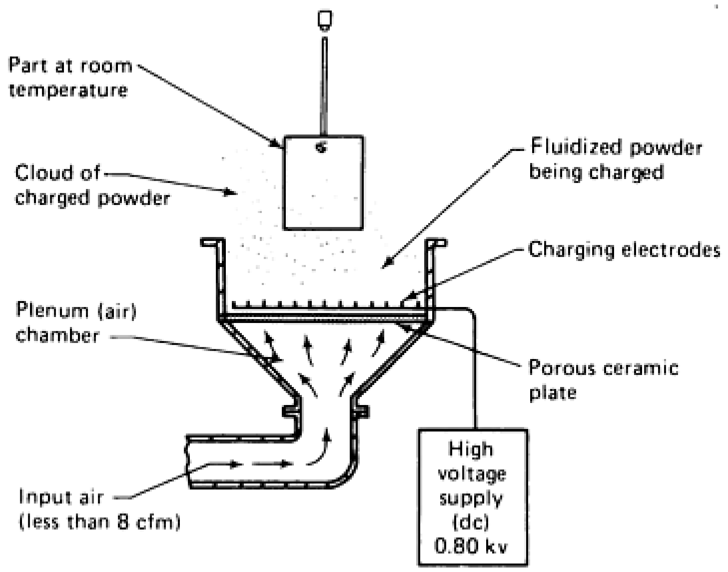


Fig. 9 Electrostatic fluidized bed for application of powder coatings

Curing of Paint Films

Curing is the process of converting an applied coating to a dry film. Baking or thermosetting coatings require heat to cure. Those coatings that dry by evaporating the solvent are air drying or thermoplastic. Ovens are used to supply the energy needed to cure the film and/or evaporate the solvent.

Heat is transferred by conduction, convection, or radiation. Convection and radiation are used in ovens for baking paint. Conduction takes place in shielded areas only incidentally. Convection baking ovens usually are heated by gas, although oil, electricity, or steam may also be used. Radiation ovens may be heated by gas or electricity, although electricity is used more frequently.

Batch ovens are used for baking paint films on parts produced intermittently, in limited quantities, or on parts not easily conveyorized. These ovens, which transfer heat by convection, consist of one or more insulated compartments equipped for heating, recirculating, and exhausting air. These compartments also regulate and control temperature.

Batch ovens range in size from small single-compartment units that accommodate only a few small pieces, to large units with single or multiple compartments for baking several bulky parts simultaneously. Multiple-compartment batch ovens may be used for simultaneous production of separate runs of parts that require different baking cycles. Batch ovens may be direct fired or indirect fired.

Direct-fired batch ovens (Fig. 10a) are used more often than indirect-fired ovens. In direct-fired ovens, fuel is burned directly in the circulated air. Direct-fired ovens are more economical to operate, because the heat does not have to be conducted through the walls of a heat exchanger. The disadvantage of direct-fired ovens is that the paint films are exposed to the products of combustion, which may harm some coatings.

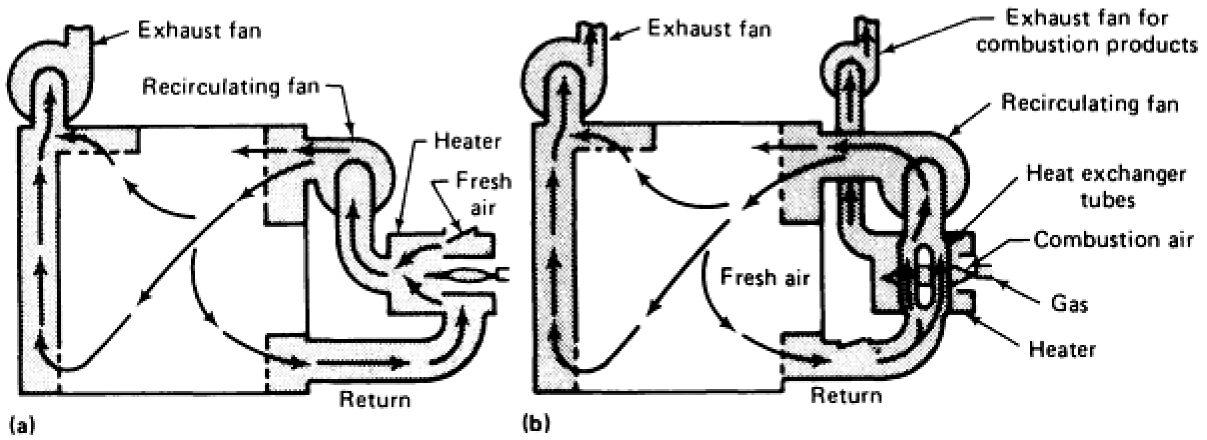


Fig. 10 Convection ovens for curing of paint coatings. (a) Direct fired. (b) Indirect fired

The solvent vapors extracted from the paint are burned when they are passed through the flame with the recirculated air. Proper circulation and introduction of a sufficient supply of fresh air are essential--particularly during the early minutes of the cycle, when the rate of solvent evaporation is greatest. The required dilution rate for safe operation depends on the total quantity of solvent present and on its lower explosive limit. Insurance and safety organizations have established minimum exhaust rates for safe operation of direct-fired baking ovens for most of the solvents used in paint films.

Most regulations require maintaining 25% or less of the lower explosive limit (LEL) of solvent in the oven. This is done by calculating solvent emission at full oven load and exhausting sufficient air to keep solvent level at or below 25% of LEL. New solvent level monitoring equipment allows automatic damper control of oven exhaust to maintain safe solvent levels, depending on actual load. This reduces energy requirements by reducing exhaust rates and provides richer solvent exhaust for more efficient use of incineration for VOC emission control.

Indirect-fired batch ovens (Fig. 10b) burn the fuel outside the oven walls, and the oven is heated by means of heat-exchange surfaces. Indirect-fired ovens are less efficient and consume more fuel than direct-fired ovens. The advantages of indirect-fired ovens are that the paint film is protected from the products of combustion, and solvent vapors are not exposed directly to the flame.

Continuous ovens are used in finishing parts produced in large quantities. Parts are conveyed through the ovens as a cycle in a continuous finishing process that may include cleaning, phosphating, drying, painting, and baking. Continuous ovens may use either convection or radiation.

Convection continuous ovens, direct fired or indirect fired, may use gas, oil, electricity, or steam as the source of heat, although steam usually limits oven temperature to 150 °C (300 °F). Figure 11 illustrates an indirect-fired continuous convection oven. Two 180° turns have been incorporated in the conveyor path to shorten the distance the heat must travel from the burner. Ductwork may be installed to direct and control the distribution of the heated air. A large volume of hot air can be directed to the area where the cold work enters and the volume of air can be limited to the area where the work has attained the desired temperature.

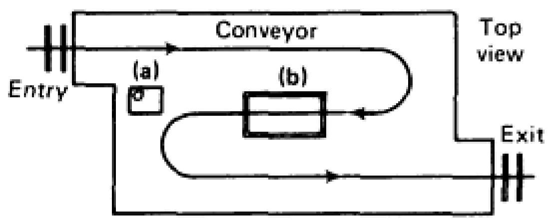


Fig. 11 Indirect-fired continuous convection oven for curing of paint coatings. (a) Exhaust system. (b) Burner

and recirculating fan

Heat retention is a problem in these ovens, because parts being conveyed must be permitted to enter and leave the oven in a continuous process without restriction. One method for heat retention is to slope entrance and exit chambers downward from the oven section, trapping rising heated air. For ovens into which the conveyor enters and exits at the same level as the hot zone, heat retention can be accomplished by high-velocity air seals (air curtains) across the entrance and exit of the oven.

Radiant continuous ovens are widely used. Using infrared radiation, radiant ovens require less insulation or heat sealing, as well as less complicated ventilation and exhaust systems. Many infrared continuous baking ovens have an enclosed tunnel construction to take advantage of the air heated by contact with the parts. A simple baking tunnel may consist only of racks of lamps on each side of the conveyor line. Heat is produced as required as parts are conveyed through the system, permitting a more flexible use of the baking facilities.

Infrared generators may be either electric or gas fired. Electric infrared generators are glass-lamp, ceramic-coated resistance wire, or quartz. Gas-fired infrared generators consist of ceramic grids heated by gas until the grids are radiant.

In infrared baking, electrical energy or heat energy from the burning gas is converted into radiant energy, which, when directed to the wet paint surface, is rapidly absorbed by both the paint film and the metal beneath it. The surface beneath the paint heats up as rapidly as the paint. This accomplishes solvent evaporation simultaneously throughout the thickness of the paint film, or in some cases, from the inside to the outside. Pits and blisters are thus minimized, and a uniform polymerization of the paint film is accomplished. This is a distinct advantage over convection baking, in which the outside paint surface is first to heat. Infrared baking decreases the tendency to form a skin or shell that traps the solvents under the surface, creating pressure and leading to the formation of pinholes or blisters when the vapors escape. Because it penetrates, infrared radiation also bakes faster than convection heat, provided that the entire painted surface is exposed to the radiant heat.

High-velocity ovens expose parts to very high temperatures for short times; 205 to 315 °C (400 to 600 °F) for 1 to 3 min is typical. If parts can tolerate high surface temperatures for a short time, high-velocity ovens may be an economical alternative to conventional ovens.

Heat Recovery. The combination of increased energy costs and stricter air pollution regulations in recent years makes the recovery of oven exhaust gases increasingly important. As much as 80% of the fuel energy may be exhausted from the oven. Considerable progress is being made in heat exchangers, afterburners, fume incinerators, and catalytic converters to recover some of the oven exhaust energy. This energy may be used to provide added heat source to preheat incoming prepared air for the oven, or to supplement the oven fuel supply. Oven manufacturers should be consulted for most recent developments in energy recovery.

Convection Baking Time and Temperature. Time and temperature of the baking cycle in convection ovens are dictated by the polymerization characteristics of the paint. Although baking temperatures often are expressed as oven temperatures, these may not be sufficient to ensure complete polymerization. Until the metal reaches baking temperature, it is conducting heat away from the paint at the interface. This may reduce the time at temperature of this part of the film enough to prevent complete polymerization. Thus, baking cycles are specified in terms of time, which makes allowance for the metal to attain the proper temperature.

The graph in Fig. 12 illustrates the importance of metal temperature in baking. Metal temperatures have been plotted against time for two panels of equal area but of different mass. Assuming that a baking temperature of 150 °C (300 °F) is desired, the 24-gage (0.607 mm, or 0.0239 in.) cold rolled steel panel can reach 150 °C (300 °F) approximately 10 min before the 13 mm ($\frac{1}{2}$ in.) thick casting.

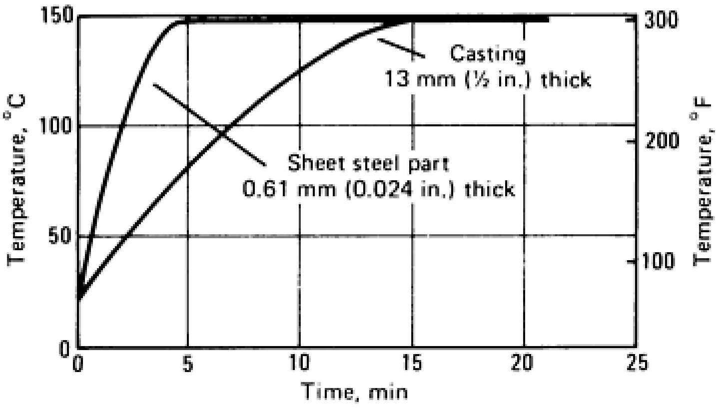


Fig. 12 Times required for interfaces of two steel parts of equal area but different mass to reach baking temperature of 150 °C (300 °F)

Adjusting the cycles so that the areas under the curves are approximately equal usually gives comparable baking results. This is not true, however, if the paint being baked has a critical curing temperature. Some urea-alkyds, for example, cannot polymerize at temperature below 120 °C (250 °F).

Prebake Solvent Evaporation. If paints are exposed to the heat of the oven too soon after being applied, particularly when infrared heat is used, the solvent materials vaporize too fast and disturb the continuity of the paint film. Vapors may also become entrapped because of incomplete ventilation in the oven. This results in a partial breakdown of the paint film and a chalky appearance. If vapor concentration is high enough, the paint film may break down completely.

To avoid these problems, sufficient time and ventilation should be allowed to permit some solvent evaporation and dispersion before baking. For batch baking, parts are allowed to stand in a well-ventilated area for a period of time before they are placed in the oven. In conveyorized painting and baking, the conveyor should pass through a well-ventilated area before carrying the parts into the oven. In this situation, forced circulation or clean air hastens the evaporation and dispersion of the solvent vapors, permitting a shorter interval of time and distance for conveyor travel.

Defects Attributable to Improper Baking. Table 7 lists some of the defects in paint films that may result from improper baking, the causes, and corrective measures that should be taken. Equipment and operating requirements for baking two specific parts are discussed in the following paragraphs.

Table 7 Causes and corrections of paint film defects associated with baking

Cause	Correction
Soft film	
Baking cycle inadequate	Increase time or temperature of baking
Metal not reaching curing temperature	Increase time or temperature of baking[(a)]
Pinholing or blistering	
Entrapment of solvent vapors because of quick drying at baking temperature	Extend air-drying time before baking to increase evaporation of solvent

Wrinkling	
Unequal curing, because of extreme temperature difference of film and metal	Extend air-drying time before baking, or change from convection to radiation
Hazing or poor gloss	
Temperature too high	Reduce temperature; decrease time
Combustion fumes in oven attacking paint	Increase input of fresh air and air circulation in oven
Venting of solvent vapors from oven not fast enough	Increase input of fresh air and air circulation in oven
Discoloration	
Temperature too high	Reduce oven temperature
Hot spots in oven	Control circulation of air in oven
Discontinuity of coating	
Solvent vapors collecting in oven to high concentration	Increase air input and circulation in oven; allow longer air-drying time
Entrapment of solvent vapors because of quick drying at baking temperature	Extend air-drying time before baking
Brittleness	
Overbaking (excessive time or temperature)	Careful control of time and temperature

(a) In convection ovens, adjust louvers to deliver greatest concentration of heated air to area in which parts have not attained baking temperature, or change to radiation heating.

Example 4: Baking of a Spray Painted Wing Bolt.

The upper half of a 64 mm (2 $\frac{1}{2}$ in.) long shouldered wing bolt was spray painted to a wet film thickness of 30 μm (1.2 mils) with glossy bronze baking enamel, using toluene as the solvent. Before being painted, the parts were placed in aluminum racks incorporating 156 holes that accepted the wing bolts up to the shoulder on the body of the bolt, serving to mask the lower part from the paint. Parts were painted, air dried for 5 to 6 min, then baked at a production rate of 1500 pieces per hour. The operating conditions were the following:

Weight of each piece	0.032 kg (0.0702 lb)
Number of pieces per rack	156
Weight of rack plus load	5.089 kg (11.22 lb)
Pieces processed per hour	1500
Type of baking enamel	Glossy bronze
Solvent used	Toluene
Baking cycle	20 min at 150 °C (300 °F)

The requirements for the baking equipment included the following:

- *Racks:* aluminum sheet, 710 by 660 mm (28 by 26 in.) and 1.0 mm (0.040 in.) thick, with 13 rows of 12 equally spaced 9.5 mm ($\frac{3}{8}$ in.) diam holes (156 holes); weight 0.12 kg (0.27 lb)
- *Oven:* electrically heated single-compartment batch oven, 750 mm (30 in.) square and 622 mm (24.5 in.) high (inside dimensions), with shelves accommodating five racks of parts, which are placed in oven every 30 min
- *Heat input:* 13.3 kW/h, assuming that oven is at heat and that 15 min is required for load to reach oven temperature
- *Exhaust air:* 0.46 m^3/s (98 ft^3/min) at room temperature; 0.670 m^3/s (142 ft^3/min) at 150 °C (300 °F)
- *Air recirculation rate inside oven:* 3.8 m^3/s (800 ft^3/min) at 150 °C (300 °F)
- *Space for oven and controls:* width, 1625 mm (64 in.); depth 915 mm (36 in.); height, 2135 mm (84 in.)

Example 5: Baking of a Spray Painted Angular Welded Frame Assembly.

A welded frame assembly, angular in shape, 2 m (8 ft) long with each leg approximately 0.9 m (3 ft) long, was produced from 6.4 mm ($\frac{1}{4}$ in.) steel plate, and weighed approximately 410 kg (900 lb). The parts were spray painted to a wet film thickness of 30 μm (1.2 mils), using a glossy yellow baking enamel with xylene as the thinner. Before baking, the parts were air dried 10 to 20 min. The parts were supported during baking by special dollies designed to have minimum contact with the parts. Three parts were processed each hour. Operating conditions used in this process included:

Weight of each assembly	408 kg (900 lb)
Assemblies painted	3 per hour
Baking enamel	Glossy yellow

Solvent used	Xylene
Baking cycle	45 min at 135 °C (275 °F)

The requirements for the baking equipment included the following:

- *Dollies:* of steel construction, designed to support frame assemblies with minimum contact during finishing; 3 m (9 ft) long, 1 m (4 ft) wide, 380 mm (15 in.) high; weight 90 kg (200 lb). Nine required, three each in spray room, oven, and cooling area
- *Oven:* electrically heated walk-in batch oven with three compartments, each 1.5 m (5 ft) wide, 3.0 m (10 ft) deep, 2 m (6 ft) high
- *Heat input:* 95.6 kW/h, assuming that one dolly and part are replaced every 20 min and that 15 min is required for one dolly and part to reach oven temperature
- *Exhaust air:* 1.26 m^3/s (267 ft^3/min) at room temperature; 1.75 m^3/s (370 ft^3/min) at 135 °C (275 °F)
- *Air recirculation rate inside oven:* 30.68 m^3/s (6500 ft^3/min) at 135 °C (275 °F)
- *Space for oven and controls:* width, 6.1 m (20 ft); depth, 3.4 m (11 ft); height, 3.0 m (10 ft)

Radiation Cure Coatings

Radiation cure coatings are organic monomer or polymer resin binders of low viscosity that polymerize to a cured film when subjected to radiation. Two main types of radiation curing are used: electron beam (EB) and ultraviolet (UV). In both processes, the materials used are solvent free and 100% reactive, giving off little vapor, creating no pollution problems. Curing time ranges from a fraction of a second to minutes depending on the source of radiation. Curing is achieved at or slightly above room temperature, which allows heat sensitive materials, such as plastics, wood, and electronic components to be coated without harm. Because no baking ovens are needed, less floor space is required for finishing. The differences between EB and UV curing systems must be considered:

- Electron-beam radiation is much stronger than UV. Ultraviolet coatings usually require activators to initiate curing, potentially shortening storage life.
- Electron-beam coatings cure almost instantaneously, whereas UV coatings may require several seconds to several minutes.
- Ultraviolet coatings are generally limited to thin clear films (up to 75 μm, or 3 mils); EB can be clear or pigmented (up to 255 μm, or 10 mils).
- Ultraviolet lamps generate heat from 38 to 49 °C (100 to 120 °F); EB does not. Thermally sensitive substrates may cause problems if UV cured.
- Electron-beam curing has higher equipment cost than UV.
- Ultraviolet coatings are more readily available than EB coatings.

Quality Control

Once a coating has been chosen for production, it is necessary to ensure that future supplies of the coating are consistent from batch to batch, maintaining satisfactory application properties, appearance, stability, and performance characteristics. Only by so doing can production quality be maintained. Testing can be costly; consequently, quality control programs should be designed using the simplest test methods and the least number of tests necessary to ensure essential quality levels. Numerous tests and equipment for evaluating and monitoring of coatings are available, most of which are described in the following publications:

- *Annual Book of ASTM Standards,* Vol 06.01, Paint--Tests for Formulated Products and Applied Coatings; Vol 06.02, Paint--Pigments, Resins, and Polymers; Cellulose; Vol 06.03, Paint--Fatty Oils and Acids, Solvents, Miscellaneous; Aromatic Hydrocarbons
- Federal Test Method Standard No. 141a, "Paint, Varnish, Lacquer and Related Materials; Methods of Inspection, Sampling and Testing"

- *Paint Testing Manual, Physical and Chemical Examination of Paint, Varnishes, Lacquers, and Color*, STP 500, American Society for Testing and Materials
- Physical Testing for Paint Finishes, *NCCA Technical Manual*, National Coil Coaters Association

Table 8 lists a number of the most common tests for paint.

Table 8 Selected test methods for paint and painted surfaces

Test	**ASTM**	**Federal method 141**
Wet or liquid tests		
Nonvolatile (solids content)	D 2369	4041
Vehicle solids	D 2698	4052
Pigment content	D 2698	4022
Weight per gallon	D 1475	4184
Flash point	D 56, D 93, D 92	4291, 4293, 4294
Viscosity		
Ford cup	D 1200	4282
Brookfield	D 2196	4287
Stormer	D 562	4281
Zahn	D 3794	. . .
Gardner Holt tubes	D 1545	4271
Fineness of grind	D 1210	4411
Reducibility and dilution stability	. . .	4203
Drying time	. . .	4061
Dry film performance tests		

Hiding power	D 344, D 2805	. . .
Color (pigmented coatings)	D 1729	4250
Specular gloss	D 523	6101
Abrasion resistance		
Falling sand	D 968	6191
Taber abraser	D 1044	6192
Adhesion	D 2197	6303
Dry film thickness		
Magnetic gage	D 1186	6181
Mechanical gage	D 1005	6183
Hardness		
Pencil	D 3363	. . .
Sward Roeker	D 2143	. . .
Indentation	D 1474	6212
Humidity resistance	D 2247	6201
Salt spray resistance	B 117	6061

Viscosity. Controlling paint viscosity is necessary to maintain the desired properties of the coating and to ensure that the process operates at the maximum possible efficiency. Pigmented materials require close control of solids content to eliminate that influence on viscosity readings. Close control of the temperature is also necessary, because viscosity varies inversely with temperature.

Viscosity may be checked by:

- The efflux cup method
- The torsional method
- The bubble viscometer

Commercial equipment is available to assist in performing any of these tests for viscosity.

The efflux cup method uses containers closely controlled in size having a precise orifice in the bottom. After the cup is filled with paint to be checked, paint is permitted to drain through the orifice. The length of time, in seconds, to the first break in the flow stream of the paint is the viscosity. Several commercial cups are available, including the Zahn and Ford cups, designed to permit rapid testing of viscosity on the production line.

The torsional method measures the resistance of paint to rotation of a disk immersed in the paint. Several instruments for measuring the rotational resistance require that the paint be placed in a special container, and other instruments permit the viscosity to be measured in the shipping container.

With the bubble viscometer, the viscosity of the liquid is measured by the speed with which a bubble of air rises in the liquid. The material is confined in a glass tube, which is completely filled, except for a small bubble, and stoppered. The viscosity determination may be made in two ways:

- Comparing the rate of rise with that of a material of known viscosity contained in a tube of the same size
- Measuring the time required for the bubble to travel between two marks on the tube, which must have been calibrated with one or more liquids of known viscosity

Color of paint is most often controlled by visual comparison against a reference standard. One deficiency of this type of control, however, is the difficulty of retaining permanent color standards. Because of this difficulty, stabilized dry drift control panels have come into use. These panels can be either paper chips coated with paints designed to have a minimum of color change on aging, or porcelain or ceramic panels properly coated with the appropriate paint. Each control has its advantages; however, both are subject to soiling. All comparisons should be made under a standardized source of light to eliminate extraneous influences of various sources of light.

Visual comparisons do not permit the assignment of numerical values to differences and are subject to wide variations of opinion. It is possible, however, to analyze color on various instruments, assign numerical tolerances, and eliminate subjective judgment to some degree.

Colorimeters measure the three attributes of color: hue, saturation, and brightness. Colorimeters require the use of some reference standard, although not necessarily of exactly the same color as the paint being tested. Because the numerical values established with the colorimeter must still be related to a reference standard, they cannot be considered as absolute.

Spectrophotometers, which measure and analyze color throughout the entire visual spectrum of 400 to 700 nm, come nearest to being absolute measuring devices. Curves obtained on the spectrophotometer are used as a permanent, reproducible reference. Figure 13 shows spectrophotometric recordings of red, gray, and blue flat paints prepared by extending cadmium red, ivory black, and Prussian blue, respectively, with zinc white. These curves indicate the variation in the light reflectance of the three colors across the entire visible spectrum.

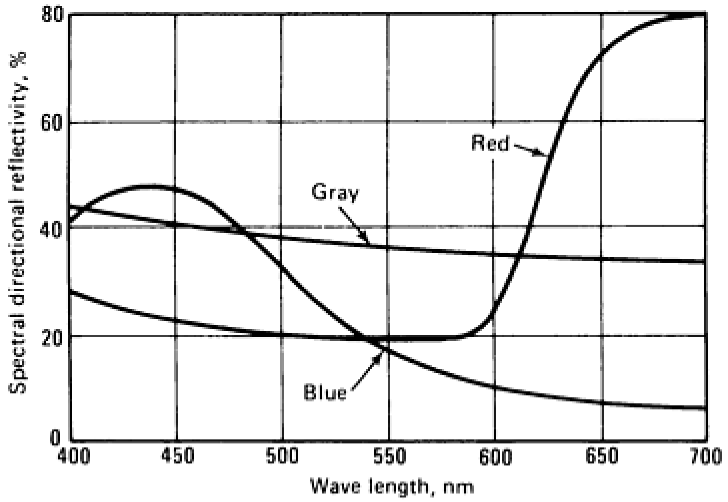


Fig. 13 Spectrophotometric curves of gray, red, and blue flat paints

Gloss. The procedure used for measuring gloss of a painted surface is by visual comparison with a known standard. By comparing the sharpness of an image reflected by a sample surface with the image reflected by a standard surface, even relatively small differences can be detected. However, because this procedure is based on human judgment and does not lend itself to the assignment of numerical values, instruments are often used for the measurement of gloss.

Photoelectric glossmeters measure gloss from various fixed angles. The viewing angle used most often is 60° from the vertical, but a viewing angle of 85° is more sensitive for low-gloss paints. The scale of glossmeters is calibrated from 0 to 100 with the higher numbers indicating higher gloss. Readings of 0 to 15 are generally considered flat, 15 to 80 are semigloss, and 80 to 100, high gloss. Instruments accurate to less than one unit are available. However, it is difficult to apply paint films to this degree of accuracy with any consistency, and a five-unit variation in gloss is acceptable.

Abrasion resistance of organic films may be determined by test methods using either falling sand or an abraser.

The falling-sand method uses a funnel-shaped hopper, which feeds sand to a vertical tube of 19 mm ($\frac{3}{4}$ in.) ID and 915 mm (36 in.) long. Sand is permitted to flow down the tube and impinge on the test panel, which is placed at a 45° angle beneath the tube. The test is complete when the sand abrades through the paint film, exposing a spot of bare metal 4 mm ($\frac{5}{32}$ in.) in diameter. The abrasion coefficient in liters per mil is found by dividing the volume (in liters) of sand used by thickness of the paint film (in mils).

The Taber Abraser method uses abrasive wheels of various grits, a method of applying loads of 250, 500, or 1000 g on the wheels, and a turntable to which the test panel can be clamped. This test can be used to obtain either the wear index (rate of wear) or the wear cycles (amount of wear) of the paint film.

Elongation properties of an applied organic film may be measured by bending a test panel over a tapered cone and measuring the length of the first continuous crack. The apparatus and test methods used are described in detail in ASTM D 522 ("Test Method for Elongation of Attached Organic Coatings with Conical Mandrel Apparatus").

Blistering. A water immersion test may be conducted to determine the resistance of organic films to failure when immersed in water in an accelerated manner. Distilled water is used to eliminate the influence of any chemicals contained in tap water. The test procedure is set forth in ASTM D 870 ("Practice for Testing Water Resistance of Coatings Using Water Immersion"). The method for evaluating degree of blistering is given in ASTM D 714 ("Method for Evaluating Degree of Blistering of Paints").

Environmental tests may be required to evaluate paint films in a particular service environment. For example, a detergent immersion test is used to determine the suitability of a particular paint for use on a home laundry machine. Tests

for resistance to acids, alkalis, industrial fumes, and other corrosive media may be established, with the criterion for failure being predetermined by agreement.

Salt spray (fog) tests (ASTM B 117) are arbitrary performance tests useful in establishing and maintaining certain standards of quality for the organic finish, particularly when correlated with field tests. For example, if spring clips, phosphate coated and painted with two coats of phenolic-based zinc chromate primer, can withstand 100 h in salt spray before failure, they may be expected to last 5 years or more in applications such as license plate brackets, molding retainers, and wire retainers on automobiles.

The test consists of placing parts or panels to be tested in a chamber in which a 5 wt% solution of sodium chloride is atomized. The exposure zone of the salt spray chamber must be maintained at 33 to 36 °C (92 to 97 °F).

Exterior-exposure tests may be conducted in accordance with ASTM D 1014 ("Method for Conducting Exterior Exposure Tests of Paints on Steel") to determine the resistance of a paint film to exposure. These tests are usually conducted in specified areas to obtain information on the influence of various atmospheres, such as industrial fumes, arid but intensely sunny climates, or salt air.

Artificial weathering tests using apparatus for exposing specimens to water and carbon-arc light are detailed in ASTM G 23, "Practice for Operating Light- and Water-Exposure Apparatus (Carbon-Arc Type) for Exposure of Nonmetallic Materials." Fluorescent UV-condensation type tests are described in G 53, "Recommended Practice for Operating Light- and Water-Exposure Apparatus (UV-Condensation Type) for Exposure of Nonmetallic Materials." These test methods simulate conditions of atmospheric exposure that act in a highly accelerated manner on the test panels. ASTM D 822, "Recommended Practice for Operating Light- and Water-Exposure Apparatus (Carbon-Arc Type) for Testing Paint, Varnish, Lacquer, and Related Products," is concerned with the variations in test conditions and the evaluation of test results. This test predicts the results of more time-consuming exterior-exposure tests with some degree of reliability.

Dry film thickness bears a direct relation to product cost and product performance. Film must be measured accurately for control of cost and performance. Several types of equipment and methods may be used for measuring the thickness of dry paint films on ferrous and nonferrous metals. Among these are dial micrometers, eddy current and magnetic thickness gages, and penetration and microscopic methods.

Dial micrometers are accurate depth-measuring devices with a calibrated dial and a pressure foot with a maximum diameter of 3.2 mm ($\frac{1}{8}$ in). The test panel is clamped firmly to a base. The pressure foot of the dial comparator is brought into contact with the paint film, and a reading is taken. Without disturbing the panel, the paint film is carefully removed from the panel where the reading was taken. The pressure foot is then brought into contact with the panel at the point of the previous reading. The difference in gage readings is the thickness of the paint film. This procedure, set forth in ASTM D 1005 ("Test Methods for Measurement of Dry-Film Thickness of Organic Coatings Using Micrometers") is not adaptable to paint films thinner than 13 μm (0.5 mil) or unusually soft films.

Eddy current thickness gages work on the principle of induced current changes in a high-frequency alternating current coil in a probe held in close proximity to a metal surface. Thickness of nonconductive films may be measured on any metal substrate.

Magnetic thickness gages are available in several types, the most useful being the portable gage using permanent magnets. These instruments measure the reduction of magnetic forces by a nonmagnetic coat of paint between a permanent magnet and the magnetic base to which the paint is applied. This reduction in magnetic force is calibrated in terms of paint-film thickness. This method is suitable for films from 13 μm to 6.3 mm (0.5 to 250 mils) thick. The instrument accuracy is generally 5% of the thickness measured.

The penetration method is practical where the paint film is applied to a surface that conducts electricity. This method measures the depth of travel of a small drill. The drill and the painted metal are connected electrically to a signal light that lights when the drill tip touches the metal panel. The drill is set with the tip just touching the surface of the paint film. The drill is then rotated and advanced slowly into the paint film until the signal light indicates contact. The measured distance of travel of the drill is a direct measurement of the paint film thickness. The accuracy of this method is approximately 10% of the film thickness. A portable scratch thickness gage also is available for determining the thickness of a dry paint film by the penetration method.

The microscopic method of measuring dry film thickness is the most accurate of the methods described. A cross section of the painted panel or part is mounted and polished. Using a calibrated eyepiece or screen, the magnified image of the paint film is measured. This method has the disadvantages of being a destructive test as well as requiring more specimen preparation than other methods. The accuracy of the microscopic method is limited only by the optical equipment used and the care exercised in preparing the specimen.

A portable microscopic method uses a cutting tip of a precise angle to slice through the coating. The exposed cross section is then measured microscopically. This instrument is accurate for thicknesses ranging from 2.5 to 1250 μm (0.1 to 50 mils). However, it is not suitable for brittle or rubbery coatings unless a power-driven cutting tip is used.

Wet Film Thickness. Inspection gages may be used to measure the thickness of wet paint films. With these gages, it is possible to determine whether the wet film is of adequate thickness to develop the desired dry film thickness.

Hardness of a paint film may be approximately determined by scratching it with pencils of different hardness sharpened in a mechanical sharpener. This test does not reveal a specific hardness, but enables one paint film to be compared either to another paint film or to an acceptable standard film. The test is run to determine the softest lead that can penetrate the surface of the paint film. If only one manufacturer's pencils are used, more consistent comparisons are obtained. The disadvantage of this test is the possible variability of the force exerted by the operator. It is a useful test, however, when one skilled operator is making empirical comparisons of two panels side by side.

Coating hardness can also be measured by using a spring-loaded penetrating needle instrument. The depth of penetration, or pressure required for penetration, provides an indication of coating hardness. Instruments of this type are available for a range of coating types, from soft elastomeric coatings to hard metallic ones.

Adhesion of the paint film can be measured by a test described in ASTM D 3359, Method A or B. Method A involves cutting an X scribe through the coating to the substrate; Method B requires a cross-hatch cutting pattern. After the cut is made, a special tape is pressed over the cut area and then briskly removed. Adhesion is determined by the amount of delamination that occurs.

Adhesion testing can be simplified and standardized by using commercially available instruments, which have a solid cutting head that makes several parallel lines with one pass. Cutting guides are also available with various spacings to enable the user to cut a precise cross-hatch pattern with a sharp utility knife. The spacing of scribed lines is usually correlated to total film thickness, with thicker films requiring spacing of cuts to be wider.

Impact resistance may be determined by the use of an instrument that consists of a 25 mm (1 in.) diam impact rod that tapers to an impact nose with a 6.4 mm ($\frac{1}{4}$ in.) spherical radius, a tube 26 mm ($\frac{1}{32}$ in.) inside diameter (ID) that serves to guide the impact rod in its downward fall, a base plate with a 13 mm ($\frac{1}{2}$ in.) diam hole through it, and a bracket to support the tube and position the base plate. The tube is graduated in inch-pounds and is slotted, so that a pin, protruding from the impact rod, can be used to raise the rod to a specific inch-pound location. The base is positioned so that its 13 mm ($\frac{1}{2}$ in.) diam hole can engage the nose of the rod at the bottom of its fall.

To test the impact characteristics of a paint film, a test panel, or an actual part, if made of sheet metal, is placed over the base, and the impact rod is permitted to fall from a height that generates the desired force. Direct impact is obtained by facing the paint film toward the falling rod; reverse impact is obtained by facing the paint film away from the rod. The impact makes a 6.4 mm ($\frac{1}{4}$ in.) spherically radiused impression in the test panel. Results are measured by the force the paint film can withstand without cracking, chipping, or flaking.

The Gravelometer (Fig. 14) is another device that is used to compare impact resistance of organic films against an accepted standard. Using air at 70 kPa (10 psi), this device propels 14 kg (30 lb) of steel shot a distance of 685 mm (27 in.) against a painted area 125 by 150 mm (5 by 6 in.). The amount of paint that is retained on the panel is indicative of the impact resistance and the adhesion of the paint film. This is a more severe test than the rod impact tester, but the Gravelometer is more revealing, because of the greater area involved. The SAE J400 test uses graded gravel instead of steel shot and is gaining wide acceptance as a standard test.

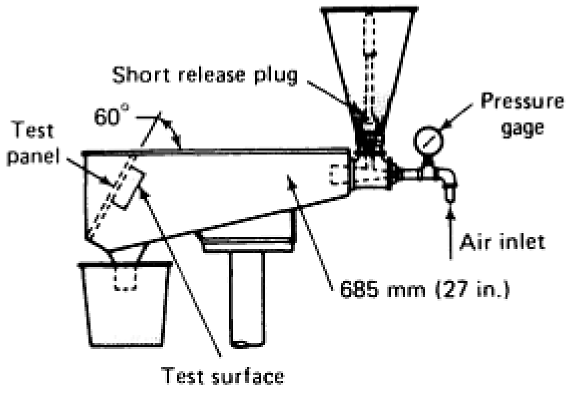


Fig. 14 Gravelometer. Used to measure impact resistance of paint films

Causes of Paint Film Defects

Defective paint films are usually the result of either improper preparation of the paint or substrate surface, or lack of control of processing variables. Paint film defects attributable to improper baking procedures are listed in Table 7; other paint film defects and frequent causes are listed in Table 9.

Table 9 Common causes of paint film defects

Defect	Cause	Susceptible application methods
Poor adhesion (peeling, flaking, poor bonding)	Paint applied over grease, oil, water, alkali residues, or other foreign materials on surface	Dip, flow, roller, spray
	Finish coat applied over incompletely dried undercoat	Dip, flow, roller, spray
	Paint applied to surface that is too hot (above 71 °C, or 160 °F) or too cold (below 16 °C, or 60 °F) or too cold (below 16 °C, or 60 °F)	Dip, flow, spray
	Film too thick	Dip, flow, roller, spray
Beading	Solvent vaporizes too rapidly	Dip, flow
	Parts drawn from paint too rapidly	Dip
Blistering (pimpling, bubbling, pinholing, pitting)	Moisture entrapped on surface of substrate	Dip, flow, roller, spray
	Air entrapment	. . .
	Improper solvents	Dip, flow, roller,

		spray
	Wide temperature differential between paint and work	Dip, flow, roller, spray
	Insufficient drying time between coats; solvent trapped in undercoat escapes through partially dried finish coat	Dip, flow, roller, spray
	Excessive air pressure and dry spraying of undercoat, causing porosity and air pockets under finish coat	Spray
	Water in air line	Spray
	Excess paint film, entrapping solvents	. . .
Brittleness	Improper composition of paint	Dip, flow, roller, spray
Checking (alligatoring, crazing, crowfooting, hairlining)	Application of finish coat over incompletely dried undercoat	Dip, flow, roller, spray
	Insufficient mixing of material to blend all pigment	Dip, flow, roller, spray
Color separation	Incomplete mixing of paint before application	Dip, flow, roller, spray
	Poor agitation during application	Dip, roller, spray
Cracking (shrinking, splitting)	Paint not thoroughly mixed before application	Dip, flow, roller, spray
	Surface not completely clean	Dip, flow, roller, spray
	Insufficient thinner	Dip, flow, roller, spray
	Undercoat too thick	Dip, flow, roller, spray
	Surfaces too hot or too cold	Dip, flow, spray
	Oil or water in air line	Spray
Cratering	Surface air bubbles	

	Silicone contamination	Dip, flow, spray
Slow drying	Application over grease, oil, or fingerprints	Dip, flow, roller, spray
	Application of too much paint	Dip, flow, roller, spray
	Poor ventilation, air drying only	Dip, flow, roller, spray
	Drying atmosphere too cold or too humid, air drying only	Dip, flow, roller, spray
	Oil in air line	Spray
	Solvent vaporizes too slowly	Dip, flow, roller, spray
Dusty or gritty appearance (dry spray)	Insufficient solvent	Spray
	Solvent vaporizes too rapidly	Spray
	Excessive air pressure	Spray
	Spray gun too far (over 305 mm, or 12 in.) from work	Spray
	Excess air movement in spray booth	Spray
	Spray pattern too wide,	. . .
	Airborne particles reach substrate	. . .
Edge pull-away	Solvent vaporizes too slowly	Dip, flow
	Too much solvent	Dip, flow
Poor flow-out	Viscosity of paint too high	Dip, flow, roller, spray
	Temperature of paint too low	Dip, flow, roller
	Solvent vaporizes too rapidly	Dip, flow, roller,

		spray
	Temperature of surface too low	Spray
Poor gloss	Paint film too thin	Dip, flow, roller, spray
	Application over incompletely dried undercoat	Dip, flow, roller, spray
	Drying atmosphere too cold or too humid, air drying only	Drip, flow, roller, spray
	Application over alkali residues	Dip, flow, roller, spray
	Too much solvent vapor in drying oven	Dip, flow, roller, spray
	Improper solvent	. . .
	Too much heat in cure cycle	Roller
Poor hiding	Pigment settling because of poor agitation	Dip, flow, roller, spray
	Solvent vaporizes too slowly	Dip, flow
	Too much solvent	Dip, flow, roller
	Withdrawal from paint too slow	Dip
	Vapor concentration too high	Dip, flow
Nonuniform film thickness (or uncoated areas)	Solvent vaporizes too slowly	Dip, flow
	Nonuniform roll pressure; roll out-of-round	Roller
	Improper hanging of panels	Dip, flow
	Paints not lapping properly when spraying	. . .
Orange peel	Excessive film thickness	Dip, flow, roller, spray

	Surface temperature too hot or too cold	Flow, dip, spray
	Improper adjustment of spray gun pattern	Spray
	Air pressure too high	Spray
	Solvent vaporizes too rapidly	Dip, flow, roller, spray
	Improper applicator/metering roll speeds	Roller
Undesirable pattern	Swelling of roll	Roller
	Roll improperly ground	Roller
	Foreign material on roll	Roller
	Poor spray gun technique	Spray
Runs (curtains, sags)	Too much solvent	Dip, flow, spray
	Paint surface or drying atmosphere too hot or too cold	Dip, flow, spray
	Solvent vaporizes too slowly	Dip, flow, spray
	Excessive paint applied	Dip, flow, spray
	Poor spray gun technique	Spray
	Distorted spray gun pattern	Spray
	Air pressure too low	Spray
	Withdrawal from paint too rapid	Dip
	Automatic equipment is jerky	Dip, flow
	Drafts	Dip
	Improper racking	Dip, flow, spray

Streaking	Metal too hot or too cold	Dip, flow, spray
	Poor spray technique; insufficient overlap between passes, should be 50%	Spray
	Distorted spray pattern	Spray
Water spotting	Rain or dew settling on finish	Dip, flow, roller, spray
	Washing before paint is completely dry	Dip, flow, roller, spray
	Uneven quenching of hot surface	Roller
Wrinkling	Excessive film thickness	Dip, flow, roller, spray
	Abnormally hot or humid drying environment, air drying only	Dip, flow, roller, spray

Calculating Coating Coverage and Costs

The cost of the applied coating is directly related to the cost per gallon of coating material, the application efficiency, the required thickness of film, and the spreading rate. To calculate the gallons needed and cost for coating an object the following information is needed.

- Volume of solids in coating
- Spreading rate of coating at application viscosity
- Dry film thickness required
- Area to be coated
- Application efficiency
- Cost per gallon

Volume solids content of the coating is the volume percentage of vehicle solids and pigments in a gallon of paint. The remaining volume percentage is the solvent that evaporates in the drying or curing process. The volume solids should not be given by the supplier and should not be confused with weight solids.

Spreading Rate. One U.S. gallon of any liquid is equivalent to 3785 cm^3 (231 $in.^3$). Thus, 100% volume solids liquid can cover 149 m^2 (1604 ft^2) at a thickness of 25 μm (1.0 mil). This figure is derived from the following formula:

$$\textit{Spreading}\ \text{rate}=\frac{\text{in}^3\text{/gal x vol solids}}{\text{in}^2\text{.ft}^2\text{ x in}}$$

Using this formula, the spreading rate for any liquid coating can be determined. For example, if the volume solids of a product is 40% at application viscosity and a 38 μm (1.5 mil) dry film is required, the area covered by 1 gal of the paint is approximately 39.7 m^2 (427 ft^2) determined as follows:

$$\frac{231\ x\ 0,40}{144\ x\ 0.0015} = 427\ ft^2/gal(spreading\ \text{rate})$$

Table 10 is an approximation of spreading rates at various volume solids and dry film thicknesses. Because cost per gallon is determined at application viscosity, any solvent, thinner, or reducer added to the paint must be included in the final cost as well as the volume solids determined at application viscosity. The cost per gallon is equal to the cost per gallon of paint plus the cost per gallon of thinner divided by the total number of gallons.

Table 10 Theoretical spreading rate for coatings

Volume solids, %	13 µm (0.5 mil)		25 µm (1.0 mil)		38 µm (1.5 mils)		51 µm (2.0 mils)		64 µm (2.5 mils)		76 µm (3.0 mils)	
	m^2/L	ft^2/gal	m^2/L	ft^2/gal	m^2/L	ft^2/gal	m^2/L	ft^2/gal	m^2/L	ft^2/gal	m^2/L	ft^2/gal
10	6.4	320	3.2	160	2.14	107	1.6	80	1.3	64	1.1	54
20	12.8	640	6.4	320	4.26	213	3.2	160	2.56	128	2.14	107
30	19.2	962	9.62	481	6.4	320	4.8	240	3.94	197	3.2	160
40	25.68	1284	12.8	641	8.54	427	6.42	321	5.14	257	4.28	214
50	32.1	1605	16.0	802	10.7	535	8.02	401	6.42	321	5.34	267
60	38.52	1926	19.2	962	12.8	641	9.62	481	7.7	385	6.42	321
70	44.8	2240	22.4	1120	14.9	747	11.2	560	8.96	448	7.46	373
80	51.2	2560	25.6	1280	17.1	853	12.8	640	10.2	512	8.54	427
90	57.6	2880	28.8	1440	19.2	960	14.4	720	11.5	576	9.6	480

Application Efficiency. In addition to cost per gallon at application viscosity, the percent of the coating deposited on the substrate by the application method must also be considered. Table 11 lists the average efficiency of various types of application methods. The cost of paint for a part can be calculated using the following formula and the data in Tables 10 and 11.

$$Cost\ \text{per square foot} = \frac{\text{Cost per gal at application viscosity}}{\text{Spreading rate x application efficiency}}$$

Table 11 Average application efficiency of painting methods

Method	Efficiency, %

Conventional spray,	
Air atomized	50
Airless atomized	65
Electrostatic spray,	
Air atomized	70
Airless atomized	80
Centrifugally atomized	90
Dip, flow, curtain coat	80
Coil and roller coat	90
Electrodeposition	90
Powder coat	90

Safety and Environmental Precautions

The 1990 Amendments to the Clean Air Act (CAAA) and the promulgation of several Constructional Industry Standards by the Occupational Safety and Health Act administered through OSHA have had a major impact on the blasting and coating industries. Several of these regulatory initiatives are of special importance to industries that use paint and other organic coatings.

Volatile Organic Compounds (VOCs). Regulatory activity required under the 1990 CAAA continues to dominate the protective coatings industry. Many items are under negotiation with the Joint Industry, Government and Regulatory Negotiation Committee. Several items in the forefront of development and negotiation include

- A national volatile organic compounds rule on architectural and industrial maintenance (AIM) coating applied to stationary sources is being developed. Under a tentative agreement, industrial maintenance coating would be restricted to a maximum VOC level of 350 g/L as applied.
- Tentative VOC levels have also been established for around 50 other categories and subcategories of coating.
- The Regulatory Negotiation Committee has also tentatively agreed to reduce current average VOC emissions (CAVE), which are based on total corporate product line levels compared to 1990 levels. Reduction is scheduled for 25% by 1996, 35% by 2000, and 45% by 2003.
- The CAAA directs the EPA to develop control technique guidelines (CTGs) on shipbuilding and shipyard repair coating operations.
- Under the National Emission Standards for Hazardous Air Pollutants (NESHAP), the EPA under the CAAA must create a national standard regarding the control and emissions of 189 hazardous air pollutants.
- The CAAA mandates a review of the current ozone standard by the EPA.

- EPA has formally revised its Method 24 for measuring VOCs in coatings to make it applicable for use with multicomponent coatings. The method is now consistent with ASTM D 2369 and ASTM D 3960.

OSHA Cadmium Exposure Regulations. In September 1992, OSHA published a Cadmium Exposure in Construction Standard (29 CFR 1926.63) to address occupational exposure to cadmium during construction activities.

In 1993, OSHA published its final rule on permit-required confined space entry (29 CFR 1910.146). It established strict provisions for facility owner and contractors involved in confined space operations. This standard was printed in the Federal Register in January 1993 and became effective 15 April 1993.

OSHA Lead Exposure Regulations. OSHA published its Interim Final Rule on Lead Exposure in Construction (29 CFR 1926.62) in May 1993 for the protection of construction workers from overexposure of airborne lead. The Rule went into full effect in August 1993. The Rule lowers the permissible exposure limit (PEL) to 50 μg/m^3, incorporates many provisions of the General Industry Standard, and establishes "trigger tasks" to establish presumed exposure levels.

Published Standards. All aspects of the OSHA and EPA VOC requirements cannot be covered within this article. The following provide greater detail:

- Interim Final Rule on Lead Exposure in Construction (29 CFR 1926.62)
- Confined space entry (29 CFR 1910.146)
- Rule on Cadmium Exposure in Construction (29 CFR 1926.63)
- The Clean Air Act (42 USC 7401)
- The Clean Air Act Amendments of 1990

Individuals and organizations involved in industrial painting and coating should maintain contact with OSHA, EPA, and state and local regulatory agencies in order to keep abreast of current, revised, and pending regulations.

Painting of Structural Steel

Painting of structural steel is done to protect the environmental area affected by the structure being coated, to preserve manufacturing or plant functionality, and to provide aesthetic appeal. Painted structures may have to withstand high-operating temperatures, adverse weather conditions, and marine, industrial (urban) and rural exposure as well as chemical exposure. All these conditions dictate the frequency of coating application, selection of the method of surface preparation, and coating system selected.

As discussed previously in the section "Safety and Environmental Precautions" in this article, the introduction of restrictive regulations has had an impact on the use of painting coating systems. For example, the federal Environmental Protection Agency has limited the amount of volatile organic compounds that can be emitted from painting facilities. For the protection of the applicator, the use of active pigments in primers, such as lead compounds and chromates, has been listed by the Occupational Safety and Health Administration.

Composition and Characteristics of Organic Coatings for Structural Steel

Coatings have three components: the volatile vehicle (solvent or dispersant), the nonvolatile vehicle (resin), and the pigment. The volatile vehicle is the portion of the coating that allows the coating to be spread or applied. This component can be ketone, ester alcohol, petroleum solvent, water, or a combination of these materials. Water, for example, acts as the dispersant in water-reducible coating systems.

The pigment portion provides opacity and color, as well as viscosity control and reduced water permeability. Other pigments also provide corrosion resistance. Materials that are considered pigments include: driers, plasticizers, ultraviolet light absorbers, emulsifiers, and dispersing agents. These materials are added to modify coating properties as required.

A number of resins are used in the preparation of coatings. These include plant-derived oleoresins (linseed oil, safflower oil, and tung oil); fish oils (menhaden, sardine, and pilchard); lacquers (nitrocellulose, cellulose acetate, ethyl cellulose,

and acrylic polymers); and synthetic resins (alkyds, aminoplast-alkyd blends, phenolic, epoxy, acrylic, vinyl, urethane, silicone, and chlorinated rubber). Table 12 provides information on some frequently used resins.

Table 12 Characteristics of the resins for coating structural steel

Resin	**Curing method**	**Solvents**	**Chemical and weather resistance**					**Remarks**
			Acid	**Alkali**	**Solvent**	**Water**	**Weather**	
Raw and boiled linseed oil	Air drying Oxidative polymerization	Aliphatic hydrocarbons	Fair	Poor	Poor	Fair	Fair	Vehicle for corrosion inhibitive primers for wire-brushed steel, slow drying
Oleoresinous varnishes	Air drying Condensation and/or oxidative polymerization	Aliphatic hydrocarbons and/or aromatic hydrocarbons	Fair	Poor	Poor	Good	Good	Pale-colored finishes that yellow on exposure
Alkyds	Air drying Oxidation Polymerization	Aliphatic hydrocarbons	Fair	Poor	Poor	Fair	Very good	Long oil alkyds are generally used, although these alkyds may be blended with medium oil alkyds
Modified alkyds	Air drying Oxidative polymerization	Dependent on modification A wide variety of solvents	Fair	Fair	Fair	Good	Very good	. . .
Epoxy, aliphatic amine or polyamide blends	Air dryingAddition polymerization	Blends rich in high ketones	Good	Very good	Very good	Very good	Good	Two-component compositions
Epoxy, fatty acid esters	Air drying Oxidative polymerization	Aliphatic and/or aromatic hydrocarbons	Fair	Fair	Poor	Fair to good	Fair	. . .
Polyester urethane	Addition polymerization	Blend rich in ketones and esters	Fair to good	Good	Very good	Fair to good	Very good	Two-component compositions
Vinyl resins	Air drying solvent evaporation	Blends usually rich in ketones	Very good	Very good	Poor	Very good	Good	Fire hazard, unless high solids compositions are used
Chlorinated rubber	Air drying solvent evaporation	Aromatic hydrocarbons	Good	Good	Poor	Very good	Good	Very poor heat resistance
Acrylic resins (water	Water evaporation and coalescing	Water dispersant	Fair	Fair	Very good	Fair	Good	Used as a maintenance coating system. Porosity of film results

emulsion)								in poor chemical and weather resistance

Linseed oil is the most important drying oil used in oil varnishes and in the preparation of alkyd resins because of its ready availability and relatively low cost. The main advantages of linseed oil are good surface wetting properties, easy preparation of surface, good application properties, and ease in coating preparation. Raw linseed has disadvantages as well, including very slow drying, lack of gloss when formulated into coatings, and poor leveling qualities.

Linseed oil is composed of a mixture of linoleic and linolenic triglycerides. Both of these acids contain a chain of 17 hydrocarbon members with an acid radical and 2 or 3 double-bonded positions. On drying (oxidizing) the double bonds cross link with other molecules to form a high molecular weight film.

Heat-treated oils fall into three categories: boiled oils, stand oils, and blown oils. Boiled oils are prepared by heating linseed oils in the presence of metal driers such as lead naphthenate and cobalt naphthenate. Boiled linseed oils have a higher viscosity and better drying properties because of higher molecular weight and more complex molecular structure. Boiled linseed oil is used in oil-based primers and in conjunction with oil varnishes and undercoats.

Stand oils have an even higher viscosity than boiled linseed oil. These oils are prepared by heat-polymerizing linseed oil alone or in a mixture with tung oil. Stand oils are mostly used in combination with oil varnishes and alkyd resins to improve application properties and increase total oil.

Blown oils are partially oxidized in addition to being polymerized. As the name implies, air is blown through the heated oil, which results in a poorly drying product. Generally, the blown oil is used as a plasticizer.

Oleoresinous varnishes are varnishes and paint media prepared from drying oils and natural or synthetic resins, such as rosins, gum congo, rosin-modified phenolics, and 100% oil-soluble phenolics. Oleoresinous varnishes are used to improve drying and film-forming properties.

The phenolic varnishes require surface preparations to provide at least a commercial blast-cleaned surface (SSPC-SP-6). (Table 13 lists Steel Structure Painting Council designations for surface preparations. Additional information is available in the section "Surface Preparation" in this article.) Tung-oil phenolic resin has very good water resistance and is mildly acid- and alkali-resistant.

Table 13 Steel Structures Painting Council (SSPC) designations of surface preparation methods for painted coatings

SSPC designation	Method of surface preparation	NACE designation	Equipment and materials	Remarks
SP1	Solvent cleaning	. . .	Mineral spirits, chlorinated solvents, coal tar solvents, using tack rags or dip tanks	For the removal of grease, oil, or other soluble materials before removing mill scale, rust, and coatings by other methods. Alkaline cleaners saponify oils and greases, but these cleaners must be neutralized with 0.1 wt% chromic acid, sodium dichromate, or potassium dichromate
SP2	Hand tool cleaning	. . .	Hand scrapers	Hand tool cleaning should be limited to removing loose material for materials for maintenance and normal atmospheric exposure; coatings with good wetting properties are brush applied
SP3	Power tool cleaning	. . .	Power wire brushes, grinders, sanders, impact tools, needle guns	For the removal of loose rust, loose mill scale, and loose paint by power tool chipping, descaling, sanding, wire brushing, and grinding without excessive roughing that causes ridges, burrs, or burnishing. Used when primer is to be brush applied

SP4	Flame cleaning	[a]	. . .	Removal of contaminants by high-velocity oxyacetylene flame burners. Usually followed by wire brushing
SP5	White metal blast	1	Abrasive blasting	Removal of 100% of oil, grease, dirt, rust, mill scale, and paint. Cleaning rate 9.3 m^2/h (100 ft^2/h), using 7.94 mm ($\frac{5}{16}$ in.) nozzle with 690 kPa (100 psig) at nozzle. Because of atmospheric contamination, maintaining this degree of cleanliness before primer application is difficult
SP6	Commercial blast	3	Abrasive blasting	Removal of 67% of oil, grease, dirt, rust, mill scale, and paint. Cleaning rate of 34 m^2/h (370 ft^2/h), using 7.94 mm ($\frac{5}{16}$ in.) nozzle with 690 kPa (100 psig) at nozzle. Used for general-purpose blast cleaning to remove all detrimental matter from the surface, but leaves staining from rust or mill scale
SP7	Brush-off blast cleaning	4	Abrasive blasting	All loose mill scale and rust are removed, with tight mill scale, paint and minor amounts of rust and other foreign matter remaining. The remaining rust is an integral part of the surface. This level of surface preparation is used for mild exposure and is suitable where a temperature change of less than 11 °C/h (20 °F/h) can be anticipated. Cleaning rate of 81 m^2/h (870 ft^2/h) using 7.94 mm ($\frac{5}{16}$ in.) nozzle
SP8	Pickling	. . .	Hydrochloric acid, sulfuric acid with inhibitors, or phosphoric acid with a final phosphate treatment	A shop method of surface preparation for removal of rust and mill scale from structural shapes, beams, and plates where there are few pockets or crevices to trap acid. Excess acid must be rinsed off with water, and painting is required as soon as possible to prevent recontamination of the surface
SP9	Weathering	[b]	. . .	Although mill scale is weathered away, this process is detrimental because surface contamination is more difficult to remove when weathered
SP10	Near-white blast	2	Abrasive blasting	Removal of 95% of oil, grease, dirt, rust, mill scale, and paint. A cost savings of 25% can be realized on average where this level of cleanliness can be tolerated. Shadows, streaks, or discolorations are distributed over the surface, but not concentrated in any area or particular spot. Cleaning rate 16 m^2/h (175 ft^2/h) using a 7.94 mm ($\frac{5}{16}$ in.) nozzle and 690 kPa (100 psig) at nozzle
	Water blasting	. . .	Inhibited water at pressures of 6900 to 69,000 kPa (1000 to 10,000 psig) used	Removal is slow and the degree of cleaning must be specified. High pressures may cause damage to substrate or structures
SP11	Power tool cleaning to bare metal	. . .	Same as SP3	Removal of all mill scale, rust, old paint, and oil, exposing bare metal. The resulting surface must be roughened as necessary to obtain a 25 μm (1 mil) surface profile

(a) Discontinued as of Jan 1982.

(b) Discontinued in 1971

Alkyd resins are produced by reacting a polyhydric alcohol with a monobasic and polybasic fatty acid to yield an ester. The more frequently used alcohols include ethylene glycol, glycerol, and pentaerythritol. Phthalic anhydride is the acid used most often because of the plentiful supply of the petrochemical orthoxylene from which it is made. Isophthalic acid is used in primers or where a harder, more weather-resistant coating is desired. Unsaturated dibasic acids, such as maleic anhydride, are used to provide higher molecular weight polymers.

For coating structural steel, air-drying alkyd resins are most frequently used. The films are formed by the oxidation of the drying oils these alkyds contain. The fatty acids are obtained from linseed, soya, sunflower, cottonseed, safflower, tung oil, and fish oils, in the form of a glycerol triester. These triesters, or the oils chemically separated, are used to prepare primers, intermediate coatings, and finishing coatings. The shorter (more reactive) the acid oil, the more brittle and less forgiving the primer. Short oil resins require more meticulous surface preparation, and they dry more quickly. Soya oil is used with other faster drying oils to produce non-yellowing white and pastel color compositions.

When additional hardness, chemical resistance, and durability may be required, alkyd resins are modified with vinyl, acrylic, silicone, and urethane and other adducts to the acid oil constituent. The resins resulting from these modifications are higher in molecular weight than the original alkyd and may require oxygenated solvents such as ketones.

Epoxy resins are long-chain polyhydric alcohols with epoxy end groups. The alcohol and epoxy groupings are available for reaction with the aliphatic polyamines, amine adducts, and polyamides to provide film formers with excellent chemical resistance at room temperature. The epoxy resins may be separated from their curing adducts such as polyamines and polyamides, as two-component coating systems. These components are mixed in the required proportions immediately before use. Epoxy coatings are used where chemical resistance is required. A surface preparation of SSPC-SP-6 or better is required.

Polyurethane resins are characterized by having isocyanate groupings at the end of the molecular chain, acting as the reactive groups that combine with moisture or a reactive polyol such as glycerol, glycol, phenols, alkyds, and many others. The latter resins are called two-component polyurethane coatings, and the former are classified as single-package for moisture-curing coatings. Two-pack urethane resins provide a chemical-resistant film of excellent quality and high gloss and are used to coat structural steel as a lining coating for petroleum storage tanks. Moisture-cured polyurethane coatings are aromatic urethanes that are less chemically resistant than the two-component systems.

Vinyl coatings, for most purposes, are prepared from polyvinyl formal, polyvinyl acetal, and polyvinyl butyral.

Vinyl resin paints are inert and are used for coatings applied to tanks, pipelines, petroleum equipment, offshore drilling rigs, railroad hopper cars, dairy and brewery equipment, and tanks that require acid and alkali resistance. Vinyl films are abrasion resistant, with low water permeability, high dielectric resistance, and high-speed drying capabilities. Vinyl paints require steel to be cleaned to an SSPC-SP10 or better, a near-white abrasive blast cleaning. Vinyl paints are ideal for immersion in fresh water and brackish water, but do not impart the same degree of protection in salt water, where coal tar or epoxy coatings would be preferred.

Chlorinated rubber resins are prepared by the chlorination of isoprene in solution to approximately 65 wt% chlorine. Natural rubber is used as the raw material, and when combined with chlorine, it results in a trichloro- and a tetrachloro-polymeric mixture. The resulting films provide excellent corrosion resistance for ferrous metals in marine environments, strong acids, and weak alkalis, but films chalk when exposed to sunlight. For a paint to be designated as a chlorinated rubber paint, it should contain not less than 60 wt% chlorinated rubber in the vehicle solids.

Acrylic resins are formed by the esterification of acrylic or methacrylic acids with alcohols. The major homopolymers are methyl, ethyl, butyl and isobutyl methacrylate, and methyl, ethyl and butyl acrylate. Lacquers and enamels, based on acrylic resins, have been developed for both ferrous and nonferrous metals. Latex emulsions are used in home painting.

Types of Paints for Structural Steel

Paints are generally described by their resin (binder) designation and sometimes their pigment composition, such as red lead alkyd or epoxy polyamide. Paints may be applied in single or multiple layers. When multiple layers are used, each layer has a special purpose.

The primer is the first layer to be applied. The main purpose of the primer is to wet the surface of the substrate and to provide adhesion and corrosion protection. Pigments such as red lead, zinc chromate, or zinc molybdate are active corrosion inhibitors. Titanium dioxide, chromium oxide, and ferric oxide pigments--while important pigments for color hiding, strength, and barrier reinforcement--are not corrosion inhibitors.

Intermediate coatings are sometimes applied to improve adhesion and impact strength between primer and topcoat and to provide a barrier layer between coats, as well as surfacers and sealers. Intermediate film also inhibits light penetration, reducing actinic degradation.

The final coating is described as the top or finish coat enamel, which provides environmental and chemical resistance. Also, the finish coat provides aesthetics of color and gloss, as well as film characteristics such as hardness and abrasion resistance. Table 14 shows the compatibility of paints applied as multiple layers.

Table 14 Paint compatibility

Primer or weathered paint	Topcoat												
	Solvent thinned				Lacquer			Water thinned (latex)		Chemically reactive			
	Oleoresinous	Alkyd	Silicone alkyd	Phenolic oleoresinous	Vinyl	Chlorinated rubber	Styrene-butadiene/ styrene-acrylate	Acrylic	Polyvinyl acetate	Epoxy	Coal tar epoxy	Polyester	Urethane
Solvent thinned													
Oleoresinous	C	C	C	C	NR	NR	NR	C	C	NR	NR	NR	NR
Alkyd	C	C	C	C	NR	NR	NR	C	C	NR	NR	NR	NR
Silicone alkyd	C	C	C	C	NR	NR	NR	C	C	NR	NR	NR	NR
Phenolic oleoresinous	C	C	C	C	NR	NR	NR	C	C	NR	NR	NR	NR
Lacquer													
Vinyl	CT	NR	NR	NR	CT	CT	CT	CT	CT	NR	NR	NR	NR
Chlorinated rubber	CT	NR	NR	NR	CT	CT	NR	CT	CT	NR	NR	NR	NR
Styrene-butadiene/styrene-	CT	CT	CT	NR	CT	NR	CT	CT	CT	NR	NR	NR	NR

Bituminous	NR	NR	NR	NR	CT	CT	CT	CT	NR	NR	NR	NR	NR
Water thinned (latex)													
Acrylic	C	C	C	NR	CT	CT	CT	CT	CT	NR	NR	NR	NR
Polyvinyl acetate	C	C	C	NR	CT	CT	CT	CT	CT	NR	NR	NR	NR
Chemically reactive													
Catalyzed epoxy	NR	NR	NR	NR	CT	CT	CT	CT	CT	CT	CT	CT	CT
Coal tar epoxy	NR	NR	NR	NR	NR	NR	NR	NR	NR	CT	CT	NR	NR
Zinc-rich epoxy	NR	NR	NR	NR	CT	CT	CT	C	NR	CT	CT	NR	NR
Polyester	NR	NR	NR	NR	CT	CT	CT	CT	CT	CT	CT	CT	CT
Inorganic zinc	NR	NR	NR	NR	CT	CT	CT	CT	NR	C	C	NR	CT
Cementitious	NR	NR	NR	NR	CT	CT	CT	CT	NR	C	C	CT	C
Urethane	NR	NR	NR	NR	NR	CT	CT	CT	CT	NR	CT	C	CT

Note: C: normally compatible. CT: compatible with special surface preparation and/or application. NR: not recommended because of known or suspected problems. Certain combinations

Enamels may be cured by air drying or oven baking. Air dry enamels are cured essentially by a combination of solvent evaporation and oxidation. Baking enamels incorporate catalysts and cross-linking agents that require heat for polymerization. Coatings may be classified according to curing method, as is shown in Table 15. Each generic type is discussed separately in the following sections.

Table 15 Classification of coatings according to methods of cure

Method of curing	**Generic type**	**Comments**
Air oxidation of drying oils (solvent thinned)	Oleoresinous	Good wetting, slow curing, soft film recommended in normal environments only
	Alkyd	Good wetting and appearance, poor in alkaline or solvent environments
	Silicone alkyd	Improved durability, gloss, and chemical resistance compared to alkyds, but still poor in alkaline or solvent environments
	Phenolic oleoresinous	Good resistance to abrasion and mild chemical environments; however, dark color of binder precludes use in white or light tints
Solvent evaporation (lacquers)	Vinyl (polyvinyl chloride-acetate)	Good water resistance, limited solvent resistance, poor adhesion unless surface has been properly prepared with abrasive blast cleaning
	Chlorinated rubber	Good water resistance, limited solvent resistance
	Styrene-butadiene, styrene-acrylate	Good water resistance, limited solvent resistance
	Coal tar	Soft, black only; of limited use, mostly on mechanically cleaned surfaces
	Polyvinyl-butyral	Exclusively used in pretreatment (wash) primers
Evaporation of water (latex, emulsion, water-thinned)	Acrylic	Recommended in normal environments only
Chemical reaction	Epoxy	Good water, chemical, abrasion, and solvent resistance, chalks freely on exterior exposure, difficult to topcoat
	Coal tar epoxy	Improved water resistance and lower raw material costs compared to epoxies, black only. Difficult to topcoat
	Polyester	Frequently used with glass fibers to give abrasion- and water-resistant coating. Only fair alkali resistance
	Zinc inorganic	Requires adequate surface preparation (SSPC No. 10, Near White Blast Cleaning); adequate curing time required; excellent corrosion protection; good abrasion, solvent, and high-temperature resistance; must be topcoated in aggressive environments; reacts with alkali-sensitive topcoats

	Cementitious	Inexpensive, requires adequate curing for best performance, and tends to chalk with aging, poor corrosion resistance
	Urethane	Good water, chemical, abrasion, and solvent resistance. Difficult to topcoat

Air-Oxidizing Coatings. Oleoresinous (oil-drying) coatings were among the earliest to be used to provide protection from environmental deterioration. These coatings contained natural vegetable or fish oils that cure to a solid by reacting with oxygen from the air. This usually slow reaction is accelerated by using driers in the coating formulation. Paints using these oils have excellent wetting properties and are used on poorly prepared surfaces such as SSPC-2 or 3.

Alkyd coatings are developed by reacting drying oils with phthalic anhydride or other polybasic acids that increase durability and hardness. Alkyd coatings are currently the most widely used coatings, because of their good wetting, flexibility, curing, and application properties. Alkyd coatings are among the most suitable for general atmospheric exposure.

Silicone alkyd coatings have a silicone resin reacted with the alkyd resin to form the resin binder. When compared to alkyd coatings, silicone alkyd coatings have superior chemical resistance, color retention, and gloss.

Phenolic coatings are prepared using resin binders that incorporate phenol-formaldehyde in dry oils. The use of phenol-formaldehyde improves water resistance, but lowers exterior durability.

Epoxy resins combined with drying oils improve the corrosion resistance of epoxy ester coatings. Epoxy ester coatings are single-component coatings and should not be confused with two-component chemically reacting epoxies.

Lacquers are coatings that dry by solvent evaporation. The major resins used are acrylics, cellulosics, and vinyl. Lacquer coatings contain dissolved solid resins that form a continuous hard film after the solvent evaporates from the coating. Because coatings are not chemically active during curing or weathering, they can be redissolved in the same solvent. This allows lacquers to be readily overcoated, resulting in excellent intercoat adhesion. Lacquer coatings have poor solvent resistance, but have excellent chemical and water resistance.

Acrylic resins are frequently used in lacquers, because of their fast drying properties and chemical and water resistance. Chlorinated rubber coatings are fast drying and are being used increasingly in this country. Chlorinated rubber coatings have excellent moisture resistance. Coal tar and asphaltic coatings are used on below-grade structural steel because of their moisture resistance and abrasion resistance. Polyvinyl-butyral coatings, such as those conforming to military specification DoD-P-15328D, are used as pretreatments for alkyd and vinyl coatings applied to steel and galvanized structures.

Two-Component Coatings. In general, coatings that cure by chemical reaction have the best combination of durability and water, solvent, and chemical resistance. Chemically cured coatings are packaged in two separate containers, and the chemical reaction is initiated after the two components are combined. Epoxy coatings have either an amine or polyamide curing agent although polyester and polyurethane constituents have been used. Amino-cured epoxies tend to have better chemical and solvent resistance. Polyamide-cured epoxies have better flexibility and water resistance. Because epoxy coatings cure to a hard, smooth, solvent-resistant finish, they are difficult to overcoat. To ensure good bonding, topcoats are applied to incompletely cured undercoats, allowing the topcoats to chemically react with the undercoats. If the solvent has not evaporated by the time the topcoat is applied the solvent can be entrapped, resulting in the blistering of the topcoat. If the undercoat is completely cured before the topcoat is applied, a fog or mist coat (thinned topcoat) is first applied to improve intercoat adhesion. Epoxy coatings chalk during weathering, although chalking occurs to a smaller extent with newer materials. When chalking occurs, it can be removed by sanding or brush-off abrasive blasting. Epoxies are exothermic when they cure; they cure slowly when applied below 8 °C (50 °F) and extremely rapidly above 32 °C (90 °F). Coal tar epoxies have coal tar pitch added to the epoxy resin. This combination increases the water resistance and makes the coating more tolerant to poor surface preparation. A coal tar epoxy cured with a low molecular weight amine is especially resistant to an alkaline environment, such as occurs on a cathodically protected structure. Some coal tar epoxy systems become brittle when exposed to the sun and must be protected. Coal tar epoxies are more difficult to overcoat than epoxies and come in colors ranging from tan to black.

Urethane coatings provide the tough, durable, smooth finish that is typical of chemically cured coatings. Aliphatic urethanes provide bright, chalk-resistant finishes with exceptional physical properties. Urethane coatings may be air dried or heat cured.

Polyester coatings are used most frequently with glass fibers or flakes for reinforcement. Polyester provides a thick coating that is tough and durable, with good resistance to abrasion.

Inorganic zinc coatings are available as primers or complete coating systems. Water-borne inorganic zinc-rich coatings are based on post- or self-curing alkali silicates (sodium, lithium, potassium), alone or in combination. Solvent-borne inorganic zinc coatings are based on an ethyl silicate vehicle. Finely divided zinc dust is added to the water- or solvent-borne binder just before application. An inorganic zinc coating applied to a well-prepared ferrous substrate can provide good protection without being topcoated at film thicknesses from 0.75 to 1.25 mm (0.03 to 0.05 in.). All topcoats applied to inorganic zinc must be alkaline resistant, or the topcoat can saponify and become water soluble. Zinc coatings should not be allowed to come in contact with gasoline, because the zinc is slightly soluble and will be leached from the film.

Organic zinc-rich coatings may be formulated with a number of resins, but the epoxy resins are most widely used. Zinc-rich coatings are not abrasion resistant and should be overcoated when required with a coating system containing a compatible binder similar to that used in the original coating. Zinc-rich organic coatings are more tolerant to poor surface preparation and are easier to topcoat.

Paint Application on Structural Steel

Basic application procedures must be followed to obtain optimum performance from a coating system regardless of the equipment selected for applying the coating. Cleaned, pretreated surfaces must first be coated within specific time limits established to prevent corrosion products, dirt, and moisture from accumulating and interfering with the coating process. Surface and ambient temperatures must generally be between 8 and 32 °C (50 and 90 °F) for water-borne coatings and 7 and 35 °C (45 and 95 °F) for solvent coatings. Some coatings that are catalyzed, such as epoxy and polyurethane coatings, dry within 4 h at 21 °C (70 °F), within 2 h at 27 °C (80 °F), and within 1 h at 32 °C (90 °F). These coatings in some circumstances may gel in the container or in the spray hoses unless two-component spray equipment is used. Paint should not be applied when temperature is expected to drop below freezing or when the relative humidity is higher than 80% and a temperature drop of more than 3 °C (5 °F) is expected. When successive coats of the same paint are used, each coat should be tinted differently to aid in determining proper application and to ensure complete coverage. Sufficient time must be allowed for each coat to dry thoroughly before overcoating. Allow the final coat to dry for as long as is practical before service is resumed.

Brush application procedures require brushes of first quality, maintained in perfect working condition. Brushes are identified by the type of bristle used, natural, synthetic, or mixed. Chinese hog bristles are the finest natural bristles, because of their length, durability, and resiliency. Hog bristles are unique; the bristle end forks out, resembling a tree branch. This flagging permits more paint to be carried on the brush and leaves finer brush marks on the applied coating that flow together more readily with the overall result of a smoother finish. Horsehair bristles are used in inexpensive brushes and are a very unsatisfactory substitute. Horsehairs do not flag, the bristles quickly become limp; they hold far less paint; and they do not spread the paint well. Badger hair brushes make good varnish brushes, and squirrel and sable bristle brushes are used in fine work in lining and lettering. Nylon brushes are used for water-thinned coatings, and these brushes are superior to horsehair. Nylon brushes cannot be used for lacquer materials, because the solvents may dissolve or soften the bristles.

Hand roller application (as opposed to roller coating, or coil coating, which was discussed previously in this article) involves the use of a roller, which consists of a cylindrical sleeve or cover that slips over a rotatable cage with attached handle. The sleeve, or cover, is generally 38 to 64 mm ($1\frac{1}{2}$ to $2\frac{1}{4}$ in.) in inside diameter and 75, 100, 175, or 230 mm (3, 4, 7, or 9 in.) in length. Special rollers are available in unusual shapes for corners and in lengths of 38 to 455 mm ($1\frac{1}{2}$ to 18 in.) for painting pipes, fences, and other hard-to-reach places. Pressure rolling equipment is available. The paint is fed to the roller under pressure, and the paint flow is controlled by a valve.

Fabrics used in covering the rollers include the following:

- *Lamb's wool (pelt):* This material is the most solvent resistant and is available in nap lengths of up to

31.8 mm ($1\frac{1}{4}$ in.). Lamb's wool is recommended for applying synthetic finishes on semismooth and rough surfaces. Lamb's wool mats badly in water and should not be used in water-thinned paints.

- *Mohair (angora):* Mohair is solvent resistant and may be used with water-thinned paints. Mohair is supplied in 4.8 and 6 mm ($\frac{3}{16}$ and $\frac{1}{4}$ in.) nap lengths.
- *Dynel (modified acrylic fiber):* Dynel has excellent water resistance and is somewhat tolerant to most solvents, except such strong solvents as ketones. Dynel is best for conventional water-thinned water paints and solvent systems, except ketone-containing lacquers. Dynel rollers are available in nap lengths from 6 to 31.8 mm ($\frac{1}{4}$ to $1\frac{1}{4}$ in.).
- *Dacron (polyester):* Dacron is a synthetic fiber softer than Dynel, suitable for exterior oil or water-thinned paints. It is available in nap lengths from 7.9 to 13 mm ($\frac{5}{16}$ to $\frac{1}{2}$ in.).
- *Rayon:* Rayon fabric should not be used because its use can lead to poor results. Rayon also mats badly in water.

Table 16 is a guide that can assist in the selection of a suitable roller.

Table 16 Roller selection guide

Product standards do not exist in the paint roller industry, and quality varies greatly among manufacturers; table is based on experience with first-line, high-quality products.

Paint	Smooth metal	Surface blasted metal	Pitted and weathered metal
Aluminum	C	A	A
Enamel or semigloss alkyd	A or B	A	. . .
Enamel undercoat	A or B	A	. . .
Epoxy coatings	B or D	D	D
Urethane coatings	B or D	D	D
Latex (water-thinned) paint	A	A	A
Metal primers	A	A or D	. . .
Varnishes, all types	A or B	. . .	. . .

Roller cover key	Material	Nap length					
		mm	in.	mm	in.	mm	in.

A	Dynel (modified acrylic)	6.4-9.5	$\frac{1}{4}$-$\frac{3}{8}$	9.5-19	$\frac{3}{8}$-$\frac{3}{4}$	25-32	1-1$\frac{1}{4}$
B	Mohair	4.8-6.4	$\frac{3}{16}$-$\frac{1}{4}$	. . .	. . .	. . .	. . .
C	Dacron (polyester)	6.4-9.5	$\frac{1}{4}$-$\frac{3}{8}$	13	$\frac{1}{2}$	. . .	. . .
D	Lamb's wool pelt	6.4-9.5	$\frac{1}{4}$-$\frac{3}{8}$	13-19	$\frac{1}{2}$-$\frac{3}{4}$	25-32	1-1$\frac{1}{4}$

Coating System Selection for Structural Steel

Selection of resin-type designations of coatings should be based on such factors as solvent limitations and chemical and weather resistance properties (as shown in Table 12), the category of the coating system based on surface preparation (see Table 17), and the estimated life of the paint (see Table 18).

Table 17 Minimum surface preparation requirements for steel with commonly used coatings

Listed coatings should not be used unless minimum surface preparation requirements can be met.

Coating	**Minimum surface preparation**
Drying oil	Hand or power tool cleaning (SSPC-SP2 or 3)[(a)]
Alkyd	Commercial blast (SSPC-SP6)
Oleoresinous phenolic	Commercial blast (SSPC-SP6)
Coal tar	Commercial blast (SSPC-SP6)
Asphaltic	Near white or commercial blast (SSPC-SP10 or 6)
Vinyl	Near white or commercial blast (SSPC-SP10 or 6)
Chlorinated rubber	Near white or commercial blast (SSPC-SP10 or 6)
Epoxy	Near white or commercial blast (SSPC-SP10 or 6)[(b)]
Coal tar epoxy	Near white or commercial (SSPC-SP10 or 6)
Urethane	Near white or commercial (SSPC-SP10 or 6)

Organic zinc	Near white or commercial (SSPC-SP10 or 6)
Inorganic zinc	White or near white (SSPC-SP5 or 10)

Note: No established criteria are available for the latex paints finding increasing use on steel.

(a) SSPC-SP: Steel Structures Painting Council Surface Preparation.

(b) Polyamide-cured epoxies require only a commercial blast.

Table 18 Estimated life of paint systems in years

Paint system	**Cleaning SSPC designation**	**Average dry film thickness**		**Climatic conditions**			**Immersion service**			**Splashes and spills**		
		μm	**mils**	**Mild**	**Moderate**	**Severe**	**Fresh water**	**Salt water**	**Petroleum products**	**Acid**	**Alkaline**	**Halogens**
Alkyd:												
3 coat	SP3	114	4.5	4	2	1.5	. . .	. . .	. . .	. . .	. . .	. . .
3 coat	SP6	114	4.5	6	4	2	. . .	. . .	. . .	. . .	. . .	. . .
Latex (acrylic):												
3 coat	SP3	127	5.0	6	3	1.5	. . .	. . .	. . .	. . .	. . .	. . .
3 coat	SP6	127	5.0	10	5	3	. . .	. . .	. . .	. . .	. . .	
Epoxy polyamide:												
2 coat	SP6	152	6.0	7	6	5	. . .	. . .	. . .	. . .	. . .	. . .
3 coat	SP6	254	10.0	10	8	5	5	. . .	. . .	5	6	5
Inorganic zinc:												
+3 coat	SP10	254	10.0	12	10	6	6	5	. . .	6	7	6

3 coat	SP10	305	12.0	14	10	7	6	. . .	12	5	6	5
Urethane-epoxy:												
Inorganic zinc + 2 coat epoxy + urethane	SP10	305	12.0	15	12	10	. . .	. . .	. . .	. . .	. . .	4
2 coat epoxy + urethane	SP10	254	10.0	15	10	8	. . .	. . .	20	7	7	5
Vinyl:												
Inorganic zinc + 3 coat	SP10	305	12.0	15	10	8	8	6	. . .	. . .	. . .	. . .
3 coat	SP10	254	10.0	12	8	6	6	4	. . .	3	5	4
Chlorinated rubber	SP6	305	10.0	10	9	8	5	5	. . .	9	6	9
Coal tar epoxy	SP6	406	16.0	8	7	6	8	6	. . .	4	. . .	4

Coating of Galvanized Steel. Special treatment must be provided for galvanized structural steel that normally has a nominal thickness of 0.13 mm (5 mils). Data indicate that in rural exposures rusting will not occur for 74 years, and in a marine environment, 33 years of rust-free service can be expected. For a marine-industrial exposure, 16 years of rust-free use can be expected. Normally, the galvanized structure must be degreased and acid phosphate etched using a vinyl butyral pretreatment similar to Mil-Spec DoD-P-15328. A primer, intermediate coat, and topcoat is then applied to the prepared surface. The primer coat must be selected to be compatible with the wash primer; the coatings manufacturer should be consulted at this point in the selection process. Careful control as to coating thickness of wash primer must be followed to provide a cohesive film. The wash primer must be between 0.006 and 0.013 mm (0.3 and 0.5 mil) thick followed by the appropriate thickness of the subsequent coating system.

Economic Factors. When painting steel structures, many economic factors need to be considered in preparing a job estimate, including:

- The area to be painted
- The surfaces to be coated, such as galvanized steel or ungalvanized steel or the combination of the two
- The complexity of the structure (e.g., the number and types of bolts, rivets, or welds)
- The type of structural member to be encountered
- The accessibility of surfaces with the tools required
- The downtime for the facility, including the time to erect scaffolds, place drop cloths, rope off the area, provide alternate parking and alternate storage if required
- The cost of scaffolding and drop cloths, which should include horticultural care such as plantings and grass
- Surface preparation and removal of debris

- Painting

Actual costs vary depending on the season and the location of the structure. Preparing some surfaces for specified paints may add to the cost. Steel that is pitted, gouged, or has discontinuous welds, requires filling with epoxy putty or similar filler material. Sometimes even rewelding and grinding are required for high value structures.

Surface Preparation

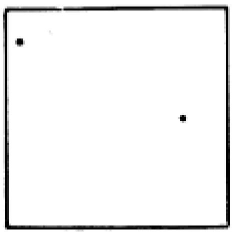
After the selection of a coating system, the most important factor to be considered is surface preparation. Surface preparation must be compatible with the primer and topcoating. Surface preparation is often the most costly phase of the corrosion prevention process for steel, averaging over half the cost of paint application exclusive of scaffolding.

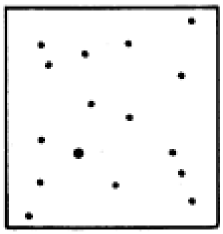
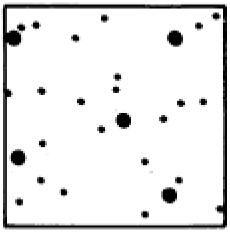
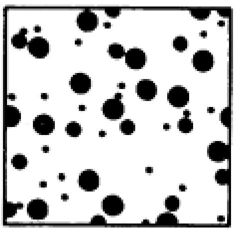
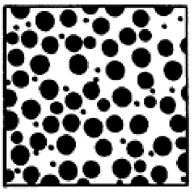
Surface preparation should remove mill scale, rust, oil, grease, atmospheric materials, weld spatter, and old coatings. Surface preparation also provides an anchor pattern to allow the primer and following coats of paint to key into the surface for a good bond. Table 17 shows minimum surface preparation requirements for steel with commonly used coatings. Table 13 summarizes various methods of surface preparation used before painting and provides the Steel Structures Painting Council (SSPC) designation for each method.

Inspection of Surface. Before proper surface preparation and painting method can be applied, the condition of the surface must be determined. For new or previously uncoated steel surfaces, the Steel Structures Painting Council visual standard (SSPC-VIS1) defines the four rust grades of structural steel and contains colored photographs presenting surface preparation standards. Shop primed coated steel would be expected to have no rusting except for small areas abraded during handling.

However, most of the steel structures encountered have been coated previously. The coating layers may be concealing as much rust as is showing on the surface. The surface condition of a previously coated steel substrate may be classified in accordance with ASTM 610/SSPC-VIS2 for the degree of rusting, as shown in Table 19 (SSPC-VIS2 for Pictorial Representation of Rust Classification). The chalking, blistering, flaking, erosion, checking, and cracking of the coating may be classified by the corresponding ASTM visual standards. Instrumentation is available for determining the presence of pinholes, the adhesion of the coating film to the substrate, and the film thickness.

Table 19 Steel Structures Painting Council standard SSPC-VIS2 for pictorial representation of rust classification for surfaces to be painted

Paint system condition	Cleaning and painting recommended	Rust grades	Area of example, %
Nondeteriorated, 0 to 0.1% rust			
Paint almost intact; some primer may show; rust covers less than 0.1% of the surface	Solvent clean (SSPC-SP1) entire repaint area, and spot prime, if necessary. If required to maintain film thickness or continuity, spot apply finish coat, then apply 38-51 μm (1.5-2.0 mils) of finish coat over entire repaint area	10-8	
Slightly to moderately deteriorated, 0.1 to 1% rust			

Finish coat somewhat weathered; primer may show slight staining or blistering; after stains are wiped off, less than 1% of area shows rust; blistering, loose mill scale, or loose paint film	Spot clean (minimum SSPC-SP2) entire repaint area, and spot prime. If required to maintain minimum film thickness or continuity, spot apply finish coat, then apply 38-51 μm (1.5-2.0 mils) of finish coat over entire repaint area	8-6	
Deteriorated, 1 to 10% rust			
Paint thoroughly weathered, blistered, or stained; up to 10% of surface is covered with rust, rust blisters, hard scale or loose paint film, very little pitting visible	Spot clean (minimum SSPC-SP2) entire repaint area, feather edges, and spot prime. If required to maintain film thickness or continuity, spot apply finish coat, then apply 38-51 μm (1.5-2.0 mils) of finish coat over entire repaint area	6-4	
Severely deteriorated, 10 to 50% rust			
Large portion of surface is covered with rust, pits, rust nodules, and non-adherent paint. Pitting is visible	Clean (minimum SSPC-SP6) entire repaint area, feather edges, and spot or full prime. If required to maintain film thickness or continuity, spot apply finish coat, then apply 38-51 μm (1.5-2.0 mils) of finish coat over entire repaint area	4-1	
Totally deteriorated, 50 to 100% rust			
	Clean (minimum SSPC-SP6) entire repaint area and apply primer, intermediate, and finish coats over entire repaint area	1-0	

Surface profile allows the coating to key into the metal substrate. Surface profile is determined by the abrasive material, including hardness, mass, and firmability, and the force with which the abrasive material impinges upon the surface. The selection of appropriate surface profile provides the bases for good primer adhesion. The coating formulator takes into account the viscosity of the primer, which allows the coating to fill the contact surface, the number of polar groups to come in contact with this surface, and the mechanical anchor or tooth that facilitates adhesion of the primer to the contact surface. Surface profile cannot expose the peaks of the metal once the primer is applied. Therefore, the abrasive blaster must use the correct angle of attack and distance from the work during the blasting operation. An abrasive-blasted surface profile of from 0.038 to 0.089 mm (1.5 to 3.5 mils), measured from the top of the highest peak to the bottom of the lowest valley, is used for most coating systems.

Surface inspection includes the determination of the condition of the surface before surface preparation and the results of the surface preparation. SSPC VIS1 provides a standard for surfaces before preparation and prepared surfaces. Surface comparison may also be made by using a surface-profile comparator and the NACE Standard TM-01-70, prepared by the National Association of Corrosion Engineers.

Structural design may limit access to the sections being prepared for painting. Access for abrasive blasting requires approximately 455 mm (18 in.) of clearance of the blast nozzle, although 150 mm (6 in.) can be sufficient if superficial cleaning can be tolerated. Sharp edges resulting from corrosion pits, deep gouges, or cut edges should be properly prepared. Pits and gouges over 3.18 mm ($\frac{1}{8}$ in.) deep should be filled with weld metal and ground flush to the surface or prepared for painting with an epoxy grout. Cut edges should be chamfered to a 3.18 mm ($\frac{1}{8}$ in.) radius by grinding. Bolts and rivets should be tight against the steel plates, not allowing crevices; areas surrounding bolts and rivets should be hand brushed with primer after the areas have been abrasive blasted. Discontinuous weldments or tack welds should be properly prepared. Continuous welds should be required, or an epoxy grout or caulk should be used to eliminate water accumulation. Where water may accumulate, in areas such as cross members joining channels and L sections that are directly exposed to the sky, weep holes are needed that are sufficiently large to allow water to drain and debris to be flushed through.

Quality Control

Paint materials should be purchased to meet the needs of the job at hand. Storage should be minimal to avoid material deterioration because of temperature variations. Coating materials, pretreatment primer, primer, intermediate coating, and topcoating, should be obtained from the same supplier and prepared by the same manufacturer to avoid incompatibility of materials and abrogation of the manufacturer's warranty. When using new and unfamiliar materials, the manufacturer's representative should be consulted and should supervise critical portions of the surface preparation and coating application.

Paint in freshly opened containers should not require straining. However, if skins, lumps, color flecks, or foreign materials are present, paints should be strained after mixing. First, remove any skins from the paint surface, thoroughly mix the paint, thin to application viscosity necessary, and strain through a fine sieve. Use straining as a standard procedure when paint is to be applied by spraying to avoid clogging the spray gun.

Paints should be ready for application by brush or roller when received. Unnecessary thinning or excessive thinning results in an inadequate film thickness and drastically reduces the longevity and protective qualities of the applied coating. In all instances, measure the viscosity of the material to determine that it is correct for the method of application established by the manufacturer. When thinning is necessary, it must be done by competent personnel using the compatible thinning agents recommended in label or specification instructions. Do not thin to improve brush or rolling of paint materials that are cold. Paint materials should be preconditioned to bring them to between 15 and 29 °C (65 and 85 °F) for application.

Sampling and testing of the coating material may be required before it is applied. This is done to confirm that the materials that have been supplied meet specifications. Tests should be performed by the supplier and if confirmation is required, additional testing should be performed by a qualified independent testing laboratory retained by the purchaser of the material.

Sending paints out to an independent testing laboratory requires accurate selection and labeling. Select samples from each lot of coating material supplied by the painting contractor, if more than 380 L (100 gal) of material of each kind is to be used on the job. A representative of the contractor should take these samples. The samples should be two full gallons if supplied in gallon containers or two 1-qt containers properly labeled. Inspect the containers to determine that full measure has been received. Record the following on each sample container: manufacturer's name and address, tradename and manufacturer's designation of the material, contractor's name and address and contract number when applicable, date and weather conditions when the sample was taken if put in a 1-qt container, batch or lot number, date of manufacture, and number of gallons represented by the sample. Forward the samples to the laboratory with a written request for the tests required, either full compliance or specific test desired. Include the above information in the request form.

Field and paint shop testing should be done if there is any doubt that materials meet specification requirements. When preparing the paint for use and during painting operations by contractors, limited testing should be done to determine if paints have been adulterated. However, limited field testing should not be considered as a substitute for standard laboratory techniques. Field testing is used to discover major flaws or adulteration in a coating material. Sampling on the job is done by the contractor in the presence of the inspector, unless other arrangements have been made.

Material storage should be at 24 °C (75 °F) plus or minus 6 °C (10 °F), because paint is a temperature sensitive product. Low temperatures cause paints to increase in viscosity and may require conditioning for 24 h before use. Freezing temperatures may ruin water-borne paints and cause container to bulge or burst. High temperatures result in lower viscosities, causing pigment to settle and thus producing poor flow characteristics. Coating materials may be extremely sensitive to heat. At temperatures over 38 °C (100 °F), gelation may occur, resulting in unusable material. At these high temperatures, pressure can build up within the containers enough to cause lids to blow off, creating a serious fire hazard. Application is seriously affected when coating materials are used after being stored at very high or low temperatures. Additional conditioning time and effort are required in these cases to ensure proper application and optimum surface protection.

Other factors to be considered are high humidity, which causes containers to corrode and labels to deteriorate, and poor ventilation, which allows the collection of excessive concentrations of solvent vapors that are both toxic and combustible. Pumps for drawing liquids from steel drums must be approved by fire underwriters. Gravity spigots, other than self-closing types, should not be used because of the possibility of accidental spillage. Stock should be stored so that all labels can be easily read and containers can be rotated to use older material first. Materials should be issued for each work shift in amounts that are consumed during that time without loss or spoilage.

Maintenance Program

The most economical approach to maintaining a coating system is the establishment of a periodic maintenance program. If the appropriate structural steel alloy is selected, uniform corrosion should be the only corrosion encountered without a protective coating system. Proper surface preparation and selection of a coating system suitable to the ambient conditions can provide a 10-year life cycle for the coating. An annual touch-up and the application of a full topcoat after 5 years of exposure can provide this 10-year life cycle.

A spotty appearance can result from periodic touch-ups, especially if the topcoat has chalked. In addition, catalyzed coating systems are difficult to topcoat, because only cohesive forces hold the freshly applied topcoat to the aged coating, and the aged coating must be roughened by brushoff blasting before applying a fresh coating. A maintenance coating must be compatible with existing coatings.

When programmed maintenance is instituted, all structural exteriors should be inspected annually to establish the following:

- Update the condition of the structure to determine the priority for painting
- Determine if washing is the only process needed to improve or maintain appearance
- Determine what portions of the structure require touch-up painting
- Determine if the structure requires a totally new coating system

Specifications and Industrial Guidance

Specifications and industrial guidance have been developed by the Steel Structures Painting Council committees. These specifications are used for industrial applications. A second source of standardization data and guidance is the Department of Defense publications. The standardization documents include military handbooks that reference federal and military specifications. All these federal and military documents are listed in the Department of Defense Index of Specifications and Standards (DoDISS). The American Society for Testing and Materials issues consensus standards on paint constituents and the testing of paints; however, these standards currently do not cover paints as supplied by industrial producers or vendors. Other specifications and guidance are available from the National Association of Corrosion Engineers and the American Society of Naval Architects. Most of the documents are available in various libraries throughout the United States.

Safety

Safety hazards are of two types--those resulting from the location of and access to the structural steel and hazards occurring as the result of exposure to paint as a possible toxic material. Hazards in the workplace are regulated by Department of Labor in the Occupational Safety and Health Administration (OSHA), which is responsible for establishing safety rules for workers and the materials they use. Hazards that are emitted to the environment are regulated by the Environmental Protection Agency.

Federal laws govern all works, and these laws established by congressional action are defined by OSHA rulings. These rulings are established by priority that is at the state and local level; therefore, the rulings can vary depending on where the work takes place and on the inspector who enforces the ruling. State safety requirements exert control in relevant areas whenever federal law or rulings do not cover projects. Municipal or township ordinances should be followed whenever specific rulings impose restrictions beyond the federal and state controls. It is at this level that safety requirement priorities are established and are moved up to the state, federal district, and national levels. Additional information is available in the section "Safety and Environmental Precautions" in this article.

Elastomeric Coatings for Automotive Plastics

Robert M. Piccirilli and John Burgman, PPG Industries

Introduction

THIS ARTICLE describes elastomeric coatings that are suitable for painting flexible plastic substrates. In particular, the coatings systems described are those that find utility in automotive exterior applications, where the requirements of appearance and durability are most severe. Wire coatings, for example, are not discussed even though they definitely have a demanding flexibility requirement. The article also focuses on substrates that have a high degree of flexibility, so it does not include coatings systems for more rigid plastics, such as fiberglass-reinforced polyester sheet molding composites or the more rigid nylon substrates, although some of the coatings systems described would certainly perform well in these applications.

More general information about the selection and application of organic coatings is available in the article "Painting" in this Volume.

Types of Elastomeric Coatings for Automotive Plastics

Flexible plastic substrates became popular for automotive use in the 1970s, when legislation mandated that automobiles should sustain little or no damage in low-speed collisions. As a result, the use of plastic bumpers and fascia capable of receiving these low-speed impacts without damage became widespread. These substrates are still widely used, including EPDM (ethylene-propylene-diene monomers), reaction injected molded polyurethane, glass-filled reaction injection molded polyurethane, and thermoplastic polyurethane. More recently, rubber-modified poly-propylene thermoplastic olefin has been used for many automotive exterior applications.

Paints that are used for these substrates must meet the automotive exterior requirements that the paint on the steel portion must meet. Among the most critical issues are durability, adhesion, appearance, and color match capability. In addition, flexibility of the painted substrate over a wide range of temperatures is a minimum requirement. Certainly the paint must be flexible enough that the part can be handled and attached to the car body in the assembly plant. However, many of the automotive specifications (e.g., Ref 1) require that the painted substrate be capable of being bent 180° over a 25 mm (1 in.) mandrel at temperatures below -18 °C (0 °F) with little or no cracking of the paint or substrate. In addition to performance requirements, elastomeric coatings must now comply with federal and local regulations that pertain to volatile organic compounds and hazardous air pollutants. All of these requirements have led to a wealth of research directed toward solving these challenges. Over the years elastomeric coatings have changed from low-solids enamels to high-solids basecoat clearcoat systems and, most recently, to water-based systems.

The types of chemistries that have been used for elastomeric coatings fall into two general categories:

- Modified polyester/polyurethane cross-linked with either melamine formaldehyde resin or polyisocyanate
- Modified acrylics cross-linked with either melamine formaldehyde resin or polyisocyanate

The details of these systems will be discussed as they pertain to structure, synthesis, and formulation.

Reference cited in this section

1. Specification ESBM 2J218A, Ford Motor Co.

Cross-linking Mechanisms

In the United States, the most popular mode of cross-linking for elastomeric coatings for exterior automotive fascia is via melamine formaldehyde chemistry. Coatings formulated in this fashion offer a number of advantages. First of all, they are single-component and therefore do not need any mixing or catalysis when applied. Melamine coatings have inherently good durability, and melamine formaldehyde resin is compatible with a wide array of resins, pigments, and solvents. One disadvantage of curing coatings with melamine formaldehyde is that somewhat elevated temperatures, approximately 120 °C (250 °F), are required to achieve adequate properties. Because many of the plastics that are used have a heat distortion temperature below 120 °C (250 °F), it is necessary to support the part during the painting and baking process. Another disadvantage of melamine cross-linked systems is susceptibility to environmental etching (i.e., spotting from acid rain), which has become a concern in recent years. It is not the purpose of this review to discuss the details of melamine formaldehyde chemistry; an excellent discussion is provided by Solomon (Ref 2).

Two-component isocyanate chemistry is finding increasing use in coating elastomeric parts. One advantage of this chemistry is its ability to cure at lower temperatures, which allows coating of unsupported plastic parts. Also, it appears that two-component isocyanate coatings offer enhanced resistance to environmental etching. These systems, however, require mixing just prior to application or at the gun because of limited pot life. Also, some care must be taken when handling the isocyanate portion because of its toxicity.

Either curing mechanism requires a polyol for cross-linking. In a given formulation, the type and amount of cross-linker required to achieve optimum performance may vary, but the basic properties of flexibility and durability are delivered by the polyol portion of the coating. Thus, this article focuses on that portion of the coating system. The types of polyols most commonly used fall into two major categories: modified acrylics and condensation polymers.

Reference cited in this section

2. D.H. Solomon, *Organic Chemistry of Film Formers,* Robert E. Krieger Publishing Co., 1982

Acrylic Polyols

Acrylic polyols that are not appropriately modified do not make good elastomeric coatings. A monomer composition with a low glass transition temperature (T_g) usually gives adequate flexibility, but the coatings are soft and do not possess good tensile strength. By raising the T_g of the acrylic polymer to improve hardness, the coating becomes too brittle to be useful over flexible substrates. Usually a modification is required that involves introducing some soft, low- T_g polymeric segment into the polymer backbone or pendant to the chain of a high-T_g acrylic polymer. This typically results in a good marriage of flexibility and hardness.

The use of polycaprolactone as a pendant group off the polymer chain is very common in the patent literature. Chang et al. (Ref 3) described the use of an adduct of hydroxyethyl acrylate and caprolactone to make useful elastomeric coatings from acrylics. Caprolactone reacts with alcohols to give adducts that contain flexible chain segments (Ref 4). If the alcohol is hydroxyethyl acrylate, an adduct is formed (Fig. 1). This adduct is further reacted with diisocyanate to form a long-chain polyester polyurethane with acrylate termination. This new low-T_g acrylate monomer can then be incorporated into a conventional acrylic by free radical polymerization. In this manner an acrylic polyol is prepared that has a polycaprolactone-based polyurethane pendant to the acrylic polymer chain.

$$CH_2 = CHCO_2CH_2CH_2OH + CO_2 - (CH_2)_5 \rightarrow CH_2 = CHCO_2CH_2CH_2O[CO(CH_2)_5O]_N - H$$

Fig. 1 Adduct of hydroxyethyl acrylate and caprolactone, used by Chang et al. (Ref 3) to make elastomeric coatings from acrylics

In another example in Ref 3, an isocyanate prepolymer was prepared by reacting methylene bis(cyclohexylisocyanate) with a polycaprolactone diol (prepared from caprolactone and diethylene glycol). This material was then reacted with hydroxyethyl acrylate to give a low-T_g acrylate functional polyurethane, which in turn was copolymerized with various

other acrylate monomers to yield an acrylic polyol with urethane-modified polycaprolactone in the side chains. These polyols could be cured with N-butoxymethylacrylamide, melamine formaldehyde resin, or polyisocyanate to produce materials with good hardness and flexibility.

In the above examples, an acrylate monomer was prepared that contained a soft segment based on polycaprolactone. The acrylate monomer was then copolymerized with other acrylate monomers to yield a useful product. A second approach that yields similar products is to prepare an acrylic interpolymer that contains hydroxyethyl acrylate or some similar monomer, then react this material with a polycaprolactone-modified isocyanate prepolymer. Such materials are described in patents by Chang (Ref 5, 6). Although the examples are directed toward polycaprolactone-modified materials, these patents address the use of other low-T_g materials to modify the acrylic polymer, including poly(oxytetramethylene) glycols and other soft acrylic polyols with T_g < 10 °C, or 50 °F. Again, these materials could be cured with melamine formaldehyde resins to obtain useful coatings for elastomeric substrates.

The materials described above are high-molecular-weight polymers and thus are not suitable for use in high-solids coatings. In patents by Etzell et al. (Ref 7, 8, 9), acrylic polymers modified with caprolactone are described. The polymers are prepared in different ways, as described in the examples, but in each case the polycaprolactone moiety is attached to the polymer backbone through a hydroxyl-containing monomer, typically hydroxyethyl acrylate or hydroxypropyl acrylate. The caprolactone can be added while the acrylic polymerization is taking place, or a polycaprolactone-containing acrylate monomer can be used in the polymerization. In a typical example, caprolactone is mixed with solvent and a free radical catalyst. To this is added a mixture of monomers consisting of methyl methacrylate, butyl methacrylate, 2-ethylhexyl acrylate hydroxyethyl acrylate, and acrylic acid, and polymerization is conducted at elevated temperature. The polymers thus prepared are low in viscosity at reasonably high solids contents. The caprolactone-modified acrylics can be blended with melamine formaldehyde resin to produce coatings that have solids contents of 50% or greater and are generally quite useful over elastomeric substrates.

It should be noted that the coatings prepared from the caprolactone-modified acrylics of the Etzell patents (Ref 7, 8, 9) require the use of microgel to provide adequate sag resistance and metallic pattern control, whereas the low-solids materials described in Ref 5 and 6 provide the rheology control for good application. In fact, all high-solids coatings need some form of rheology control to maintain good application properties. The structure, synthesis, and function of pattern control agents are complex enough to be discussed in a separate review and will not be discussed here.

In general, acrylic polymers can be modified by caprolactone to make polyols suitable for cross-linking with melamine formaldehyde resin. In these cases, the working hypothesis is that one needs a relatively high-T_g acrylic backbone that can be modified with a relatively low-T_g side chain to achieve a good balance of hardness and flexibility. Polycaprolactone provides this soft side chain without any adverse effects on adhesion or durability. When the acrylic polyol is modified solely with caprolactone, high-solids coatings are possible. If the side chain is further modified with urethane linkages, lower-solids coatings are possible that do not require the use of rheology control agents for good application properties.

Soft side chains other than polycaprolactone can be incorporated into the acrylic polymer. Ryntz has shown a number of ways to incorporate a polyester into the backbone of an acrylic. In one invention, vinyl benzyl chloride is used to introduce copolymerizable vinyl groups onto a relatively soft polyester urethane (Ref 10). Thus, in a typical example, a polyester was prepared from 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate, trimethylolpropane, and adipic acid. The polyester was reacted with diisocyanate and then further modified with vinyl benzyl chloride. This hydroxy functional carbon-carbon double bond bearing branched polyester was then copolymerized with butylmethacrylate, hydroxypropylmethacrylate, and methyl methacrylate to produce a graft copolymer of the invention. Finally, the graft copolymer was formulated into a high-solids coating composition with melamine formaldehyde resins, additives, and solvents to produce flexible, durable coatings.

Ryntz has described other methods of preparing polyester graft copolymers (Ref 11, 12). Instead of using vinylbenzylchloride to incorporate polymerizable moieties into a branched polyester, one can use a vinyl functional methoxy silane. Alkoxy silanes react with organic alcohols in a type of exchange reaction where the lower-molecular-weight alcohol is replaced by the higher-molecular-weight polymeric alcohol, in this case the polyester polyol, according to the equation

$$RSi(OR')_3 + R''OH \rightarrow RSi(OR')_2(OR'') + R'OH$$

where R'' is a polyester polyol. In Ref 11 and 12, a polyester is prepared from 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate and Tone 301 (polycaprolactone triol). This material is then reacted with g-

methacryloxypropyl trimethoxysilane to liberate methanol and to produce the polyester containing a polymerizable double bond. Copolymerization of the methacrylate-modified polyester with other durable acrylic monomers produces the grafted acrylic polymer described. Formulation of the grafted polymer with melamine formaldehyde resin produces coatings with good elongation and durability, as evidenced by gloss retention in cyclic ultraviolet accelerated weathering tests. It is believed that the use of the silicon compound in forming the vinyl functional polyester is responsible for the superior durability of these coatings.

An interesting approach to synthesizing polymers useful for elastomeric coatings is to attach a soft acrylic chain to a hard acrylic backbone. This can be accomplished through the use of mercaptoethanol. In patents by Simms (Ref 13, 14), a mercaptoisocyanate is prepared by reacting a diisocyanate with 2-mercaptoethanol. The mercaptoisocyanate thus formed is then reacted with a hydroxyethyl-methacrylate-containing acrylic to give an acrylic copolymer that has mercapto groups pendant to the polymer chain. (It should be noted that the T_g of this acrylic is too high to make a useful elastomeric coating.) The mercapto-modified acrylic copolymer is then grafted with a soft monomer composition (e.g., butyl acrylate) to yield a material with essentially two chains that are significantly different in T_g. These graft copolymers can be cured with polyisocyanate or melamine formaldehyde resin to give films with good elongation and excellent tensile strength.

Another approach to modifying acrylics to make good elastomeric coatings involves making a block copolymer of the A-B-A type (Ref 15). The B portion of the block copolymer is a urethane-modified polyester that contains terminal mercapto groups. The polyester is a linear, difunctional material that is reacted with diisocyanate to give a urethane-modified polyester with terminal isocyanate groups. Mercaptoethanol is added to the isocyanate-terminated polymer, resulting in the thiol-terminated B segment. A hard acrylic segment is grafted onto both ends of the B block through the thiol groups to provide the block copolymer of the invention. The block copolymer is formulated with another hard acrylic polymer, then cured with melamine formaldehyde resin or polyisocyanate to yield elastomeric coatings with excellent flexibility and durability.

Polysiloxane chains can also be grafted onto acrylic polymer backbones (Ref 16, 17). In a typical example, a hydroxy functional oligomeric polysiloxane reactant was prepared by reacting triethylene glycol with a commercially available methoxy functional polysiloxane, adipic acid, and trimethylol propane. The hydroxy-functional, polyester-containing polysiloxane unit was made acrylate functional by reacting with glycidyl methacrylate in such a way as to promote the epoxy hydroxyl reaction. This new carbon-carbon double bond bearing branched polysiloxane macromer was then copolymerized with styrene, butyl methacrylate, hydroxyethyl acrylate, and acrylic acid to produce an acrylic copolymer with polysiloxane grafted side chains. These materials have the advantage of having high solids at relatively low viscosity, which makes them suitable for high-solids coatings. Coatings prepared from these polymers are reported to have good durability, ability to adhere to a wide variety of substrates, and good flexibility. As with many of the polymers reported here, these materials need to be cured with melamine formaldehyde resin or polyisocyanate to produce useful coatings. Coatings of the high-solids type also need the appropriate rheology control agents to prevent sag and improve appearance.

In general, the types of acrylics useful for elastomeric coatings are those with a relatively hard polymer backbone, as defined by T_g, and a low-T_g or soft segment, usually pendant to the acrylic chain. The molecular weight of the two segments should be high enough that these materials exhibit the properties of both, in terms of phase transitions that are typical for multiphase systems. High-solids systems are possible with the appropriately modified acrylic, but to achieve good application properties, the proper rheology control additives are needed in the coating formulation.

References cited in this section

3. W.H. Chang, J.A. Erikson, and R.L. Scriven, U.S. Patent 4,034,017, July 1977
4. A. Schindler, *J. Coatings Technol.,* Vol 54, Oct 1982, p 693
5. W.H. Chang, J.A. Erikson, and S. Porter, U.S. Patent 4,208,494, June 1980
6. W.H. Chang, J.A. Erikson, and S. Porter, U.S. Patent 4,208,495, June 1980
7. R.A. Etzell, B.J. Miller, and D.J. Dziekan, U.S. Patent 4,546,046, Oct 1985
8. R.A. Etzell, B.J. Miller, and D.J. Dziekan, U.S. Patent 4,720,528, Oct 1985
9. R.A. Etzell, B.J. Miller, and D.J. Dziekan, Canadian Patent 1,246,769, Dec 1988
10. R.A. Ryntz, U.S. Patent 4,873,285, Oct 1989

11. R.A. Ryntz, U.S. Patent 4,870,140, Sept 1989
12. R.A. Ryntz, U.S. Patent 4,810,759, March 1989
13. J.A. Simms, U.S. Patent 4,243,573, Jan 1981
14. J.A. Simms, U.S. Patent 4,206,108, June 1980
15. J.A. Simms, U.S. Patent 4,346,201, Aug 1982
16. R.A. Ryntz and K.R. Kurple, U.S. Patent 4,673,718, June 1987
17. R.A. Ryntz and K.R. Kurple, U.S. Patent 4,754,014, June 1988

Condensation Polymers

Condensation polymers are polymers that are defined by condensation polymer kinetics, including polyesters, polyurethanes, or a combination of both. As will be shown below, these polymers are designed to be hydroxyl functional to enable cure with melamine formaldehyde resins or polyfunctional isocyanate. This class of polymers covers a large extent of the patent literature and can be divided into two major groups: high-molecular-weight, low-solids materials and low-molecular-weight, high-solids materials. Two factors are particularly important to good performance in this class of coatings: the branching or cross-link density of the condensation polymer employed, and the balance of low-T_g and high-T_g materials.

An early patent by Chang (Ref 18) described high-molecular-weight polyester polyurethanes that were useful for elastomeric coatings. In this patent, a polyester polyol that is subsequently modified with isocyanate is prepared from neopentyl glycol, trimethylolpropane, adipic acid, and isophthalic acid. The degree of branching of this polyester polyol is key to the performance of the resin in the coating. In this case the branching is defined as the number of moles of polyol or polyacid in 500 g of the polyhydric material, typically the polyester. The patent recommends that no more than one mole of material with a functionality of 3 or greater should be present per 500 g of material. Any amount higher than that results in poor flexibility of the coating.

A second key to good performance is the incorporation of urethane linkages through the use of polyisocyanate. The polyester polyol is reacted with diisocyanate to produce a polyurethane of sufficiently high molecular weight to provide good application properties and elasticity. The polyurethane polyols thus prepared are cured with melamine formaldehyde resin to give highly durable elastomeric coatings with excellent appearance. Elasticity can be further enhanced through the addition of a low-T_g polyol such as poly(oxytetramethylene)glycol to the coating formulation. Specifically, when one uses a soft, low-T_g polyol in the coating formulation it is best to employ a "harder," high-T_g polyol to achieve a balance of flexibility and hardness.

A variation on the aforementioned example was used to seal EPDM substrates, thereby preventing oil from the substrate from spewing out onto the coating (Ref 19). It was found that modification of the polyurethane polymer with a polyacid or anhydride in the later stages of the reaction gave good sealing properties. Thus, in a typical example, a polyurethane polyol was prepared from poly(hexanediol adipate), trimethylolpropane, 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate, triethylenediamine, and bis(isocyanatohexyl)-methane. To this polyurethane polyol was added maleic anhydride, and the reaction was carried out at a low enough temperature to allow only opening of the anhydride ring. The resin thus produced was cured with melamine formaldehyde resin to provide a good sealing primer for EPDM rubber. Even after accelerated weathering, EPDM rubber that was primed with the acid-modified polyurethane and then topcoated showed no yellowing or migration of plasticizing oils to the surface of the coating, whereas unprimed controls showed severe yellowing and loss of gloss.

In still another example of polyester polyols modified with isocyanate for melamine-cured elastomeric coatings, Guagliardo (Ref 20) recommends the incorporation of dimer fatty acid into the polyester portion of the polymer to improve the solvent and gasoline resistance of the coating.

A more classic example of elastomeric coatings is provided by Chang and Hartman (Ref 21). A polyurethane polyol is prepared from a high-molecular-weight, low-T_g polyol; a low-molecular-weight short-chain diol; and a diisocyanate. A typical experiment is described as follows: To a mixture of poly(oxytetramethylene)-glycol (molecular weight 1000), poly(neopentyl adipate), and 1,6-hexanediol in an appropriate solvent, methane bis(cyclohexyl-isocyanate) is added, followed by diethylenetriamine in cyclohexanone. The mixture is heated until all the isocyanate has reacted. The above polymer was formulated with melamine formaldehyde resin to give a coating with good low-temperature impact resistance and tensile strength. The key elements for good performance are a low-T_g polyol (T_g < 25 °C, or 77 °F), a short-chain diol or diamine, minimal branching in the polymer, and a polyisocyanate. The low-T_g polyol, which was

poly(oxytetramethylene)-glycol in the above example, provides a soft, flexible matrix in which are embedded hard segments formed by the diisocyanate and short-chain diols and diamines. The molecular weight of the soft segment should be high enough to provide some phase separation of the smaller urethane segments. The diamine or polyamine delivers additional hard segments as well as sights for minimal branching.

A patent by Porter et al. (Ref 22) describes the use of polymeric polyol with a low T_g in combination with an excess of melamine formaldehyde resin. The low-T_g polyol is also low in hydroxyl content, and if it were cured with a stoichiometric amount of melamine resin a rather soft coating would result. However, when one uses a melamine formaldehyde resin that can homopolymerize in combination with the low-T_g polyol, coatings with excellent low-temperature flexibility result. Melamine formaldehyde resins that can homopolymerize are those that contain a high number of methylol groups, and these are well known.

In the above examples, it has been shown that urethane linkages are required for good elastomeric properties. They not only provide crystalline domains in the softer low-T_g matrix, but they also build viscosity by increasing molecular weight and hydrogen bonding. The higher molecular weight is a key factor in the durability and appearance of the coatings. However, Piccirilli et al. (Ref 23) have shown that polyesters alone can be made suitable for elastomeric coatings. The polyesters described are hydroxyl functional and are intended to be cured with melamine formaldehyde resin. Much like the polyurethanes, one of their keys to good performance is the minimal branching described above: 1 gram mole of polyol per 500 g of polyester. However, the major element required for good elastomeric performance is to keep the average molecular weight of these materials greater than 80,000, as measured by gel permeation chromatography. Examples described in Ref 23 show coatings having typical elongations of 80 to 150%. In addition, coatings made from the polyesters showed durability superior to that of some polyurethane coatings. These results indicate that molecular weight of the polyol is a factor in producing useful elastomeric coatings.

The above discussion of condensation polymers is intended to show the characteristics necessary to achieve elastomeric properties. These include polyurethane linkages, a mixture of low-T_g and high-T_g polymeric materials, a minimum of branching (as defined by the content of compounds having functionality of 3 or greater), and relatively high molecular weight. With respect to the last characteristic, it would appear that high-solids elastomeric coatings cannot be formulated, because they would require the use of low-viscosity, low-molecular-weight material. However, high-solids elastomeric coatings based on condensation polymers are described in a number of patents (Ref 24, 25, 26). Hard polyester polyols of low molecular weight are combined with soft polyurethane polyols of a defined molecular weight and an aminoplast or polyisocyanate curing agent.

The hard polyester polyol is characterized by its molecular weight, content of cyclic moieties, and hydroxyl functionality. The molecular weight of the polyester polyol is greater than 300, but usually less than 1000, to achieve the highest possible solids contents in the coating formulation. The hydroxyl equivalent weight is inversely proportional to the molecular weight and is generally kept low, approximately 200, to ensure adequate hardness characteristics from the hard polyester in the cured film. The hydroxyl functionality is typically 2, although it can be raised somewhat for special applications. The most important feature of the hard polyester polyol is the content of cyclic moieties present. These cyclic moieties can be either aliphatic or aromatic, although the aliphatic are preferred to achieve maximum flexibility. The cyclic moieties help to provide adequate hardness from the polyester polyol. Thus, in a typical example, 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate is reacted with hexahydrophthalic anhydride to give a polyester polyol with a molecular weight of 544, a hydroxyl equivalent weight of 267, and a cyclic content of 27 wt%. The soft polyurethane polyol is prepared from a low-T_g polyol such as polycaprolactone or poly(oxytetramethylene)-glycol and a diisocyanate. The molecular weight of this material can be as low as 2000 or as high as 20,000, depending on the degree of flexibility required. The higher the molecular weight, the more flexible the coating becomes. These materials can be cured with melamine formaldehyde resin or polyisocyanate to obtain high-solids coatings with good durability and flexibility.

Alexander et al. (Ref 27, 28) describe the use of linear polyurethanes in combination with a hydroxyl-containing, urethane-modified polyester. In the specific examples given, a low-molecular-weight urethane diol is prepared and is subsequently reacted with other diacids, glycols, and polyols to give a relatively high-hydroxyl-containing material. The advantage of this procedure for preparing hydroxyl-containing urethanes is that it allows one to incorporate a high level of urethane linkages while avoiding gellation. It is proposed that the increased number of urethane linkages leads to a greater degree of flexibility. The hydroxyl-containing, urethane-modified polyester is relatively low in molecular weight, making it suitable for high-solids coatings, and the linear polyurethane is high enough in molecular weight to provide adequate flexibility. These materials are curable with melamine formaldehyde resin or polyisocyanate to give coatings with excellent elongation and weathering resistance.

Chang et al. (Ref 29) have described high-solids coating compositions that do not need higher-molecular-weight polyurethanes to achieve adequate flexibility. The polyol of this invention is characterized as above, by its content of cyclic moieties necessary for good hardness and durability, its hydroxyl content, and its urethane content. A representative composition involved the preparation of a polyester from neopentyl glycol, 1,6-hexanediol, and hexahydrophthalic anhydride. The polyester was subsequently modified with trimethylhexamethylene diisocyanate, resulting in a urethane-modified polyester. The resin was formulated into a coating composition with melamine formaldehyde resin that produced a paint with good hardness and moderate flexibility.

Elastomeric coatings cured with melamine formaldehyde are generally susceptible to environmental etching. A patent by Stephenson (Ref 30) describes compositions that have improved resistance to environmental etching. The coating compositions comprise a polyester, a silane-containing acrylic, a silsesquioxane (Fig. 2), and a melamine formaldehyde curing agent. The polyester portion of the formulation is very similar to the types of polyesters described above for the lower-solids elastomeric coatings. The silane-containing acrylic is a copolymer of standard acrylic monomers and an acrylatosilane such as g-acryloxypropyltrimethoxy silane. These are generally known in the art, and although the function of this polymer is not stated in the patent, it is presumed that it is necessary for some interaction with the silsesquioxane. The silsesquioxane is the key ingredient; coatings prepared with this additive show significantly improved acid etch resistance compared to controls that contain no silsesquioxane additive, without any compromise of other elastomeric coating properties except recoat adhesion. This drawback would be significant in a commercial application.

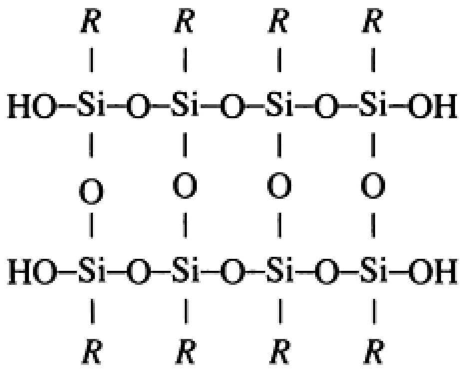


Fig. 2 Silsesquioxane used by Stephenson (Ref 30) to improve resistance to environmental etching

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References cited in this section

18. W.H. Chang and M.E. Hartman, U.S. Patent 3,954,899, May 1976
19. W.H. Chang, R.L. Scriven, and P.J. Prucnal, U.S. Patent 3,962,369, June 1976
20. M. Guagliardo, U.S. Patent 4,423,179, Dec 1983
21. W.H. Chang and M.E. Hartman, U.S. Patent 3,912,790, Oct 1975
22. S. Porter, Jr., R.L. Scriven, W.H. Chang, and J.B. O'Dwyer, U.S. Patent 4,154,891, May 1979
23. R.M. Piccirilli, W.H. Chang, D.T. McKeough, and S. Porter, U.S. Patent 4,205,115, May 1980
24. S. Porter, Jr., R.M. Piccirilli, W.H. Chang, J.B. O'Dwyer, and K.W. Lee, U.S. Patent 4,410,667, Oct 1983
25. R.M. Piccirilli, W.H. Chang, S. Porter, Jr., J.B. O'Dwyer, and K.W. Lee, U.S. Patent 4,410,668, Oct 1983
26. R.M. Piccirilli, W.H. Chang, S. Porter, Jr., J.B. O'Dwyer, and K.W. Lee, U.S. Patent 4,419,407, Dec 1983
27. D.J. Alexander, K.R. Kurple, and P.I. Kordomenos, U.S. Patent 4,524,192, June 1985
28. P.I. Kordomenos, K.R. Kurple, and D.J. Alexander, U.S. Patent 4,588,787, May 1986
29. W.H. Chang, R.R. Ambrose, D.T. McKeough, S. Porter, Jr., and D.R. Eslinger, U.S. Patent 4,540,766, Sept 1985
30. M.A.S. Stephenson, U.S. Patent 5,182,174, Jan 1993

Vapor Curing Systems

The above discussion has centered on polyols suitable for use with melamine formaldehyde resin or polyisocyanates. These two means of curing elastomeric coatings are the overwhelming choice for painting of fascia, bumpers, and other flexible automotive components. One other means of curing paint for elastomeric substrates that has not received much attention is vapor permeation curing, which offers the advantage of much lower baking temperatures, even as low as room temperature. Its disadvantage is the requirement of vaporous tertiary amine catalyst, which may be difficult to control in a production situation. Nevertheless, this coating technology can provide some very useful elastomeric coatings.

A good example is described in a patent by Blegen (Ref 31). In this case, a polyester is blended with a polyisocyanate, and the coating composition is applied to a suitable substrate. The film is then cured by exposure to tertiary amine vapor in an appropriate curing chamber. Cure times are as low as 20 to 60 s at room temperature. The polyester is unique in that it uses phenolic end groups, which apparently enhance the cure. A useful material for introducing the phenolic end groups is phydroxyphenylacetic acid, which is added at the very end of the polyesterification process. The coatings in the patent are reported to have good solvent resistance and excellent flexibility, as indicated by reverse impact testing.

In another example of amine vapor catalysis, Nahas et al. (Ref 32) made use of an amine functional acrylic in combination with polyisocyanate. An acrylic polymer was prepared from 4-vinyl pyridine, styrene, ethyl methacrylate, lauryl methacrylate, and hydroxyethyl acrylate. This polymer was blended with a polyisocyanate and cured for 4 min in the presence of vaporous dimethylaminoethanol. The resultant film was tough and flexible, whereas a film prepared from a similar acrylic polymer without the 4-vinyl pyridine did not cure at all. Obviously the extremely short cure times associated with amine vapor cure seem quite advantageous, but that has not offset difficulties associated with working with vaporous amines.

References cited in this section

31. J.R. Blegen, U.S. Patent 4,374,181, Feb 1983

32. R.C. Nahas and C.H. Strolle, U.S. Patent 4,713,265, Dec 1987

Water-Based Systems

Water-based coatings for elastomeric substrates have only recently begun to see commercial use, in particular as basecoats for use with solvent-based clearcoats. However, the literature is abundant with references to water-based polymers, particularly polyurethanes, that have excellent elastomeric properties. To cover all of these references adequately would require a review article in itself. However, discussion of one patent can describe the general theme.

Scriven et al. (Ref 33) describe water-based polyurethanes that are useful as elastomeric coatings. In this case the now fairly classical polyurethane is prepared from a soft, low-T_g, long-chain diol; a low-molecular-weight, short-chain diol; a short-chain, carboxylic-acid-containing diol; a diisocyanate; and a chain extender, which is usually some sort of diamine. Specifically, an isocyanate-terminated prepolymer is prepared in a water-miscible solvent, and then this solution is added to water that contains a neutralizing amine and a chain-extending amine. The isocyanate prepolymer contains the long- and short-chain polyols as well as the acid-containing diol. Particularly useful as the acid-containing diol is dimethylolpropionic acid (Fig. 3), which provides carboxyl groups for neutralization with amine to render the material water-dispersible.

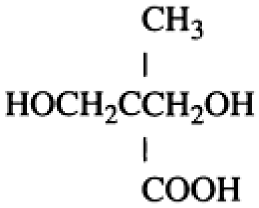


Fig. 3 Dimethylolpropionic acid, used to make polyurethane water-dispersible

The carboxylic acid group in this material is sufficiently unreactive toward isocyanate that it can be introduced into the polymer backbone while the prepolymer is being formed. The prepolymer is relatively low in molecular weight, but after

chain extension in water it becomes very high in molecular weight. The chain extension in water takes place almost exclusively with amine, because amine is about 10,000 times more reactive with isocyanate than water. Water-based polyurethanes prepared in this fashion are fairly common now, and because of their high molecular weight, they can be used as lacquers or cured with melamine formaldehyde resin.

At present, other water-based systems are being developed for use in elastomeric coatings, but they are still proprietary and will not be discussed here. However, the reader is referred to the review by Piccirilli (Ref 34) for a discussion of the idiosyncrasies in application of water-based coatings.

References cited in this section

33. R.L. Scriven and W.H. Chang, U.S. Patent 4,066,591, Jan 1978
34. R.M. Piccirilli and R. Pelo, "Waterbase Coatings for Plastics," paper presented at Finishing Automotive Plastics Conference, SME, Dec 1993

Coatings for Thermoplastic Olefins

The use of thermoplastic polyolefin (TPO) for exterior automotive parts has grown dramatically in recent years due to its low cost, low density, wide range of moduli, excellent appearance, and recyclability. However, due to its low surface energy, a pretreatment is required for good paint adhesion. Most TPOs have a total surface tension of about 30 dynes/cm, with a polar contribution of less than 3 dynes/cm. Although plasma or flame treatment of TPO can increase surface tension (Ref 35) and result in good adhesion, adhesion-promoting organic coatings are the pretreatments most often used in North America. Adhesion promoters are typically low-solids (5 to 10%), solvent-based coatings that contain chlorinated polypropylene. They are applied to power-washed or vapor-degreased substrates at low film thickness (5 to 10 μm) prior to priming and/or topcoating. Adhesion is provided by the chlorinated polypropylene. Other polymers have been reported to provide good adhesion to TPO, but they apparently have not found widespread use (Ref 36, 37, 38, 39, 40).

The chemistry and properties of chlorinated polypropylene have been described by Fujimoto (Ref 41). Chlorine content and crystallinity are key parameters that must be balanced to achieve sufficient solvent solubility and adhesive strength. The base polymer is isotactic poly-propylene. As the chlorine content of the polypropylene increases, the solvent solubility increases and the melting point and adhesive strength decrease due to lower crystallinity. A melting point minimum is reached at 20 to 30% Cl. Above this minimum, the softening point increases as the polymer becomes more amorphous. Although adhesive strength is higher at low chlorination levels, the polypropylene must contain enough chlorine to be soluble in organic solvents, which are used either to reduce the coating viscosity for spray application or to promote film formation following application. This balance is typically achieved with 20 to 30% chlorination.

Waddington and Briggs (Ref 42) suggest that chlorinated polypropylene promotes adhesion by diffusing into the substrate and forming a chain-entangled interface between the substrate and the adhesion promoter. These researchers used secondary ion mass spectroscopy and x-ray photoelectron spectroscopy to study the peeling failure between an adhesion promoter and two grades of TPO: one that exhibited strong adhesion and one that exhibited weak adhesion. Chlorine was detected on the surface of the TPO that exhibited strong adhesion, but not on the surface of the TPO that exhibited weak adhesion. In a separate experiment, the researchers coated the two grades of TPO with adhesion promoter and measured the amount of chlorine at the air interface of the adhesion promoter. Lower levels of chlorine were found over the TPO grade that exhibited better adhesion. This depletion of chlorine supports the theory that chlorinated polypropylene diffuses into the TPO. Also consistent with a diffusion mechanism is the improved adhesion, presumably due to increased mobility, that has been found when levels of rubber in TPO are increased (Ref 43).

Chlorinated polypropylenes are often modified for use in adhesion promoters. Each of the modifications described in the list below was intended to improve performance in some of the following key areas: adhesive strength, fuel resistance, humidity resistance, compatibility, and hardness. The first step is often to free radically graft acid or anhydride functionality onto the backbone. Maleic anhydride is commonly used at levels of less than 10 wt%. For example:

- Urata et al. (Ref 44) grafted maleic anhydride onto polypropylene using di-tert-butyl peroxide as an initiator. Following chlorination, the anhydride groups were partially reacted with a diepoxide such as Epon 828 to form a resin that could be blended with additional diepoxide to form a cross-linkable

coating with good properties.

- Martz et al. (Ref 45) grafted maleic anhydride onto chlorinated polypropylene, then reacted the anhydride with a monohydric alcohol to form an esterified polymer with acid functionality. The polymer was then reacted with an excess of diepoxide to form an ungelled modified chlorinated polyolefin.
- Asato et al. (Ref 46) grafted maleic anhydride onto a chlorinated polypropylene, then esterified all of the carboxylic acid functionality. This polymer was blended with a polyurethane polyol to form a composition with good properties over nonpolar and polar substrates.
- Kinosada et al. (Ref 47) modified chlorinated polypropylene by reacting it with maleic anhydride and acryl- or methacryl-modified hydrogenated polybutadiene.
- Frey et al. (Ref 48) reacted a hydroxy amine with an anhydride functional chlorinated polypropylene to form an imidized polymer.
- Ashihara et al. (Ref 49, 50) did not graft maleic anhydride, but instead improved properties by copolymerizing acrylic oligomers, acrylic monomers, and polydienes with chlorinated polypropylenes.

Each of the above modifications led to some improvement in the performance of the adhesion promoter, but it must be realized that the key ingredient for adhesion is the chlorinated polyolefin. Water-based adhesion promoters for TPO are only now becoming available. As patents are issued and more publications become available, we will learn more about the vehicles that have been developed for water-based adhesion promoters for TPO.

References cited in this section

35. R.A. Ryntz, *J. Coatings Technol.,* Vol 63, 1991, p 63-68
36. J. Mayumi et al., European Patent Application EP 193126A1, 1985
37. T. Ito, M. Mogami, and K. Kobayashi, European Patent Application EP 226387A2, 1987
38. A.J. Kielbania, European Patent Application EP 18847 (1980)
39. C.H. Coney and J.R. Gossett, U.S. Patent 884,004, 1971
40. N. Miyazaki and T. Takayanagi, *Asahi Garasu Kenkyu Kokoku,* Vol 36 (No. 1), 1986, p 155-166
41. F. Fujimoto, *Paint & Resin,* Feb 1986, p 36-40
42. S. Waddington and D. Briggs, *Polymer Comm.,* Vol 32, 1991, p 506-508
43. E.J. West, *Polymers Paint Colour J.,* Vol 177, 1987, p 778-784
44. K. Urata and Y. Kurome, U.S. Patent 4,683,264, July 1987
45. J.T. Martz, J.B. O'Dwyer, and M.E. Hartman, U.S. Patent 4,997,882, March 1991
46. I. Asato, T. Nagatani, A. Inoue, and I. Fukuyama, U.S. Patent 5,030,681, July 1991
47. M. Kinosada, R. Orita, S. Tone, and T. Saito, U.S. Patent 5,135,984, Aug 1992
48. S.E. Frey, D.W. Magouyrk, A.J. Blankenship, P.J. Greene, and L.K. Johnson, U.S. Patent 4,954,573, Sept 1990
49. T. Ashihara, S. Tone, and R. Orita, U.S. Patent 5,130,373, July 1992
50. T. Ashihara, S. Tone, and R. Orita, U.S. Patent 5,143,976, Sept 1992

Porcelain Enameling

Technical Publications Committee of the Porcelain Enamel Institute, Inc.*

Introduction

PORCELAIN ENAMELS are glass coatings applied primarily to products or parts made of sheet steel, cast iron, or aluminum to improve appearance and to protect the metal surface. Porcelain enamels are distinguished from other ceramic coatings on metallic substrates by their predominantly vitreous nature and the types of applications for which

they are used. These coatings are differentiated from paint by their inorganic composition and coating properties. They are fused to the metallic substrate at temperatures above 425 °C (800 °F) during the firing process.

The most common applications for porcelain enamels are major appliances, water heater tanks, sanitary ware, and cookware. In addition, porcelain enamels are used in a wide variety of coating applications, including chemical processing vessels, agricultural storage tanks, piping, pump components, and barbecue grills. They also are used for coatings on architectural panels, signage, specially executed murals, and substrates for microcircuitry. Porcelain enamels are selected for products or components where there is a need for one or more special service requirements that porcelain enamel can provide. These include chemical resistance, corrosion protection, weather resistance, abrasion resistance, specific mechanical or electrical properties, appearance or color needs, cleanability, heat resistance, or thermal shock capability.

Note

* John C. Oliver, Consultant to the Porcelain Enamel Institute, Inc. (Project Chairman); Douglas D. Giese, G.E. Appliances (Co-Chairman); Jeffrey F. Wright, Ferro Corp. (Co-Chairman); Ronald L. Allen, Ronalco, Inc.; Terry Conrad, Amana/Raytheon Corp.; John K. Cook, Chi-Vit Corp.; Ted Furr, Bethlehem Steel Corp.; Andrew Gordon, U.S. Steel, USX Corp.; Bernard L. Hall, Jr., JennAir/Maytag Co.; Michael Horton, Industrial Heating and Finishing Co.; William Huyser, Mapes & Sprowl Steel, Ltd.; Robert J. Long, American Porcelain Enamel Co.; Anthony R. Mazzuca, Miles, Inc.; Herbert Oliveira, Nordson Corp.; Arnold Preban, Inland Steel Co.; Charles R. Rarey, LTV Steel Co.; Donald R. Sauder, Porcelain Enamel Institute, Inc.; Narayan M. Sedalia, Whirlpool Corp.; Jeffrey Sellins, Magic Chef/Maytag Co.; Lester N. Smith, Porcelain Consultants, Inc.; Larry L. Steele, Armco Steel Corp.; Ted J. Wolowicz, G.E. Appliances

Types of Porcelain Enamels

Porcelain enamels for sheet steel and cast iron are classified as either ground-coat or cover-coat enamels. Ground-coat enamels contain metallic oxides, such as cobalt oxide and/or nickel oxide, that promote adherence of the glass/enamel to the metal substrate. Cover-coat enamels are applied over fired ground coats to improve the appearance and properties of the coating. Also, cover-coat enamels may be applied over unfired ground coats, with both coats being fired at the same time (i.e., two-coat/one-fire systems). Cover coats may also be applied directly to properly prepared decarburized steel substrates. The color of ground coats is limited to various shades of blue, black, brown, and gray. Cover coats, which may be clear, semiopaque, or opaque, may be pigmented to take on a great variety of colors. Colors may also be smelted into the basic coating material. Opaque cover coats are usually white.

Porcelain enamels for aluminum are normally one-coat systems. They are applied only by spraying. When two coats are desired, the first coat can be any color. Frits for porcelain enamels for aluminum are usually transparent and may be colored and opacified with inorganic pigments to produce the desired appearance.

Frits for Porcelain Enameling

The basic material of the porcelain enamel coating is called frit. Frits are smelted complex borosilicate glasses that are produced by quenching a molten glassy mixture. Frits generally are compounded from 5 to 20 or more components, which are thoroughly mixed together and melted into a glassy system. The molten glass is then quenched to a friable (easily broken up) condition by being either poured into water or rolled into a thin sheet between water-cooled rolls. When quenched in water, the frit is dried before use. When quenched in sheet form by water-cooled rolls, the sheet ordinarily is shattered into small flakes by mechanical means before use or shipment. Because porcelain enamels are usually designed for specific applications, the compositions of the frits from which they are made vary widely. A number of compositions of frits for enamels for sheet steel, cast iron, and aluminum are discussed below; however, many variations of these compositions are used commercially.

Enamel Frits for Sheet Steel. All the frits for which compositions are given in Table 1 are classified as alkali borosilicates and are used as ground coats on sheet steel. One of the functions of ground-coat enamels is to promote bond to the steel substrate. The addition of cobalt oxide and/or nickel oxide promotes adherence to the substrate. Compositions differ, depending on the end use application of the enameled product. For example, acid resistance is obtained by the addition of titanium dioxide and high levels of silicon dioxide with a corresponding decrease in the boron level. Resistance of the enamel to alkalis or to water can be improved by adding zirconium oxide or aluminum oxide (usually as

zircon or alumina) to the frit while maintaining a high content of silicon dioxide. It is common practice to blend soft (low melting temperature), medium, and hard (high melting temperature) frits to obtain the maximum desired properties.

Table 1 Melted oxide compositions of frits for groundcoat enamels for sheet steel

Constituent	Composition, wt%			
	Regular blue-black enamel	Alkali-resistant enamel	Acid-resistant enamel	Water-resistant enamel
SiO_2	37.17	42.02	56.44	48.00
B_2O_3	22.21	18.41	14.90	12.82
Na_2O	18.44	15.05	16.59	18.48
K_2O	0.99	2.71	0.51	. . .
Li_2O	. . .	1.06	0.72	1.14
CaO	9.34	4.47	3.06	2.90
ZnO	. . .	. . .	. . .	. . .
Al_2O_3	4.53	4.38	0.27	. . .
ZrO_2	. . .	5.04	. . .	8.52
TiO_2	. . .	. . .	3.10	3.46
CuO	. . .	0.07	0.39	. . .
MnO_2	1.58	1.39	1.12	0.52
NiO	1.37	1.04	. . .	1.21
Co_3O_4	0.65	0.93	1.27	0.81
P_2O_5	1.15	0.68	. . .	0.20

Weather resistance has been shown to be a function of acid resistance. Porcelain enamels for use outdoors are made from various types of frits that produce the necessary acid resistance along with the specific color desired. Resistance to thermal shock and to high temperature is obtained by controlling the coefficient of expansion of the glass coating; this is accomplished by adjusting the frit composition and adding refractory materials, such as silicon dioxide, aluminum dioxide, and zirconium oxide, to the mill formula.

Cover coats for sheet steel are applied over ground coats or directly to properly prepared decarburized steel. Compositions of frits for cover-coat enamels are shown in Table 2. Electrostatic dry powder cover coats may be applied over an electrostatic dry powder base coat; then the entire two-coat/one-fire system is matured in a single firing. Electrostatic dry powder cover coats may also be applied over fired ground coats in a two-coat/two-fire process.

Table 2 Melted oxide compositions of frits for cover coat enamels for sheet steel

Constituent	Composition, wt%		
	Titania white enamel	Semiopaque enamel	Clear enamel
SiO_2	44.67	44.92	54.26
B_2O_3	14.28	16.40	12.38
Na_2O	8.27	8.67	6.55
K_2O	6.99	8.12	11.32
Li_2O	0.98	0.45	1.14
ZnO	. . .	0.74	. . .
ZrO_2	1.98	3.34	1.40
Al_2O_3	0.31	0.16	. . .
TiO_2	18.49	13.05	10.04
P_2O_5	1.32	0.88	. . .
MgO	0.5	. . .	. . .

Cover-coat enamels fall into three groups: clear, semiclear or semiopaque, and opaque. The clear frits do not contain high levels of titanium dioxide, and they remain clear when fired. The semiopaque frits are translucent and are used for light colors. The opaque frits, which contain high levels of titanium dioxide, become white upon firing.

Cover-coat enamels made from titanium-dioxide-opacified frits are generally quite acid resistant; even in amounts too small to provide any opacity, titania imparts acid resistance. For alkali resistance, zirconium oxide is a desirable constituent. Clear frits containing 8 to 11% titanium dioxide are used for strong to medium-strength colors. Semiopaque frits containing 12 to 15% titanium dioxide are used for medium-strength colors, and opaque frits containing 17 to 20% titanium dioxide are used for pastel colors.

Enamel Frits for Cast Iron. Compositions of frits for enamels for cast iron vary, depending on whether the frit is applied by the dry process or by the wet process (Table 3). Dry-process enamels are commonly used for large cast iron plumbing fixtures, such as bathtubs and sinks, where the enamel's brilliance and ability to cover small surface irregularities in the casting itself are useful characteristics. Acid resistance is imparted to these enamels by reducing the alumina content, increasing silica, and adding up to about 8% titanium dioxide. Ground coats are normally used to fill surface voids in castings. Ground coats for wet process enamels often are mixtures of frit, enamel reclaim, and refractory raw material used at very low application weight. Ground coats for the dry process method are applied by the wet process and are fused in thin, viscous coatings that protect the casting surface from excessive oxidation while it is heated to fusing temperature.

Table 3 Melted oxide compositions of frits for enamels for cast iron

Constituent	Composition, wt%				
	Groundcoats		Cover coats		
	Lead-bearing	Non-lead-bearing	Zirconium-opacified[a]	Titania-opacified[a]	Titania-opacified[b]
SiO_2	77.7	63.4	28.0	51.4	44.80
B_2O_3	6.8	10.9	8.8	9.6	13.14
Na_2O	4.3	7.1	10.0	10.1	6.48
K_2O	. . .	2.4	4.1	3.0	7.67
PbO	4.0	. . .	17.8	. . .	0.94
CaO	. . .	0.6	8.7	1.9	0.55
ZnO	. . .	. . .	6.1	0.9	. . .
Al_2O_3	7.2	15.1	4.5	2.1	. . .
Sb_2O_3	. . .	. . .	. . .	. . .	19.74
ZrO_2	. . .	. . .	6.1	. . .	1.64
TiO_2	. . .	. . .	. . .	18.4	. . .

F_2	. . .	0.5	5.9	2.6	5.04

(a) For dry process.

(b) For wet process

Enamel Frits for Aluminum. Enamel frits for aluminum are usually based on lead silicate or on cadmium silicate, but they may also be based on phosphate, vanadium, or barium. Table 4 gives the compositions of some frits for aluminum. Enamels for aluminum have a high gloss, good acid weather resistance, and good mechanical properties. They melt at relatively low temperatures.

Table 4 Melted oxide compositons of frits for enamels for aluminum

Constituent	Composition, wt%		
	Lead-base enamel	Non-lead-base enamel	Barium enamel
PbO	14-45	. . .	. . .
SiO_2	30-40	30-40	25
Na_2O	14-20	20-25	20
K_2O	7-12	7-11	25
Li_2O	2-4	3-5	. . .
B_2O_3	1-2	1-2	15
Al_2O_3	. . .	. . .	3
BaO	2-6	3-5	12
P_2O_5	2-4	2-4	. . .
F_2	. . .	. . .	. . .
TiO_2	15-20	15-20	. . .

Preparation of Enamel Frits

Frits for porcelain enameling are typically formulated and smelted by commercial frit manufacturers to meet the end use application requirements of their enamel shop customers.

Enamel shops using the wet application process normally receive their frit from their frit manufacturer in 100 lb bags. At the enamel plant, the frit is ground in a ball mill to prepare it for application to fabricated parts. The milling operations are described under the section "Grinding and Blending," which follows. Today most frit manufacturers are able to supply premilled, ready-to-use frit materials for wet application systems at plants not desiring to handle the milling operations at their facilities.

Porcelain enamel may also be applied to sheet steel components using the electrostatic dry spray application method. Frits for electrostatic dry application are ground without water by the frit manufacturer and are shipped to the porcelain enamel plant in a ready-to-use form. Small amounts of proprietary additives are included by the frit manufacturer during grinding to aid in electric charge retention during application and firing. Particle size is fitted to the appropriate level for each particular application. (See the section "Electrostatic Dry Powder Spray Process on Steel" in this article and Porcelain Enamel Institute Bulletin P-300, "Electrostatic Porcelain Enamel Powder Applications.")

Grinding and Blending. In the wet application method, porcelain enamel is applied as a suspension of finely milled frit in water. The frit is reduced to a fine particle size in the ball milling operation. For milling of the porcelain enamel material, the ball charge should occupy 50 to 55% of the volume of the mill. After loading the frit and mill additions such as clay, bentonite, electrolytes, and coloring oxides into the mill, the water is added. The mill is allowed to "grind" for a specific length of time in order to achieve the recommended fineness.

The recommended fineness of various types of porcelain enamels for sheet steel, cast iron, and aluminum is shown in Table 5. Typical end uses for porcelain enamels and the required service criteria are shown in Table 6.

Table 5 Fineness of various types of porcelain enamels for sheet steel, cast iron, and aluminum

Type of enamel	Milled fineness, % on 200-mesh screen[a]
Sheet steel	
Ground coat	4-9
Cover coat	
Non-acid resistant	4-8
Titania, acid resistant	0.5-3.0
Colored, non-acid resistant	0.5-5.0
Colored, acid resistant	0.5-3.0
Wet electrostatic	1-6[b]
Dry powder, electrostatic	0-6

Cast iron	
Ground coat	0.5-4.0
Wet process cover coat	3-6
Dry process	60-80[c]
Aluminum	
Ground and cover coats	0.2-1.5[b]

(a) Percentage of washed and dried wet-milled enamel sample remaining on 200-mesh screen.

(b) Percentage on 325-mesh screen, which replaces the 200-mesh screen in standard fineness test.

(c) Through a 200-mesh screen, dry test

Table 6 Typical end uses and required service criteria

Product	**Service criteria**
Wet process and dry powder, electrostatic	
Architectural panels	Acid and weather resistant
Chemicalware	Very acid resistant
Cookware	Acid and thermal shock resistant
Heaters and heat exchangers	Thermal shock resistant
Laundry units	
Exteriors	Alkali resistant
Interiors	Alkali resistant
Oven liners	

Conventional	Acid resistant
Pyrolytic	Acid and thermal shock resistant
Ranges	
Exteriors	Acid resistant
Top	Acid and thermal shock resistant
Grates and burners	Acid and thermal shock resistant
Reflectors, electric light	High reflectance, white
Refrigerators	Acid resistant
Sanitary ware, sheet steel	Acid resistant
Signs	Acid and weather resistant
Water heater tanks	Water resistant
Dry process	
Sanitary ware, cast iron	Acid resistant
Chemicalware	Very acid resistant

The enamel slip is unloaded either by gravity flow or by applying air pressure. Centrifugal or vibratory screening and magnetic separation of the slip as it is transferred from the mill to the storage tank is a recommended practice. To minimize contamination, separate mills should be used for grinding frits for ground coats, white cover coats, and colors. More complete information on ball milling is provided in Porcelain Enamel Institute Bulletin P-305, "Ball Mill Wet Grinding of Slips for Porcelain Enameling."

Premilled ready-to-use frit materials are available from frit manufacturers. These prepared products, are mixed and blended (blunged) by the enameler into a suitable enamel slip, using a high-speed blunger operating at 900 to 2000 rev/min.

Mill Additions. For sheet steel enamels, clays and electrolytes are used with frit to control the properties of the prepared porcelain enamel (slip) that is applied by the wet process. Refractory materials and pigments may be added to impart desired properties to the fired enamel. Table 7 lists some of the common mill addition materials used with wet process frits; also shown is the amount commonly used, along with the effect of each mill addition.

Table 7 Mill additions for wet-process enamel frits for sheet steel and cast iron

Additional material	Amount added, %	Effect of addition
Clay	2-8	Suspends glass; increases set; hardens bisque
Bentonite	0-0.5	Suspends glass; increases set; hardens bisque
Borax	0-0.75	Stabilizes suspension
Gum tragacanth	0-0.06	Hardens bisque
Alginates	0-0.06	Hardens bisque
Urea[(a)]	0-1	Reduces tearing
Sodium nitrite[(a)]	0-0.75	Increases set; reduces tearing
Magnesium carbonate	0-0.25	Increases set; moderately softens bisque
Potassium carbonate[(a)]	0-0.5	Hardens bisque; retards poppers; reduces tearing
Sodium aluminate	0-0.5	Increases set; stabilizes suspension
Potassium chloride[(a)(b)]	0-0.5	Increases set
Potassium nitrite[(a)]	0-0.75	Strongly increases set; reduces tearing
Potassium nitrate	0-0.06	Slightly increases set
Tetrasodium pyrophosphate[(a)]	0-0.33	Strongly decreases set
Zinc oxide	0-2	Fluxes enamel for lower firing temperature
Formaldehyde[(a)]	0-0.1	Prevents bacterial growth
Titanium dioxide	0-3	Increases opacity
Silica	0-15	Lowers gloss; increases resistance to chemicals and heat; increases refractoriness
Pigments	0-4	Produces desired color in fired enamels

Opacifiers	0-4	Produces opacity in fired enamels

(a) May be added to the slip after milling.

(b) Never used in direct-to-steel enamel slips

The soluble electrolytes that are highly alkaline, such as potassium carbonate and sodium aluminate, are responsible for flocculation of the clays. Flocculation is necessary to permit proper suspending action by the clays. Minor adjustments in the flow properties of the slip are made by varying the content of the clay and the electrolytes.

Mill additions for wet-process enamel frits for aluminum include boric acid, potassium silicate, sodium silicate, and other additives. These materials are used to control the wet suspension of the frits and to contribute to the characteristics of the fired enamel. Also, titanium dioxide is added to produce opacity, and inorganic pigments are added for the desired color.

Steels for Porcelain Enameling

There are a number of flat-rolled carbon steel products available today for porcelain enameling. The general categories are:

- Low-carbon enameling steels (enameling iron replacements)
- Decarburized steels
- Interstitial free steels
- Titanium-stabilized steels
- Common cold-rolled steels
- Common hot-rolled steels

Within each of these categories are products differing in chemical composition and/or method of production.

Aluminum killing and the steel industry's movement from ingot casting to continuous casting have added new sheet steel products for the porcelain enamel industry. At the same time, these industry changes have resulted in the gradual withdrawal of some long-time enameling-grade products from the market.

Low-Carbon Enameling Steels (Enameling Iron Replacements). For many years, enameling iron, a rimmed-ingot poured product with a low metalloid content, was used extensively for porcelain enameling. The enameling characteristics were excellent, with the caveat that the product required a separate ground coat before applying a cover coat. Because enameling iron is a rimmed steel, it cannot be continuously cast. The steel industry's movement to continuous casting has resulted in the recent withdrawal of the product from the market.

A number of highly serviceable enameling iron replacement products are now available for porcelain enameling. These aluminum killed steels have low carbon (0.02 to 0.04 wt%) and low manganese (0.15 to 0.30 wt%), along with 0.015 wt% P max, 0.015 wt% S max, 0.015 wt% Si max, and 0.03 to 0.07 wt% Al. Some contain a boron addition (0.006 wt% max) to aid in grain size control and to help improve resistance to enamel fishscale. The yield strength is 172 to 221 MPa (25 to 32 ksi), the tensile strength is 303 to 338 MPa (44 to 49 ksi), and the elongation is 38 to 46%.

Unlike the old enameling iron, these products do not require normalizing; they are either box annealed or continuously annealed. These processing changes result in steels that are more formable than their predecessors. Experience to date indicates that the enameling characteristics are similar to those of enameling iron, and these steels are being used in the same applications. They perform well with both ground-coat and two-coat/two-fire systems.

Decarburized Steels. The manufacture of fully decarburized sheet for direct-on cover coat enameling became practical following the development of the open coil annealing process. Different melting and teeming practices may be

used to produce decarburized sheets: ladle aluminum killed-ingot poured, and ladle aluminum killed-continuously cast. These aluminum killed products are not subject to the return of yield point elongation following temper rolling. As killed steels, the hot coiling off the hot strip mill eliminates the possibility of having deep drawability as measured by the *R* value (plastic strain ratio), but in stretch and plane strain conditions, the decarburized products are excellent performers.

Enameling characteristics for decarburized steels are excellent, and these steels are being used in all types of today's enamel systems. The low carbon content eliminates primary boiling and consequent defects such as black specks, pullthrough, and dimples caused by the evolution of carbon monoxide and carbon dioxide through the porcelain enamel coating during firing.

These steels have excellent resistance to warpage. They also exhibit good resistance to defects such as "fishscale" and ground-coat reboiling during firing of the cover coat, both of which are caused by the evolution of hydrogen gas. If overpickled using the acid etch/nickel deposition metal preparation method, ladle killed steels will tend to have a "gassy" enamel surface, and enamel adherence is likely to be substandard. Ladle killing with aluminum and continuously casting is becoming the predominant way to produce these steels. It is expected that all decarburized steels will soon be manufactured by this method.

Interstitial-free steels are products in which all of the carbon and nitrogen contained in them are combined with an alloying element. Titanium or niobium (columbium), or a combination of titanium and niobium additions, are used to fully stabilize the steel. Domestically produced interstitial-free steels contain from <0.008 to 0.020 wt% C, 0.15 to 0.25 wt% Mn, 0.06 to 0.15 wt% Ti, and 0 to 0.10 wt% Nb. Vacuum degassing is used to produce the very-low-carbon versions, whereas the higher-carbon version is controlled by the basic oxygen shop. The yield strength is 138 to 165 MPa (20 to 24 ksi), the tensile strength is 290 to 317 MPa (42 to 46 ksi), and the elongation is 41 to 45%.

These steels have superior formability, particularly deep drawability as measured by the *R* value, which is in the range of 1.8 to 2.0. This permits extremely deep draws to be made successfully.

These steels exhibit excellent strength retention after strain and firing, as well as good base metal sag properties. They do not exhibit stretcher strain and are nonaging and nonfluting. Because titanium can effect the development of ground-coat adherence, enamel systems should be optimized to ensure satisfactory adherence with these steels.

There are many specific applications in the appliance and plumbingware sector where these steels have proved to be valuable, especially where deep drawing is required. Also, these products can be produced by either ingot pouring or continuous casting, thereby ensuring their future availability.

Titanium-stabilized steels are a variation of interstitial free steels. These steels are popular for large panels where maximum flatness can be achieved because of the product's resistance to warpage. Not being vacuum degassed, these steels are somewhat higher in carbon content than interstitial free steels.

This carbon is stabilized as titanium carbide by the addition of titanium. Stabilization provides carbon boil resistance, a high after-fire strength, and excellent deep drawability as measured by the *R* value. The higher titanium carbide content increases yield strength and reduces overall ductility. These steels offer high-temperature strength and resulting warp resistance, and they are now being produced as continuous-cast products.

Common cold-rolled steels have been used for many years in the porcelain enamel industry. They have been typically rimmed-ingot poured steels, but they are now being produced as continuous-cast products. They typically contain 0.04 to 0.07 wt% C and 0.25 to 0.040 wt% Mn. For cold-rolled drawing-quality steels, yield strength is 193 to 220 MPa (28 to 32 ksi), tensile strength is 295 to 330 MPa (43 to 48 ksi), and elongation is 40 to 44%. Enameling of cold-rolled steels should be restricted to ground coats and to noncritical appearance components.

Cold-rolled steels may also be used for two-coat enameling, where appearance is less important than in such components as range tops and other exterior parts for major appliances. Because of the high tendency of cold-rolled steel to warp and to carbon boil during porcelain enameling, the use of this material is generally restricted to components for which appreciable distortion during firing can be tolerated, applications using a low enamel firing temperature, or parts where a greater metal thickness is provided to minimize warpage. Most authorities recommend that parts fabricated from cold-rolled steels be porcelain enameled on one side only to minimize fishscale defects.

Common Hot-Rolled Steels. Hot-rolled sheets have a high susceptibility to fishscaling when porcelain enameled, especially if both sides of the steel are coated. When the use of hot-rolled steels is necessitated by the thickness and/or strength requirements for a given application, such as for water heater tanks, porcelain enameling should be limited to only one side of the sheet. This permits hydrogen gas, which produces the fishscaling, to escape from the unenameled side of the sheet.

Steel plate, tubes, pipes, and rolled sections may be porcelain enameled for specific applications. Examples include low-alloy steel pipe and tubing that is fabricated and porcelain enameled (i.e., glass-lined) for chemical pressure vessels and for sewage treatment plant piping systems, and low-carbon hot-rolled steel sections that are enameled for use as architectural components. The sheet should be thick enough so that sagging is reduced to an acceptable level.

Factors in Selecting Steel

The most important factors in the selection of steel for porcelain enameling are enamelability, freedom from surface defects, formability, sag characteristics, strength, and weldability. The relative importance of each depends on the requirements of the finished product.

Enamelability. Oxidation of carbon in the steel during enamel firing is the source of the carbon monoxide that causes primary boiling of the enamel. A limited amount of such gas evolution can e tolerated in two-coat/two-fire porcelain enameling, because the ground-coat enamel has high fluidity and tends to heal over defects. Because primary boiling does not reoccur on subsequent firing, a defect-free cover coat can be obtained.

In direct-on cover-coat enameling, however, very little gas evolution can be tolerated. Therefore, it is important to select a steel that is relatively free of carbon or one that has the carbon stabilized by the addition of titanium or a combination of titanium and/or niobium. When the higher-carbon steels are being selected for porcelain enameling, surfaces must be free of large angular cementite (iron carbide) particles.

Surface Defects. It is imperative that the surface of the steel be free of defects such as deep scratches, pits, slivers, scale, and open laminations. These defects are particularly troublesome in steels that are used for direct-on cover-coat applications.

Jagged metal burrs along scratches can protrude through the ground-coat enamel. Oxidation of these burrs during firing can cause copperheads in the ground coat and blistering in the cover coat. Folded-over burrs, deep scratches, and surface laminations can entrap dirt, drawing compounds, or cleaning and pickling solutions, all of which promote the formation of blisters in the porcelain enamel during firing.

Formability. Sheet steels for porcelain enameling are available in conventional commercial-quality, drawing-quality, and drawing-quality special-killed grades for varying severity of draw. The steels are usually supplied with a light application of oil to minimize rusting. This is particularly important in systems where acid etching is not employed during metal preparation.

Sag Characteristics. Sag is the permanent deformation or creep of steel due to its own weight during enamel firing. The sag resistance of steel is related to its strength at elevated temperatures and to the temperature at which the steel starts to transform from ferrite to austenite on heating. In general, the higher the strength and the higher the transformation temperature, the better the sag resistance of the steel. Figure 1 is a plot of typical metal sag of different enameling steels as a function of temperature. Thickness of these steels was 0.89 mm (0.035 in.).

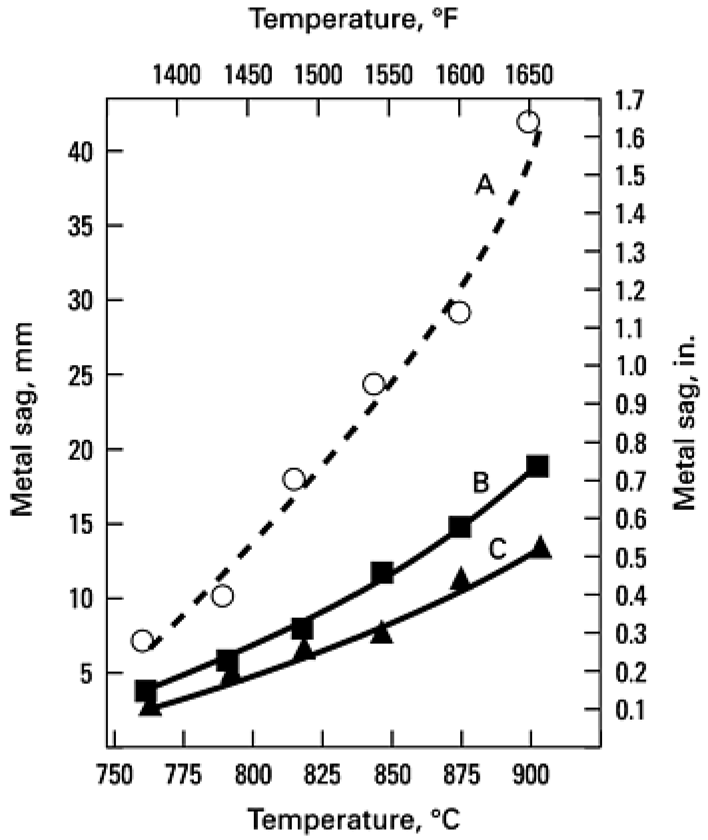


Fig. 1 Comparison of sag resistance of selected enameling steels. A, low-carbon enameling steels; B, decarburized steels; C, interstitial-free steels

Strength Retention. Some steels will exhibit critical grain growth and resulting loss of strength during the firing of the enamel coating 790 to 840 °C (1450 to 1550 °F) temperature range. Because the fired enamel coating is normally fractured when the base metal is strained beyond the elastic limit of 0.002 mm/mm (0.002 in./in.), the ability of a steel substrate to retain its strength after firing becomes an important factor when selecting steels for many service applications of the enameled component. In addition, the contour and thickness of the metal are other factors for consideration. Figure 2 shows the relative strength-after-firing characteristics of some commonly used enameling steels.

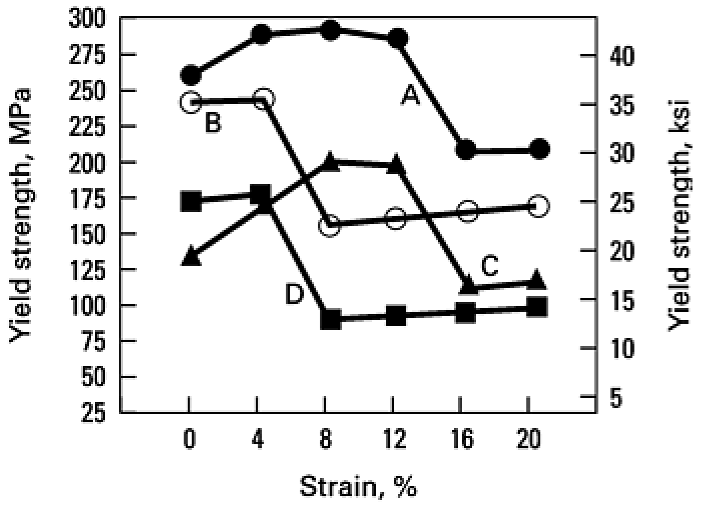


Fig. 2 Comparison of yield strength of four enameling steels after firing at 870 °C (1600 °F). A, low-carbon

enameling steels (drawing quality); B, low-carbon enameling steels; C, interstitial-free steels; D, decarburized

Weldability. Good welding characteristics are required for fabricated shapes. Welds must be free of inclusions, blowholes, and laminations.

Design of Metal Parts for Porcelain Enameling

The glasslike nature of porcelain enamel and the high firing temperatures used in its application impose limitations on the design of parts to be enameled. Proper design of each part is essential to ensure that finished work is within dimensional tolerances and has the durability for the intended service.

In general, the size of products or parts that can be porcelain enameled is limited only by the ability of fabricating and enameling facilities to accommodate their size. Table 8 indicates the maximum dimensions of workpieces that can be enameled in several types of conventional facilities.

Table 8 Maximum dimensions accommodated by enameling facilities

Type of enameling facility	Maximum dimensions of workpiece					
	Length		Width		Height	
	m	ft	m	ft	m	ft
Dial, small sign, or art	0.3	1	0.3	1	0.08	$\frac{1}{4}$
Range or laundry equipment	1.2	4	0.8	$2\frac{1}{2}$	1.2	4
Architectural; job shop	3.7	12	0.6	2	1.5	5
Special; chemical	18	60	4.6	15	4.6	15
Cast iron, dry process	1.8	6	0.9	3	0.8	$2\frac{1}{2}$

Steel Parts. The size relations for steel sheet given in Table 9 are recommended as a guide to ensure adequate flatness, rigidity, and sag resistance.

Table 9 Suggested sizes of steel sheet for adequate flatness, rigidity, and sag resistance

Sheet width	Maximum total area

mm	in.	m^2	ft^2
24-gage sheet			
150	6	0.05	$\frac{1}{2}$
305	12	0.3	3[(a)]
455	18	0.5	5[(a)]
22-gage sheet			
150	6	0.09	1
305	12	0.3	$3\frac{1}{2}$
455	18	0.5	6[(a)]
610	24	0.7	8[(a)]
20-gage sheet			
150	6	0.1	$1\frac{1}{2}$
305	12	0.5	5
455	18	0.7	8[(a)(b)]
610	24	0.9-1.4	10-15[(a)(b)]

(a) Should be embossed, flanged, or otherwise reinforced.

(b) All parts exceeding this area should be made from 18-gage 1.21 mm (0.0478 in.) or heavier thicknesses of steel sheet.

Distortion during firing is minimized by uniformity of stress and temperature during the cycle. Nonuniform thicknesses will heat at different rates and cause distortion and variations in enamel maturity. Specific aspects of design that should be considered are:

- Flatness requirements in a porcelain enameled part must be maintained at all processing stages. Wavy or

buckled areas in the original sheet, as well as those introduced in forming and handling, will persist in the fired part.

- Bend and corner radii should be at least 4.7 mm ($\frac{3}{16}$ in.). In drawn parts, the use of symmetrical embossed ridges and panels increases resistance to distortion caused by uneven residual forming stresses.
- Flanges increase strength and flatness, but they can cause irregular stresses in firing. Flanges on one side only may require welded braces. Flanges meeting at a corner must be welded and should not vary in depth by a factor of more than three.
- Cutouts should have round corners; when cutouts are located on flange edges, at least 6.3 mm ($\frac{1}{4}$ in.) of flange should remain.
- Welded lugs and ears for attachment and assembly result in double metal thickness. They should be of the same or lighter gage as the main part and as small as possible.
- Spot and seam welds also result in double metal thickness. Spot welds are difficult to enamel because of metal movement during firing and possible entrapment of solutions used in preparing the metal part for enameling. Spot welds must be at least 0.32 mm (0.0125 in.) in diameter to minimize compression failure. Seam welds should be flattened to prevent burrs, rough projections, and protruding edges, all of which enamel poorly.
- Fusion welds must be free of crevices and oxide seams. Weld spatter must be removed to avoid coating defects.
- Sharp edges are subject to burnoff of enamel when the iron oxide formed during firing exceeds the amount of iron oxide that is soluble in the coating. The tight, matte-finish layer that results is protective, but it may not meet appearance or severe corrosion requirements.
- Holes must be designed up to 1.5 mm ($\frac{1}{16}$ in.) oversize to allow for enamel buildup. To avoid sharp areas on the appearance side of punched holes, the holes may be extruded inward, allowing maximum coverage on the face side but intensifying the burnoff on the reverse side.
- Fasteners should be provided with flexible washers or gaskets to distribute stresses and prevent crazing of the enamel.
- Processing requires some means of support for handling, usually by brackets or flanges. Holes, which may be required for drainage of metal preparation solutions and excess enamel slip, may also be used.

Figures 3, 4, 5, and 6 illustrate guidelines for proper design. For further reference, see Porcelain Enamel Institute Bulletin P-306, "Design and Fabrication of Sheet Steel Parts for Porcelain Enameling."

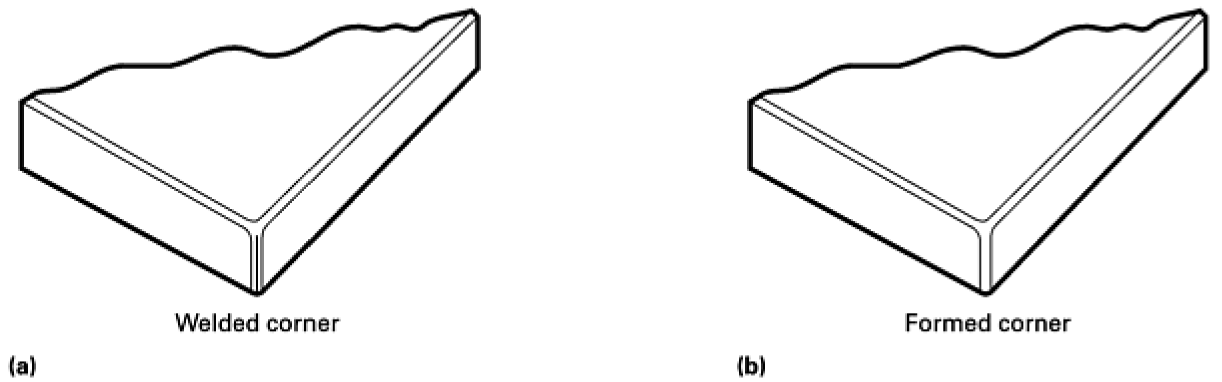


Fig. 3 Flange forming. (a) Flanges can be formed from blanks with notched corners, but they must be welded in the corner for strength, shape retention, and chip resistance. (b) Flanges can be formed with drawn shapes. Here, no welding is required.

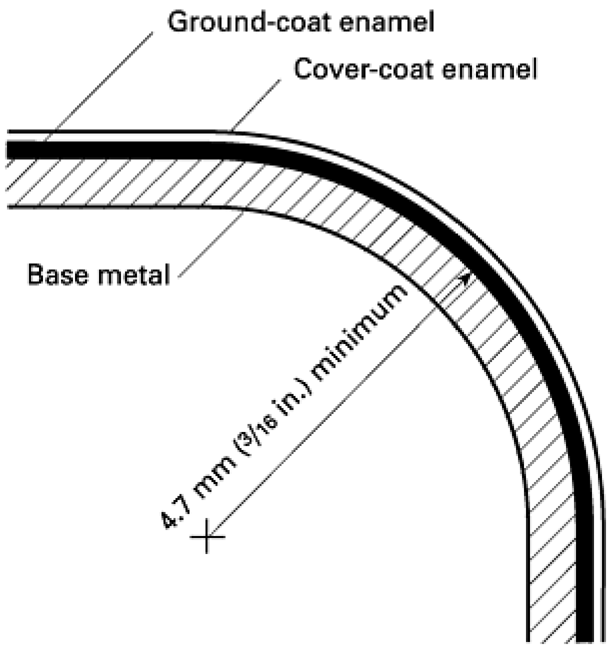


Fig. 4 Radius of curvature, two-coat enameling process. A minimum radius of 4.8 mm ($\frac{3}{16}$ in.) must be maintained at flanges, corners, and embossments to minimize assembly and field damage to parts coated by the two-coat enameling process.

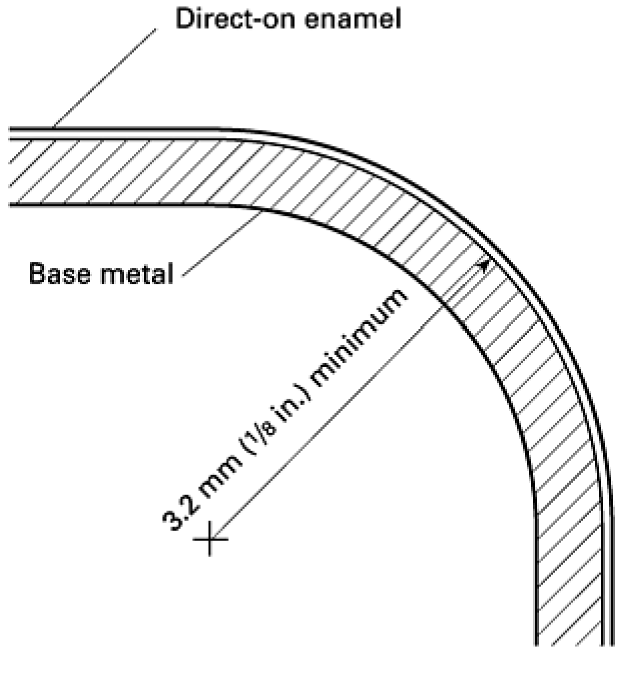


Fig. 5 Radius of curvature, one-coat enameling process. A minimum radius of 3.2 mm ($\frac{1}{8}$ in.) must be maintained at flanges, corners, and embossments to minimize assembly and field damage to parts coated by the one-coat enameling process.

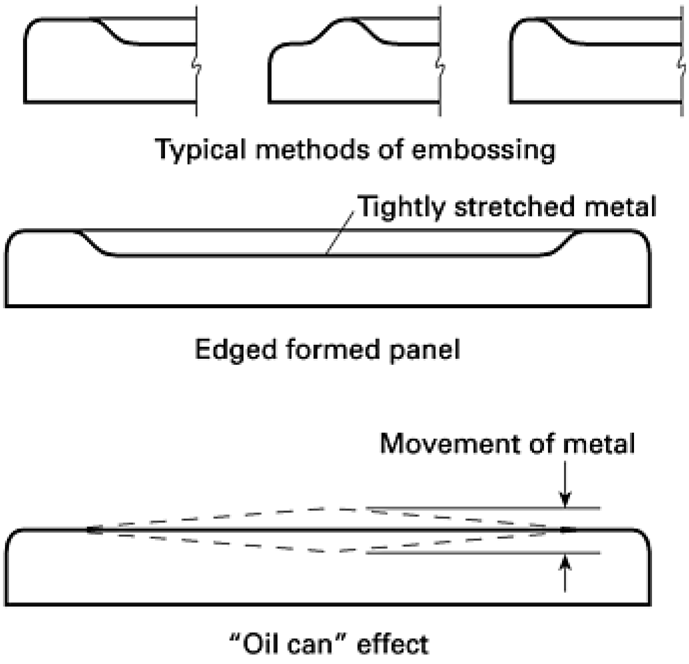


Fig. 6 Embossed panels. Panels may be embossed to increase strength of the part and to provide design relief for flat areas. Embossing also stretches the metal, thus reducing "oil canning." In embossing, an outside radius of 9.5 mm ($\frac{3}{8}$ in.) and an inside radius of 4.8 mm ($\frac{3}{16}$ in.) should be maintained for optimum enamelability and service life.

Cast Iron Parts. Uniformity of section, simplicity of design, and minimizing of lugs and braces are desirable characteristics for cast iron parts to be enameled. Radii of curved sections should be as generous as design limitations permit. The minimum radius may be 6.3 mm ($\frac{1}{4}$ in.) for decorative beading on a flat or slightly curved surface, or as large as 38 mm ($1\frac{1}{2}$ in.) for one of the components of a compound curve on a large casting.

Aluminum Parts. Because enamel ordinarily is applied to aluminum at only about half the thickness to which it is applied to steel, freedom from surface scratches, burrs, and irregularities is of double importance for the aluminum surface. Most shaping of aluminum is done before enameling, but the thin coating permits some bending, shearing, punching, and sawing of the part after it has been porcelain enameled.

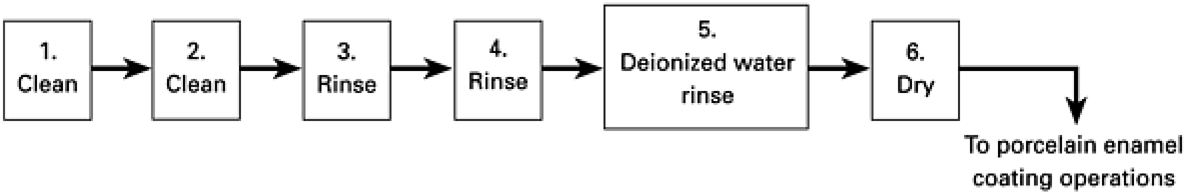
Surfaces to be enameled should have generous inside radii of not less than 4.8 mm ($\frac{3}{16}$ in.). Surfaces should have outside radii of not less than 1.6 mm ($\frac{1}{16}$ in.); 3.2 mm ($\frac{1}{8}$ in.) is preferred for both light and dark colors. Attachments should be welded to the unenameled backside of enameled heavy-gage aluminum sheet or extrusions. The visible metal surfaces must not be overheated; overheating causes the aluminum to blister and alters the color and gloss of the enamel. Welding can be done before enameling provided that the weld area is cleaned properly before coating.

Metal Preparation

The bond and appearance of porcelain enamel is heavily dependent on closely controlled cleaning of the metal surface. Complete removal of oil, drawing compounds, and other surface contaminants is essential. Steel may be prepared for porcelain enameling by the "clean only" method, and acid etch/nickel deposition process, or mechanical procedures.

Preparation of Steel for Porcelain Enameling

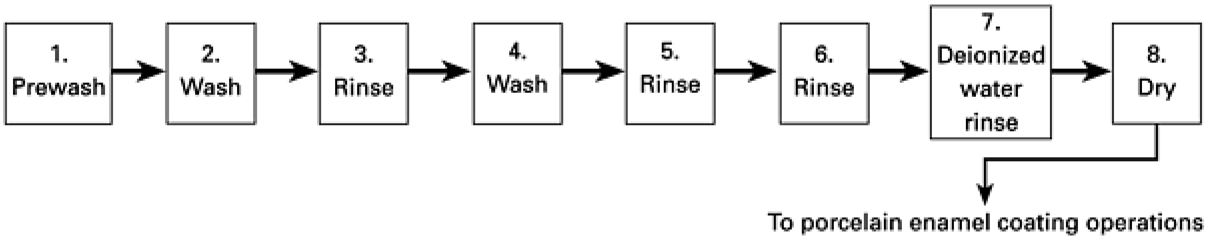
The "clean only " process has emerged in recent years as the dominant method for preparing steel components for porcelain enameling, especially for large-volume production using electrostatic dry powder application systems. Metal preparation using the "clean only" system requires at least the same amount of cleaning as is achieved using the acid etch/nickel deposition method, but no acid etching or nickel deposition is used. Benefits realized from using the "clean only" method include reduced operating costs, lower equipment costs, increased yield, reduced environmental problems, lower chemical usage, and reduced water consumption. Figures 7 and 8 illustrate the "clean only" cycle for both the spray process and the immersion process.



Stage	Solution composition	Temperature		Cycle time, min
		°C	°F	
1-Clean	Alkaline cleaner 30-60 g/L (4-8 oz/gal)	82-100	180-212	5-15
2-Clean	Alkaline cleaner 30-60 g/L (4-8 oz/gal)	82-100	180-212	5-15
3-Rinse	Tap water	49-71	120-60	1-2
4-Rinse	Tap water	Ambient	Ambient	1-2
5-Rinse[(a)]	Deionized water	Ambient	Ambient	$\frac{1}{2}$-1

(a) Deionized water rinse is required for two-coat/one-fire finish with excellent appearance

Fig. 7 "Clean only" metal preparation, immersion process

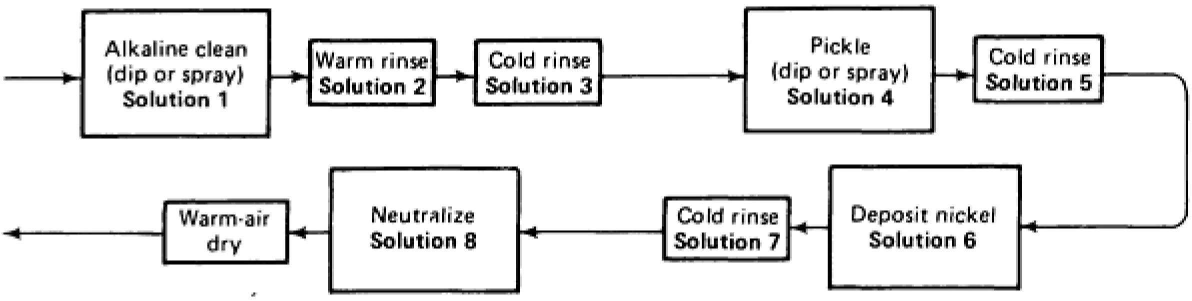


Stage	Solution composition	Temperature		Cycle time, seconds
		°C	°F	
1-Prewash	Tap water	Ambient to 71	Ambient to 160	30-60
2-Wash	Alkaline cleaner, 7.5-22.5 g/L (1-3 oz/gal)	60-71	140-160	60-90
3-Rinse	Tap water	60-71	140-160	30-60
4-Wash	Alkaline cleaner, 7.5-22.5 g/L (1-3 oz/gal)	60-71	140-160	60-90
5-Rinse	Tap water	Ambient to 71	Ambient to 160	30-60
6-Rinse	Tap water	Ambient	Ambient	30-60
7-Rinse[(a)]	Deionized water	Ambient	Ambient	10-30

(a) Deionized water rinse is required for a two-coat/one-fire finish with excellent appearance.

Fig. 8 "Clean only" metal preparation, spray process

In the acid etch/nickel deposition process, parts are placed on corrosion-resistant racks and dipped in or sprayed with a series of solutions. Mechanized equipment is required for high-production operations. The sequence of processing steps and the solutions used for the acid etch/nickel deposition method in production operations are indicated in Fig. 9. As is indicated in Stage 4, sulfuric acid is normally used to etch the metal. After drying at 93 to 150 °C (200 to 300 °F), the steel parts have a light straw color.



No.	Solution	Composition	Temperature		Cycle time, min	
			°C	°F	Dip	Spray
1	Alkaline cleaner[a]	Cleaner, 15-60 g/L (2-8 oz/gal)[b]	Ambient to 100[c]	Ambient to 212[c]	6-12	1-3
2	Warm rinse	Water	49-60	120-140	$\frac{1}{2}$-4	$\frac{1}{2}$-1
3	Cold rinse	Water	Ambient	Ambient	2-4	$\frac{1}{2}$-1
4	Pickle[d]	H_2SO_4, 6-8%	66-71	150-160	5-10	3-5
5	Cold rinse	Water, H_2SO_4[e]	Ambient	Ambient	$\frac{1}{2}$-4	$\frac{1}{2}$-1
6	Nickel-deposition[f]	$NiSO_46H_2O$, 5.6-7.5 g/L (0.75-1.0 oz/gal)[e]	60-82	140-180	5-10	4-6
7	Cold rinse	Water, H_2SO_4[e]	Ambient	Ambient	$\frac{1}{2}$-4	$\frac{1}{2}$-1
8	Neutralize	2/3 Na_2CO_3 and 1/3 borax, 0.60-2.10 g/L (0.008-0.28	49-71	120-160	1-6	1-2

(a) For spray cleaning, use a two-stage process.

(b) For spray cleaning, use 3.8 to 15 g/L (0.5 to 2.0 oz/gal).

(c) 60 to 82 °C (140 to 180 °F) for spray cleaner.

(d) Weight loss of metal is 3 to 5 g/m^2 (0.3 to 0.5 g/ft^2).

(e) Solution pH, 3 to 3.5, to prevent formation of ferric iron.

(f) Nickel deposit should be 0.2 to 0.6 g/m^2 (0.02 to 0.06 g/ft^2). Continuous filtration is commonly used to remove $Fe(OH)_3$.

Fig. 9 Ground-coat enameling, acid-etch/nickel-deposition process (dip or spray application)

When low-carbon decarburized steel is enameled in a direct-on cover-coat operation, parts must be etched to remove 11 to 22 g/m^2 (1 to 2 g/ft^2) of metal surface, and they must receive a nickel deposit of 0.9 to 1.3 g/m^2 (0.08 to 0.12 g/ft^2) of surface. Table 10 indicates modifications of the solutions and operating conditions for the acid pickling and nickel deposition cycles shown in Fig. 9 that have been used to provide increased metal removal and an increase in the amount of nickel deposited. Also, a ferric sulfate etching solution is sometimes used.

Table 10 Acid-etch and nickel-deposition solutions for preparing decarburized steels for direct-on cover coating

Solution[(a)]	Composition of solution	Operating temperature		Cycle time, min	
		°C	°F	Dip	Spray
Acid solutions[(b)]					
1	H_2SO_4, 6-8 wt%	71	160	15-30[(c)]	8-15[(c)]
2[(d)]	H_2PO_4, 17-20 wt%	60	140	4-8	2-5
3[(e)] First stage	Ferric sulfate[(f)], 5 wt%	65	150	2-4	$1\frac{1}{2}$-3
Second stage	H_2SO_4, 6-8 wt%	65	150	2-4	$1\frac{1}{2}$-3
4 Oxyacid	H_2SO_4, 6-9 wt%; $Fe_2(SO_4)_3$, 3-5 wt%; $FeSO_4$, 3-20 wt%	74	165	$1\frac{1}{2}$-4	$1\frac{1}{2}$-3
Nickel deposition solution[(g)]					

(a) Except for the use of these solutions, preparation entails processing as indicated in Fig. 9.

(b) Any of these solutions may be used in place of solution 4 in Fig. 9. Minimum metal removal required is 22 g/m^2 (2 g/ft^2) of metal.

(c) Cycle time may be reduced to that indicated in Fig. 9 for ground coats by oxidizing the metal 16 g/m^2 ($1\frac{1}{2}$ g of iron/ft^2) at 680 °C (1250 °F) in

an air atmosphere, or by blasting with sand or steel grit to remove metal prior to pickling.

(d) Equipment containing lead or Monel cannot be used.

(e) Equipment containing lead cannot be used.

(f) Convert ferrous to ferric by adding hydrogen peroxide, sulfuric acid, and water.

(g) Nickel deposit should be 0.6 to 1 g/m^2 (0.06 to 0.10 g/ft^2).

(h) pH of solution, 3.2 to 3.5. Sulfuric acid or sodium hydroxide is used to adjust pH. The addition of 0.3 to 0.8 g/L (1 to 3 g/gal) of sodium hypophosphite to solution will increase the rate of nickel deposition and permit the use of the lower end of the temperature range without excessive cycle time.

A modification of the above-described system, identified as oxyacid, is also used. Oxyacid etchant solution is a mixture of sulfuric acid and ferric sulfate. The sulfuric acid and the ferric sulfate etch the metal, producing ferrous sulfate. The ferrous sulfate is then oxidized to ferric sulfate in the presence of sulfuric acid. In this system, all of the reactions take place in only one etching tank.

Mechanical preparation requires abrasive blasting using steel shot or steel grit. Grit or shot blasting is used on parts designed without pockets or crevices and with configuration and thickness that permit blasting without distortion. Parts with flat areas should be fabricated from sheet steel thicker than 16-gage, 1.52 mm (0.0598 in.) to avoid excessive distortion when cleaned by this method.

Abrasive blasting is often used for preparing hot-rolled steel and parts that are to be enameled on one side only, as for water heater tanks. The process is also used for preparing large parts and parts having enamels with poor bonding characteristics. Before blasting, oil and drawing compounds may be removed by alkaline cleaning or by heating at 425 to 455 °C (800 to 850 °F) to burn off the organic contaminants.

Preparation of Cast Iron and Aluminum for Porcelain Enameling

Cast iron is prepared by blasting to remove adhering mold sand and the thin surface layer from chilled iron. Because the surface contains more combined carbon than is present in the remainder of the casting, this carbon-heavy layer must be removed to prevent excessive evolution of gas during firing of the enamel.

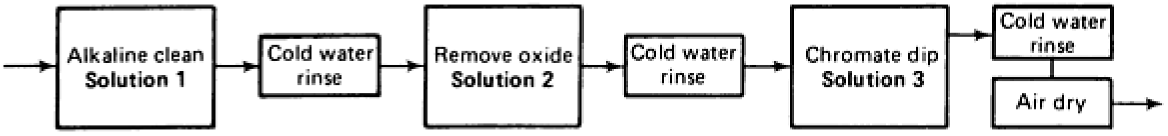
Quartz sand of nearly spherical grains, propelled by compressed air, is commonly used for abrasive cleaning of cast iron; however, steel shot, steel grit, and chilled cast iron grit propelled centrifugally from rotating wheels are generally used for cleaning sanitary ware. Zircon sand and fused alumina grit are used for special purposes.

After blasting, the casting should be inspected for cracks, sand holes, slag holes, blowholes, fins, and washes. Cracks and larger holes need to be filled by welding, and the welds require spot grinding to blend the area with the surrounding surface. Also, fins and washes must be removed by grinding. The repaired casting is blasted a second time prior to enameling. Small holes need not be repaired by welding; usually they can be filled with a ceramic paste after final blasting.

Cast iron parts should be enameled within a few hours after cleaning, especially during periods of high humidity; even a very thin layer of rust will reduce the adherence of the enamel. Parts that have rusted excessively can be reconditioned by being heated to a red heat, cooled to room temperature, and cleaned abrasively.

Aluminum. The preparation of parts made of heat-treatable aluminum alloys for porcelain enameling involves the removal of soil and surface oxide and the application of a chromate coating. Figure 10 shows the sequence of these surface preparation treatments and gives operating conditions. Final drying removes all surface moisture; drying must be

accomplished without contaminating the cleaned surface of the aluminum. Parts made of non-heat-treatable aluminum alloys or aluminum sheet require only the removal of soil, which can be done by alkaline cleaning or vapor degreasing.



No.	Type	Composition of solution		Operating temperature		Cycle time, min
		Constituent	wt%	°C	°F	
1	Alkaline cleaner[(a)]	[(b)]	[(b)]	60-82	140-180	2-5
2	Oxide removal	Chromic acid	3.5	82	180	3-10
		Sulfuric acid	18.0	. . .	. . .	. . .
3	Chromate dip	Chromic sulfate	0.2	Ambient	Ambient	1-6
		Potassium dichromate	14.4	. . .	. . .	. . .

(a) Vapor degreasing may be used instead of alkaline cleaning.

(b) Either inhibited or mildly etching (uninhibited) cleaners can be used.

Fig. 10 Process for preparing heat-treatable aluminum alloys for porcelain enameling

The Porcelain Enameling Process

Porcelain enamel may be applied to the base metal by either the wet process or the dry process. Wet process methods include manual spraying, electrostatic spraying, dipping, flowcoating, and electrodeposition (electrophoresis). Dry process methods are electrostatic dry powder spraying for application to sheet steel and, for application of the cover coat to cast iron, sprinkling the dry powder by means of a vibrating sieve onto the hot cast iron part.

The best method of application for a particular part is determined by quantity and quality requirements, the type of material being applied, units produced per hour, capital investment, labor cost, environmental considerations, and, ultimately, cost per part. Application techniques can be manual or mechanized. Manual application is necessary for parts having a variety of sizes and shapes that must go through the same enameling process system. Mechanization is essential for high-volume production of parts of the same or similar shape.

Wet-Process Porcelain Enameling of Steel

The prepared porcelain enamel (slip) may be applied to sheet steel using the wet process in a variety of ways.

Dipping is widely used as a method to apply the porcelain enamel, particularly when both sides of the parts require coverage. Dipping can be used for both ground-coat application and cover-coat application. It is performed by immersing the part in the prepared porcelain enamel slip, then withdrawing it and allowing the excess material to drain from the part. Sometimes it is necessary to rotate, tilt, spin, or shake complex shapes to ensure uniform coverage. In areas where excessive porcelain enamel slip is retained on the part after draining, the excess is removed with a siphon or a wiping device before the part is dried. In dipping, a wet coating thickness is applied to achieve a fired coating thickness of 50 to 125 μm (2 to 5 mils).

Automatic equipment is recommended when part configuration allows dipping and production volume warrants the investment. The rheology of the porcelain enamel slip can be better controlled if the dip tank is constructed with a double wall to allow the insertion of a heat exchanger to maintain the porcelain enamel slip at a uniform temperature. The dip tank walls should slope toward a central sump to facilitate recirculation and drainage from the tank.

Equipment to provide recirculation of the porcelain enamel slip consists of a diaphragm pump that continuously circulates the porcelain enamel slip through a magnetic separator and screens to remove iron particles and other foreign materials. The recirculation system helps maintain the consistency and uniformity of the porcelain enamel slip. AISI 300-series stainless steels are the preferred materials for the tank, piping, separators, and screens.

In flow coating, the prepared porcelain enamel slip is flowed onto the surface of the part. The process is especially applicable for high-volume continuous processing of parts requiring the same porcelain enamel coating. In automatic flow coating, the parts are placed on hangers at the proper angle for draining and carried by conveyor through the flow coating chamber. The porcelain enamel slip is pumped at a high volume, 570 L/min (150 gal/min), and low pressure, 70 to 105 kPa (10 to 15 psi) through a series of nozzles that are directed at various areas of the part to ensure complete coverage.

When flow coating a surface that must have a good appearance, such as the top of a kitchen range, it is necessary to incorporate a curtain of porcelain enamel slip near the exit of the flow coating chamber. This curtain, which is provided by flood plates, flows out the porcelain enamel slip into an even coating free of drain lines and splatter marks. On emerging from the flow coating chamber, flow-coated parts drain as they would in the dip method. Various devices can be added along the length of the conveyor to cause repositioning of the parts to provide a more even coating.

Another version of automatic flow coating involves the use of a constant-head tank to supply enamel slip at a constant velocity to headers and nozzles that flood parts with slip as they are conveyed through the flow-coat chamber. The advantage of this system is that the flow to the nozzles is constant and not subject to variations present in pumped systems.

Automatic flow coating is favored over hand dipping because it offers higher rates of production, improved coating quality, and reduced cost of the applied film. Control of the porcelain enamel slip and proper operation of the machine are important functions of flow coating. It is common practice to check the specific gravity and pickup of the porcelain enamel slip three or four times each hour. All parts of the flow-coating machine that come in contact with the porcelain enamel slip should be constructed of 300-series stainless steel.

Additional details on dipping and flow coating are available from Porcelain Enamel Institute Bulletin P-302, "Manual of Dipping and Flow Coating for Porcelain Enameling."

Spraying of the porcelain enamel slip is done primarily to achieve maximum appearance results and provide one-side coverage. It is also used for reinforcing enamel bisque and for making repairs on enameled surfaces. Spraying can be used for parts that are too large for hand or mechanical manipulation.

Figure 11 schematically illustrates equipment for the manual spray application of porcelain enamel slip. The prepared porcelain enamel slip is placed in the pressure feed tank and is constantly agitated to keep the material homogeneous. Regulated air pressure is applied to the pressure feed tank at 55 to 125 kPa (8 to 18 psi) to force the porcelain enamel slip through the fluid hose to the tip of the spray gun nozzle. Here, the slip is atomized by clean compressed air, regulated at 170 to 415 kPa (25 to 60 psi), and then directed to the part. The amount of air pressure required depends on the specific porcelain enamel slip and the shape of the part being sprayed.

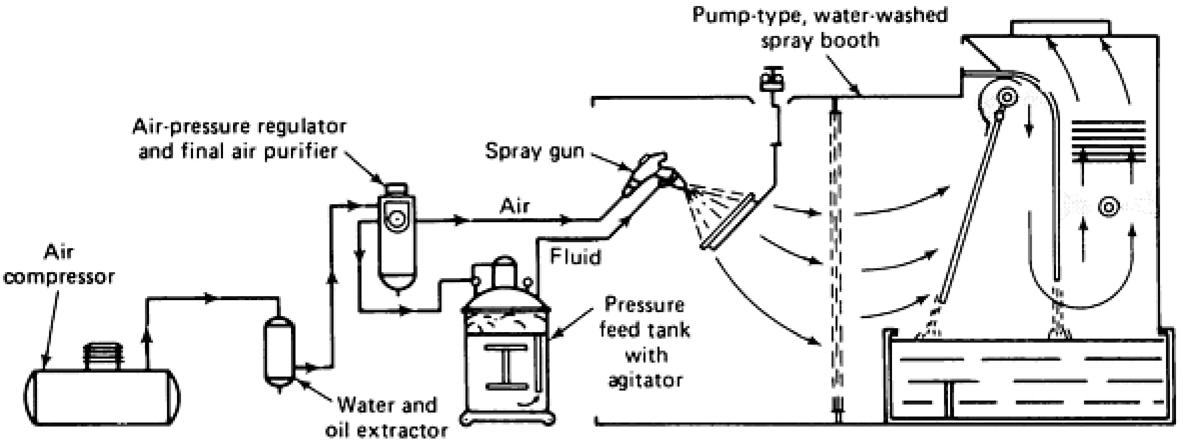


Fig. 11 Schematic of equipment for manual wet spray application

Wet electrostatic spraying is another method used to apply porcelain enamel. Here the porcelain enamel slip is charged during atomization to a potential of 100,000 to 120,000 V, and the electrostatically charged droplets are attracted to the grounded parts being sprayed. A major advantage is greater material utilization. A well-operated electrostatic unit can deposit up to 85% of the sprayed material on the part as compared to 30 to 50% in conventional spraying operations. Additional details on spraying are available from Porcelain Enamel Institute Bulletin P-301, "Manual of Spraying for Porcelain Enameling."

Electrodeposition, or electrophoresis, is another process used to apply porcelain enamel slip to steel. The process uses a series of tanks in which the parts are submerged, and enamel is deposited electrophoretically within 10 to 20 s, depending on the thickness requirements. This process is basically intended for direct-on enameling, but it can be considered for two-coat/one-fire applications. The advantages offered by electrodeposition include a very uniform coating, exceptionally thin enamel layers, and excellent edge coverage.

Drying of Porcelain Enamel Parts. Parts coated with porcelain enamel slip in any of the above wet-process methods are dried before firing to:

- Permit the application of additional porcelain enamel slip, when required, without disturbing the previously applied coating
- Permit brushing of the coated parts, if required
- Allow parts to be handled more easily for transfer to the holding fixture used during firing
- Reduce the amount of water vapor introduced into the firing furnace

Parts are normally placed in or conveyed through dryers using radiant heating or heated circulated air. Drying by radiant heating is at least 20% faster than by convection. For convection dryers, the air temperature is gradually increased to 120 °C (250 °F). A cycle time of 2 to 5 min is required to dry the coating completely in continuous dryers. Batch and intermittent dryers are also used; cycle time for these dryers ranges from 10 to 20 min, depending on the size of the load and the type of dryer used. Sufficient circulation of the air is needed to ensure uniform drying of the porcelain enamel slip. Moisture-laden air from both convection heating and radiant heating dryers must be exhausted from the dryers.

If drying temperature is too high, a hard film forms on the coating and traps moisture under the film. This condition results in tearing in the finished enamel. The rate of drying can be varied by controlling the temperature or the humidity (dew point). Humidity is generally controlled by regulating the amount of outside air entering the dryer.

The drying temperature can directly affect the strength of the dried porcelain enamel film (bisque), which in turn determines the relative ease with which the dried piece can be brushed or handled. In general, low dryer temperatures produce a film that is easily brushed, but that may be easily damaged when the piece is handled; on the other hand, high

dryer temperatures produce a hard film that is easily handled but difficult to brush. Mill additions also affect the bisque strength and the brushability of the bisque.

The coating is absorbent during drying and collects gases that are present in the dryer. Most porcelain enamels do not tolerate the absorption of sulfur gases. Sulfur from any source causes a scum on the surface of the parts or pitting in the enamel surface. Therefore, dryers usually are indirect-fired to minimize the absorption of products of combustion of fuel gases.

During the initial stages of drying, the coating is still wet and is subject to contamination from dirt and other foreign particles that cannot be removed before firing. Therefore, drying must be accomplished in an atmosphere free of dirt, scale, and dust.

Auxiliary Coating Procedures. After drying and before firing, the coating may require reinforcing or brushing.

Reinforcing is the application of more porcelain enamel slip to areas where the coating is of insufficient thickness. It is usually performed on parts after the application of ground coat by dipping or flow coating when the coating thickness needs to be built up to prevent burnoff. Reinforcing is done by manual spraying, usually with a spray gun having a nozzle with a smaller opening than is used for full-coverage spraying.

Brushing is required to uncover an area of bare metal for electrical contact and to reduce the enamel thickness for areas with holes for screws or other attachments. Brushing removes the bisque; it can be done on both ground-coat and cover-coat bisques.

Electrostatic Dry Powder Spray Process for Steel

The electrostatic dry powder spray process is an excellent method to use for high-volume production of parts requiring the same porcelain enamel coating. Although parts need not be identical in shape or size, it is necessary that they all be of a configuration that can be evenly coated by this process. It is a highly efficient system, with up to 99% of the porcelain enamel powder material applied to the parts; at the same time, little or no direct labor is required for application of the coating. Further savings result from the elimination of mill room and related enamel preparation operations. Also, solid waste disposal problems and a host of environmental considerations are eliminated.

In this process, powder is delivered to the spray guns from a fluidized bed feed hopper, where it is diffused by clean compressed air into a fluidlike state. The fluidized powder is then siphoned from the feed hopper by the movement of high-velocity air flowing through a venturi-type pump. Here, it is mixed with air and propelled through flexible urethane feed tubes to the spray gun. The powder feed hopper, when equipped with an automatic level control, delivers a steady, controlled flow of powder to the guns. Independent control of powder and air volume ensures proper ratios to coat the part to the desired thickness.

The powder leaves the spray gun in the form of a diffused cloud that is propelled toward the workpiece. A high-voltage, low-amperage power unit supplies the voltage to the electrode in the spray gun. When the voltage is applied, charge builds up on the electrode. The concentration of a charge creates a very strong electric field that causes the air to ionize and a corona to form. The powder is transported through this field to the grounded part, picking up charge in the area where the field is strongest. Variable voltage allows the operator to make application adjustments and to change the various application parameters.

The powder recovery booth collects the unused powder material that did not remain on the parts being coated. The collected material moves through a closed-loop system with the use of primary and secondary/final filters, ensuring that none of the powder escapes into the environment.

The development of "clean only" metal preparation systems, along with the accompanying "for clean only" ground coats, has broadened the utility and increased the use of the porcelain enamel powder process. Using this process, coating materials are available for a variety of base-coat or full-ground-coat applications such as pyrolitic surfaces, reflectors, and oven liners, as well as a full range of cover coats.

The powder coating process is used for:

- *Direct-on ground-coat application over parts prepared by the "clean only" method:* Here, parts requiring only a ground coat may be enameled. Also, the ground coat may be applied and fired, providing the initial part of a two-coat/two-fire process when cover coats are later applied using the wet-process method.
- *Cover-coat application only:* Here, powder cover coats are applied over wet-system ground coats that have been fired earlier.
- *Two-coat/one-fire application:* Here, a thin base coat (1 mil) is applied over a "clean only" prepared metal surface. The cover coat powder is then applied directly to the base coat powder layer at a thickness of 5 mils, making a total thickness of 6 mils. Then both the base and cover coats are fired together.

For an electrostatic powder system of maximum efficiency, a well-designed and smooth-running conveyor system is essential to avoid loss of powder from the parts prior to firing. Also, the application of the powder to parts in process should be done in enclosures where temperature and humidity are fully controlled. Very low humidity limits the buildup of the powder layer, and very high humidity causes electrical charge loss that may result in falloff. Additional details on the electrostatic porcelain enamel dry powder process are available in Porcelain Enamel Institute Bulletin P-300, "Electrostatic Porcelain Enamel Powder Application."

Porcelain enameling of cast iron is done by either the dry process or by the same wet process used for enameling sheet steel.

In the dry process, a thin coat of ground-coat enamel slip is applied to the cold casting, generally by spraying, but sometimes by dipping or other methods. After the ground coat is dry, the casting is put in a furnace and heated to a bright red heat. It is then withdrawn from the furnace. While the casting is still hot the cover coat (in the form of dry powder) is sprinkled by means of a vibrating sieve over the surfaces to be coated. The enamel melts as it falls on the hot surface. The application of powdered enamel continues until the temperature of the casting drops to the point at which the enamel will not melt. Then the piece is returned to the furnace and heated until the enamel is properly fused. For some types of products, such as lavatories, one application of powdered enamel is sufficient; other products, such as bathtubs and combination sinks, require two or more applications.

In the wet process, the enamel is applied to the part when it is cold. Handling of the part is easier, and more uniform coats of enamel are applied than in the dry process. However, because of the composition of cast iron and because of casting irregularities, it is very difficult to satisfactorily enamel large articles (such as sanitary ware) by the wet process.

During heating, gas is evolved from surface reactions of carbon in the cast iron after the temperature reaches approximately 675 °C (1250 °F). Gases produce bubbles or blisters in enamel systems that mature at temperatures higher than the temperature at which the gas evolution begins. This varies with the composition and processing history of the cast iron. Flaws in the casting act as focal points for the evolution of the gas and produce large blisters at these areas than at areas where no flaws are present.

The dry process can be used for castings of almost any size or shape. The thin ground coat allows the gas to escape from the iron during the initial firing without forming large blisters. Many castings that can be enameled by the dry process without difficulty would encounter blistering in the wet process.

Thicker coats of enamel are applied by the dry process so that the normal roughness of iron castings can be hidden with one or two applications of cover-coat enamel. These thicker coats can be fired out to a finish that has more gloss and less waviness than is common when a wet-process slip is applied by spraying to a cast iron part.

Although cast iron enameled by the wet process represents only a small portion of the total tonnage of enameled cast iron products, the wet process is used in a great variety of products and parts. These include cookware, range grates, pump impellers, and piping. Ordinarily, a dark-colored enamel whose maturing temperature is below the temperature of gas evolution is used.

Porcelain Enameling of Aluminum. Porcelain enamel slips for aluminum usually are applied by spraying, using either manual or automatic equipment with agitated pressure tanks. Slips for aluminum are not self-leveling, and therefore they must be applied smoothly in an even thickness and without runs or ripples.

Many aluminum parts are coated satisfactorily by the one-coat/one-fire method. Although the heat-treatable alloys can be recoated one or more times, the opacity and color of the coating will change with the thickness of the porcelain coating and with repeated firing. The desirable minimum fired enameled thickness is 65 μm (2.5 mils) and the desirable maximum fired thickness is 90 μm (3.5 mils).

Enameling Furnaces

Fusing of the porcelain enamel coating to its metal substrate or to a ground coat can be done in a continuous, intermittent, or batch furnace. The furnace may be heated by oil, natural gas, propane gas, or electricity. With oil heating, a muffle furnace is required to prevent the products of combustion from contaminating the enamel coating. Gas-fired furnaces are either muffle or radiant-tube, with a limited number of luminous-wall, direct-fired furnaces being used.

Continuous furnaces are of either straight-through or U-type (Fig. 12) design; furnaces of both designs use air curtains to prevent heat losses through the end openings. A laydown wire-mesh-belt conveyor is used for small signs, dials, microcircuitry, and other small flat pieces. Most continuous furnaces, however, are equipped with overhead monorail conveyors located above the furnace roof. Alloy hook or drop rods extend down from the conveyor trolleys through a narrow slot in the furnace roof to transport the parts. Sealing of this slot is accomplished by the use of articulated steel or alloy seal plates carried by the conveyor. When over the furnace, these plates ride on a cast or fabricated alloy seal track that is incorporated into the furnace roof. Cycles for continuous-furnace firing of ground coats and cover coats on a number of different types of steel parts are given in Table 11.

Table 11 Cycles for firing ground-coated and cover-coated sheet steel parts in a continuous furnace

Type of part	Gage of steel	Operating temperature[(a)]		Firing time, min[(b)]
		°C	°F	
Architectural panels	16-22	805	1480	2-4
Home laundry equipment	18-22	805	1480	4-5
Water heater tanks	7-16	870	1600	8-12
Range equipment	18-24	805	1480	3-5
Sanitary ware	14-18	815	1500	4-6

(a) Temperature varies with composition of frit.

(b) Time in hot zone of furnace

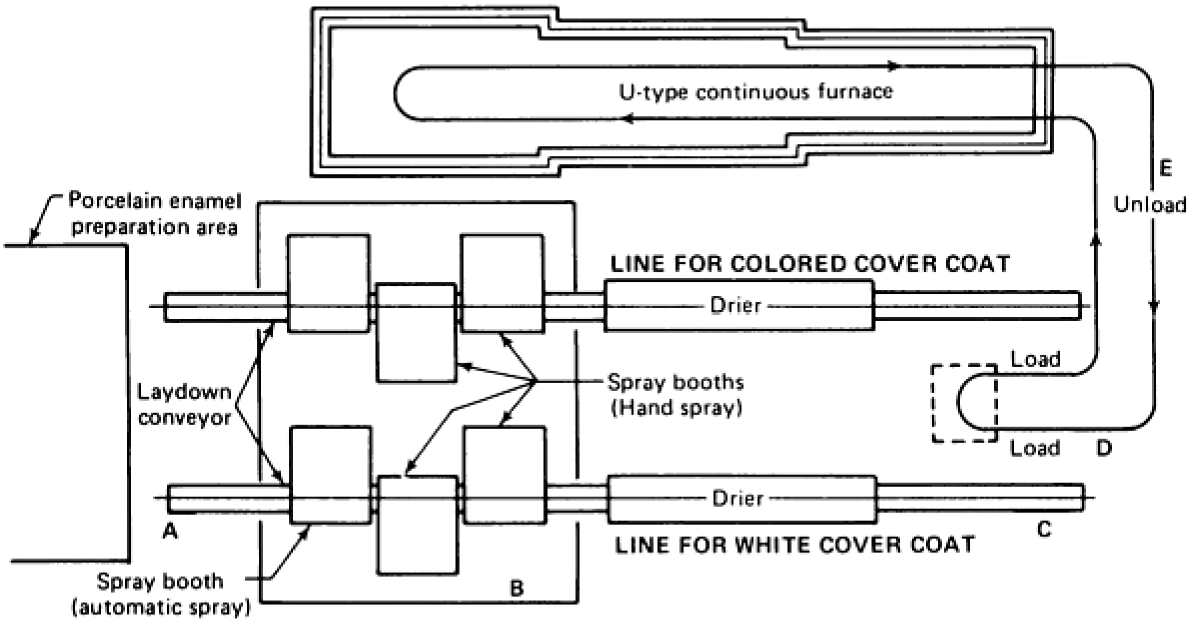


Fig. 12 Coating and firing installation using a U-type continuous furnace. Personnel stations: A, loader and stoner; B, spray operator; C, brusher; D, loader; E, unloader and inspector

Intermittent furnaces are equipped at both ends with split side-opening or articulating doors, air-cylinder operated, and have an overhead monorail conveyor similar to that of the continuous furnaces. With this type of furnace, however, the conveyor moves in increments, so that when one load is discharged, a new load enters the furnace where it remains until the firing cycle is completed. Doors and conveyor are electronically interlocked so that the firing cycle can be timer controlled. Figure 13 illustrates the small difference in temperature between the center and bottom of an intermittent 5 m (16 ft) radiant tube furnace set at 825 °C (1520 °F) for firing a load of sheet steel parts.

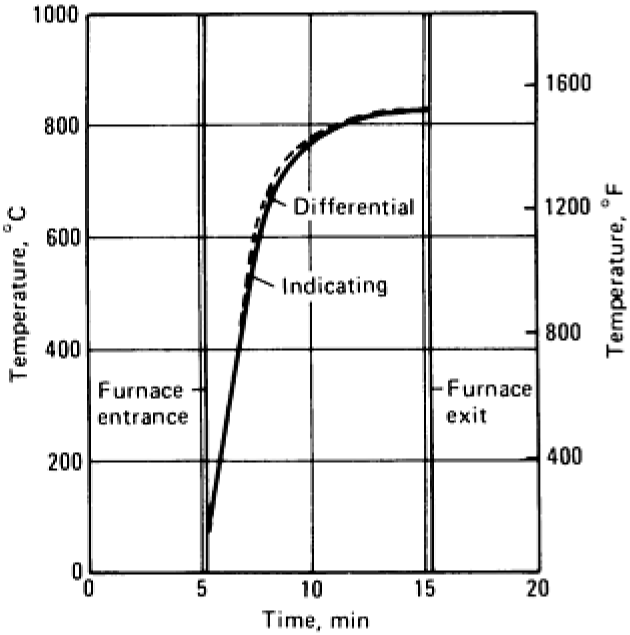


Fig. 13 Temperature and time data for an intermittent furnace. Difference in temperature between two sheet steel parts during a 10 min firing cycle at 825 °C (1520 °F) in a 4.9 m (16 ft) intermittent furnace with radiant-tube heating. Indicating thermocouple was 710 mm (28 in.) below the top of the conveyor and 580 mm (22.75 in.) above the differential thermocouple. Both thermocouples were attached to the parts.

Batch furnaces used for porcelain enameling are of two types. One type has a vertical-lift single door through which the load is charged and withdrawn by means of a charger fork. The second type has a slot in the roof and a manually operated overhead conveyor. The load for this furnace design is supported by alloy rods from overhead trolleys and is manually pushed into the furnace for firing.

Furnace construction for aluminum enameling generally requires the use of stainless steel inner liner sheets, low-density wall insulation, and plain carbon steel exterior shell. Current technology for either retrofitting existing furnaces or erecting new porcelain enameling furnaces, both continuous and batch units, uses a thin-wall lining; it is typically 150 to 205 mm (6 to 8 in.) of ceramic fiber in conjunction with radiant tubes in both the preheat and hot zones. This permits very short heat-up and cool-down periods with no resulting refractory damage. Consequently, these furnaces can be turned off during nonproduction hours, which achieves dramatic fuel savings.

Forced convection is the preferred method of heating furnaces for firing porcelain enamel on aluminum. The heat is provided by quartz-tube electric heaters, metal-sheath heaters, or electric package heaters; all are designed for operation at high ambient air temperature. Quartz-tube and metal-sheath heaters are adapted to the furnace so that radiant heat is available in the firing zone along with forced circulation. Package heaters are placed far from the firing zone to eliminate direct radiation and hot spots. Heat from the package heater requires adequate air circulation to maintain a temperature uniformity of ±1% of the normal operating temperature throughout the furnace.

Forced convection heating is also accomplished with gas-fired radiant tubes as the heat source. The tubes are baffled from the work or firing zone so that air circulation provides the same advantages as in electric-package forced convection heating.

Firing temperatures for enamel on aluminum range between 525 and 550 °C (980 and 1020 °F); cycles are shown in Table 12. To control the color and gloss of the enamel within acceptable limits, the temperature throughout the work must be held to $\pm 1\frac{1}{2}$ °C ($\pm 2\frac{1}{2}$ °F).

Table 12 Cycles for firing porcelain enamel on aluminum

Type of part	Section thickness, 0.025 mm (001 in.)	Firing time, min	Firing temperature	
			°C	°F
Any configuration	26-40	$5\text{-}6\frac{1}{2}$	540	1000
Any configuration	51-64	7-8	540	1000
Extrusions	125	10	550	1020

Role of Coating Thickness, Firing Time and Temperature, Metal Substrate, and Color

The properties and performance of the final porcelain enamel surface are markedly affected by the thickness of the applied coating, the firing time and temperature, and the selection and fabrication of the metal substrate. Color matching and control are often vital to the quality of the product or part.

Coating Thickness. The optimum thickness of porcelain enamel depends on the substrate metal and the service requirements of the part. In any application, however, the enamel coating should be applied at the minimum thickness to achieve the desired appearance and functionality.

On sheet steel, a wet ground coat 50 to 100 μm (2 to 4 mils) thick is applied to promote adhesion. To cover the ground coat, a very opaque white or pastel cover coat 100 to 150 μm (4 to 6 mils) thick is required. Thus, a two-coat wet system has a thickness ranging from 150 to 255 μm (6 to 10 mils). Brightly colored porcelain enamels are produced by applying less-opaque coats with more saturated colors over a white intermediate coating. For these, the total thickness of the coating system should range from 200 to 350 μm (8 to 10 mils). Some decorative finishes are textured; the thickest parts of these coatings may be up to 635 μm (25 mils). Coating thickness of 125 to 150 μm (5 to 6 mils) is required for cover-coat porcelain enamels applied directly to decarburized or to specially stabilized steels.

The thickness of wet porcelain enamel on a large steel part of simple configuration can be closely controlled when application is by a mechanical spraying system that is adapted to the part. For example, mechanically applied porcelain enamel on curved silo panels 2 by 3 m (5 by 9 ft) can be maintained within ±13 μm (±0.5 mil); however, when application is by hand spraying, the variation in enamel thickness may be as much as ±50 μm (±2 mils).

On aluminum, porcelain enamel is applied to produce a fired enamel thickness ranging from about 65 to 100 μm (2.5 to 4 mils). A tolerance of ±13 μm (± 0.5 mil) is required for a white enamel coating 65 μm (2.5 mils) thick, to achieve acceptable opacity.

Coatings for cast iron products are much thicker than those for sheet steel or aluminum. Dry process coatings on cast iron products, such as sanitary ware, range from 1020 to 1780 μm (40 to 70 mils) in thickness. Coatings applied to cast iron by the wet process range from 255 to 635 μm (10 to 25 mils) in thickness.

Firing Time and Temperature. Firing of porcelain enamel involves the flow and consolidation of a viscous liquid and the escape of gases through the coating during its formation. Within limits, time and temperature are varied in a compensating manner. For example, similar properties and appearance may result when a coated steel part is fired at either 805 °C (1480 °F) for $3\frac{1}{2}$ min or at 790 °C (1450 °F) for 4 min. Of course, there is a minimum practical temperature for the attainment of complete fusion, acceptable adherence, and desired appearance. Most wet ground-coat enamels for high-production steel parts exhibit acceptable properties over a firing range of 55 °C (100 °F) at an optimum firing time. However, control within 11 °C (20 °F) is ordinarily maintained to produce uniform appearance and to allow interchangeability of parts. The combined effects of increased firing time and temperature result in more thorough firing, and, up to a maximum, the following conditions occur:

- Colors shift dramatically, particularly reds and yellows. In general, white and colors shift toward yellow.
- Gloss of the enamel coating changes.
- Chemical resistance of the enamel coating increases.
- Gas bubbles are eliminated.
- Enamel coating becomes more dense and brittle and less resistant to chipping.
- Maximum adherence is attained in the optimum portion of the firing range.

Avoiding Metal Distortion. Sag and distortion of sheet metal parts result from low metal strength at the firing temperature, thermal stresses due to nonuniform heating and cooling, and transformation to austenite. Changes in design of the parts and firing practice alleviate the first two causes, and the use of extra-low-carbon content or of special stabilized steels minimizes transformation from ferrite to austenite.

Ground-coat enamels do not contribute significantly to any distortion of parts because their coefficients of thermal expansion approach that of steel. When ground coat is applied to both sides of the metal, there is a counterbalancing of expansion and contraction stresses.

The effect of cover-coat enamels on the flatness of porcelain enameled parts can be pronounced because of their lower coefficients of expansion and their one-side application. The likelihood of distortion is greatly increased when multiple or thicker coats of cover-coat enamels are necessary on one surface. Sometimes cover coats must be applied to the back side of parts to equalize the stresses.

Adjustments in the firing cycle can sometimes help minimize distortion. A cycle with relatively slow heating and cooling rates is preferable to rapid heating and cooling.

Variations in the method of supporting the work during firing can often reduce the sagging characteristics. Furnace supports and fixtures can be designed to distribute the load and equalize heating and cooling rates. Porcelain Enamel Institute Bulletin P-306, "Design and Fabrication of Sheet Steel Parts for Porcelain Enameling," has more information.

Color Matching and Control. In color matching, primary coloring oxides are normally used. In most instances, two or three oxides are sufficient to match any specific color. A minimum number of oxides should be used; for example, a stable green oxide is preferred to a blend of blue and yellow oxides. Usually, the proper color intensity is obtained first; then adjustment is made for the desired color shade.

Color stability can be adversely affected by improper mill additions. However, a color with only fair stability may be improved by the proper mill additions, and minor color adjustments.

Finer grinding reduces the intensity of the color. It is imperative that the fineness of the milled color be controlled within specified limits. The thickness of the fired enamel coating affects many colors. In general, thick coatings produce lighter colors and thin coatings result in darker colors.

The set and specific gravity of a colored enamel slip are important to the finished results. Color corrections of electrostatic dry powder cannot be made by the enameler.

Process Control

Proper workability during application of wet-process porcelain enamels depends on control of the prepared porcelain enamel slip, particularly with respect to stability of suspension; weight of enamel slip deposited and retained per unit area; specific gravity, consistency, and particle size of the enamel slip; and stability while aging at ambient temperature.

Stability of suspension, or the ability of the various mill additions to keep the milled frit in suspension, is determined by both slip measurements and visual observation of any separation that occurs. The enameler should note the accumulation of clear liquid on top of the enamel or of a heavier sludge on the bottom. Stability of the suspension is a function of many factors, but it is usually controlled by the quantity of colloid, in the form of clay or bentonite, and electrolytes used to flocculate the clay.

Pickup weight of enamel deposited and retained per unit area is measured by draining the enamel on a flat or cylindrical shape of known weight and area, then actually weighing the pickup of enamel in wet or dry form. This is a most useful test, particularly for dipping enamels, and one that closely simulates actual production operations. During the test, the operator can observe any tendency toward sliding, excessively long or short drain time, and variations in setting time. The pickup of an enamel is a function of specific gravity, colloid content, total salts content and type, and consistency. These are controlled by varying water content, addition of salts, and fineness of grind.

Specific gravity of enamel slips is measured by comparing the weight of a known volume with the weight of an equivalent volume of water or by using a hydrometer. Control of specific gravity is almost entirely a function of the ratio of water to solids. To ensure uniformity, testing for specific gravity is required for the preparation of all porcelain enamel slips.

Consistency of a porcelain enamel slip for spraying is commonly determined by the slump test. A fixed volume of the porcelain enamel slip is allowed to flow out suddenly in a circular pattern on a calibrated plate, and the diameter of the resulting pool is measured immediately. This is a simple and useful test for porcelain enamels that are to be sprayed because it indicates uniformity of slip conditions between various millings.

Other tests for consistency involve the use of viscosimeters of various types, including those that use the rotational, flow, and falling piston methods. However, enamel slips do not behave like ordinary liquids and do not follow the laws of

viscous flow. With enamel slips, a certain amount of force is required to start the flow. This force is the yield value, and the rate of flow is referred to as the mobility. These can be determined by using a consistometer; however, in plant practice, careful control of specific gravity and slump should be adequate. A study of the flow properties of porcelain enamel slips indicates that they are non-Newtonian liquids and consequently show variable rates of shear with varying stresses.

For porcelain enamel slips applied by dipping, a measure of drain time is a useful test. Drain time is the total elapsed interval between the time a standard-size sample plate is removed from a container of well-stirred porcelain enamel slip and the time at which the draining motion of the slurry on the sample stops.

Particle size of the frit for porcelain enamel slips is commonly determined by standard screen analysis. Reproducible measurements are easily obtained when a standardized shaking device is used. The particle size of the frit is important to the suspension characteristics of the porcelain enamel slip, and slight solubility of the frit shows a major change with variation in the size of the particles.

Stability while aging is measured by exposing a tested sample of the porcelain enamel to whatever temperatures are expected in normal service. Exposure is for many hours and days, and retests of the critical properties are made at intervals during testing. Aging usually has an effect on the stability of the suspension, pickup, setting time, and consistency of the porcelain enamel slip. Aging can cause poor surface quality of the fired enamel.

Leaching of soluble elements, such as sodium or boron, from the frit is a cause of aging. This problem is encountered more with frits that are less water-resistant. The leaching effect is greater at higher temperatures.

In-Process Quality Actions

Ground Coat. Parts rejected at the ground-coat stage are repaired and refired, if necessary, before the cover coat is applied. It is good practice to confine repair techniques to the defective areas. It is important to remove dirt particles, scale, and similar contaminants with a sharp-pointed instrument. The disturbed area around the site should be lightly stoned. The dust generated should be blown off. Ground-coat enamel is spotted-in at the repair area, and the entire piece is lightly dust coated. The piece is then dried and fired.

Lumps, handling defects, chips, and similar flaws in the ground coat are normally lightly stoned, and if this proves satisfactory, the parts are ready for cover coating. Otherwise they are treated as described above.

Defects that cover more extensive areas or are located at or near the steel enamel interface, such as burnoff, blisters, "copperheads," embedded grit particles, and dents, require different repair techniques; it is often necessary to grind down to bare steel. Grinding may be accomplished with a power grinder, using an 80-grit silicon carbide disk. A damp sponge placed under the work area prevents overheating. After firing, the repaired ground coat area should be hand stoned to blend it into the surrounding area of the surface.

Cover Coat. Defects that are missed during inspection of the ground coat usually become visible in the cover coat. Specks, blisters, copperheads, and dents are typical of such transmitted defects; they need to be removed by grinding into the ground coat. The ground coat is then repaired as described above, before another coat is applied. Cover-coat defects such as lumps, handling defects, chips, and thin coating areas are repaired by stoning, respraying lightly, and refiring the piece.

Direct-on cover-coat applications are repaired in much the same manner as ground coats. If the defect area is small, a light grinding or stoning is all that is required. This is followed by a localized application of cover coat and then a full dust coat, drying, and firing. If the repair requires grinding into the steel, then a ground coat patch in that area is required for adherence. A half coat of cover-coat enamel over the fired ground-coat patch is required, followed by a dust coat over the entire piece.

Properties of Porcelain Enamels

Porcelain enamels possess an unusually wide array of properties that can be specially designed and formulated for a variety of demanding environments. Some of the special properties are summarized below. (See the Porcelain Enamel Institute "Properties Data Sheets," P-401, P-402, P-403, P-404, and P-405, for more detailed information).

Chemical Resistance. Porcelain enamel is widely used because of its resistance to household chemicals and foods. Mild alkaline or acid environments are generally involved in household applications. Table 13 presents examples of corrosive environments for which porcelain enamels are widely used for long periods of service. Special enamel compositions are available to resist most acids, except for hydrofluoric or concentrated phosphorics, to temperatures of 230 °C (450 °F). These compositions also resist alkali concentration to pH 12 at 93 °C (200 °F).

Table 13 Applications in which porcelain enamels are used for resistance to corrosive environments

Application	Corrosive environment			
	Temperature		pH	Corrosive medium
	°C	°F		
Bathtubs	≤ 49	≤ 120	5-9	Water; cleansers
Chemical ware	≤ 100	≤ 212	12	Alkaline solutions
	≤ 100	≤ 212	1-2	All acids except hydrofluoric
	175-230	350-450	1-2	Concentrated sulfuric acid, nitric acid, and hydrochloric acid
Home laundry equipment	≤ 71	≤ 160	11	Water; detergents; bleach
Range exteriors	21-66	70-150	2-10	Food acids; cleansers
Range oven lines, conventional	66-315	70-600	2-10	Food acids; cleansers
Range burner grates	66-590	70-1100	2-10	Food acids; cleansers
Kitchen sinks	≤ 71	≤ 160	2-10	Food acids; water; cleansers

Weather Resistance. Factors that determine the weather resistance of porcelain enamels are chemical durability, color stability, cleanability, and continuity of coating. Gloss and enamel texture do not necessarily affect weather resistance.

Appearance for Indoor Exposure. Where corrosive attack is unlikely and appearance is the principal requirement, enamel selection and processing are directed toward providing reproducible color matching and optimum gloss and smoothness. Often, different enamels are used on different parts of the same product to ensure the best balance of properties and cost, particularly if high volume is involved. For example, somewhat different enamel compositions are used for range tops and dishwasher liners because of differing property and appearance requirements, even though these parts may be processed in the same plant. Appearance standards, in particular, are established to respond to end use requirements. Small surface defects may be tolerated in areas not heavily used or readily seen in the finished part, provided that they do not affect basic serviceability.

Surface Temperatures. Softening of the glassy matrix limits the temperature to which porcelain enamels can be exposed. Softening releases gases remaining from reactions between the enamel and the metal substrate, producing random defects known as reboil. Service-temperature limits for porcelain enamels are shown in Table 14.

Table 14 Service-temperature limits for porcelain enamels

Service temperature		Limiting conditions
°C	°F	
425	800	Usual limit for enamels maturing at about 815 °C (1500 °F)
540	1000	Maximum for enamels maturing at about 815 °C (1500 °F), without reboil
760	1400	Operating limit for special high-temperature enamels
1095	2000	Refractory enamels useful for short periods for protection of stainless steels and special alloys

Thermal shock intensifies the effect of elevated temperature, as does operation under severe temperature gradients. Enamels are formulated so that expansion characteristics place the enamel in compression under service conditions. If combinations of mechanical stress and elevated temperatures place the enamel in tension, crazing forms a pattern of fine cracks perpendicular to the tensile stress. The relation between enamel and metal expansion patterns on heating and cooling is shown in Fig. 14.

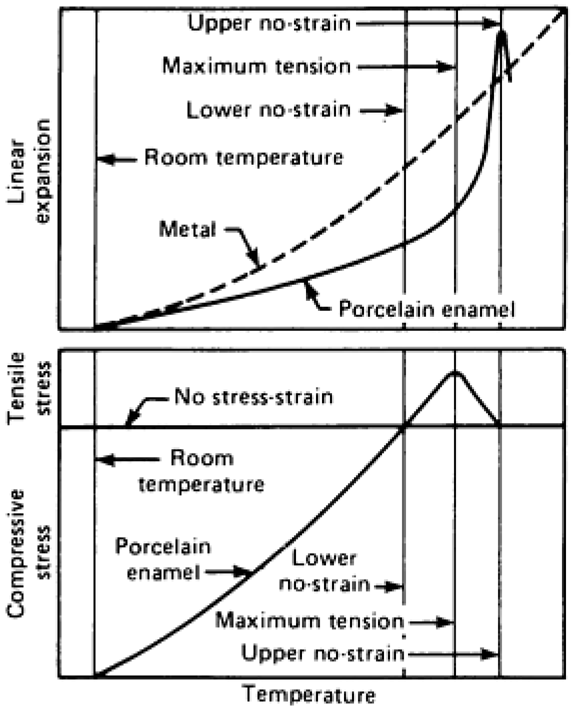


Fig. 14 Enamel/metal expansion and stress patterns. Linear expansion and stress in a composite of acid-

resistant cover-coat porcelain enamel and low-carbon steel

Mechanical Properties. The hardness of porcelain enamels ranges from 3.5 to 6.0 on the Mohs scale. Porcelain enamels show a high degree of abrasion resistance. Under abrasive test conditions where plate glass retains 50% specular gloss, porcelain enamel compositions retain from 35 to 85% specular gloss. Subsurface abrasion resistance varies with processing variables that affect the bubble structure of the enamel, that is, gas bubbles frozen in during cooling of the enamel. A decrease in abrasion resistance occurs with an increase in the number or size of gas bubbles. Enamel compositions are available that contain crystalline particles (from mill additions or devitrification heat treatment) that increase abrasion resistance as much as 50%.

The porcelain enamel coating contributes to the strength of sheet metal parts. Table 15 indicates the increased resistance to torsion provided by porcelain enamel on metal angles made of three different materials. Metal failure occurs at the point of maximum stress, which is followed by buckling of the angle.

Table 15 Effect if porcelain enamels on torsion resistance of metal angles

Material	Increase of stress, %[(a)]		
	Ground coat	One coat	Two coats
Cold-rolled steel	27	18	33
Electric steel	22	13	32
Enameling iron	22	16	42

(a) Increase of stress for metal failure, as provided by porcelain enamel, over stress for failure of annealed unenameled material

Electrical Properties. Porcelain enamels are electrical insulators. The electrical resistance per unit area is a function of thickness and enamel composition. In addition to resistance, usually expressed as resistivity, other electrical properties of interest are dielectric constant, dissipation factor, and dielectric strength. As with many glassy materials, these properties vary with temperature. In general, as the temperature increases, the resistivity and dielectric strength decrease, while the dielectric constant and dissipation factor increase. The dielectric constant and the dissipation factor also vary with frequency.

When porcelain enamel is used for its electrical properties, the selection of the enamel composition and the enameling process requires careful attention. For electronic applications, such as porcelain enameled substrates for hybrid circuits, special electronic-grade enamels are used. These compositions have considerably higher resistivities and dielectric strengths and are less sensitive to temperature changes than conventional porcelain enamels. Such specialty porcelain coatings are being used increasingly often in sophisticated electronic circuitry.

Evaluation of Porcelain Enameled Surfaces

Specifications and quality control for porcelain enamel coatings require the evaluation of a range of properties for the intended service of the porcelain enameled product. Although material and process variables can be brought into approximate control using small test panels, process control is maintained by the evaluation of finished parts, even though some of the mechanical and chemical tests are destructive. Standard test procedures are available for many porcelain enamel properties. Specific test methods for various properties are listed in Table 16. Some of these tests are discussed below.

Table 16 ASTM test methods for porcelain enamels (under jurisdiction of ASTM Porcelain Enamel Subcommittee B.08.12)

Designation	Title
C 282	"Acid Resistance of Porcelain Enamels (Citric Acid Spot Test)"
C 283	"Resistance of Porcelain Enameled Utensils to Boiling Acid"
C 285	"Standard Test Methods for Sieve Analysis of Wet Milled and Dry Milled Porcelain Enamel"
C 286	"Definitions of Terms Relating to Porcelain Enamel and Ceramic Metal Systems"
C 313	"Standard Test Method for Adherence of Porcelain Enamel and Ceramic Coatings to Sheet Metal"
C 346[(a)]	"Standard Test Method for 45° Specular Gloss of Ceramic Materials"
C 347	"Standard Test Method for Reflectance, Reflectivity and Coefficient of Scatter of White Porcelain Enamels"
C 374	"Standard Test Method for Fusion Flow of Porcelain Enamel Frits by the Flow Button Methods"
C 375	"Classification of Water Used in Milling in Porcelain Enamel"
C 385	"Standard Test Method for Thermal Shock Resistance of Porcelain-Enameled Utensils"
C 409[(a)]	"Torsion Resistance of Laboratory Specimens of Porcelain Enameled Iron and Steel"
C 448	"Standard Test Methods for Abrasion Resistance of Porcelain Enamels"
C 536	"Standard Test Method for Continuity of Coatings in Glassed Steel Equipment by Electrical Testing"
C 537	"Standard Test Method for Reliability of Glass Coatings on Glassed Steel Reaction Equipment by High Voltage"
C 538	"Standard Test Method for Color Retention of Red, Orange and Yellow Porcelain Enamels"
C 539	"Standard Test Method for Linear Thermal Expansion of Porcelain Enamel and Glaze Frits and Ceramic Whiteware Materials by the Interferometric Method"
C 540[(a)]	"Standard Test Method for Image Gloss of Porcelain Enamel Surfaces"
C 614	"Standard Test Method for Alkali Resistance of Porcelain Enamels"

C 632	"Standard Test Method for Reboiling Tendency of Sheet Steel for Porcelain Enameling"
C 633	"Standard Test Method for Adhesion or Cohesive Strength of Flame-Sprayed Coatings"
C 660	"Practices for Production and Preparation of Gray Iron Castings for Porcelain Enameling"
C 664	"Standard Test Method for Thickness of Diffusion Coating"
C 694	"Standard Test Method for Weight Loss (Mass Loss) of Sheet Steel during Immersion in Sulfuric Acid Solution"
C 703	"Standard Test Methods for Spalling Resistance of Porcelain Enameled Aluminum"
C 715	"Standard Test Method for Nickel on Steel for Porcelain Enameling by Photometric Analysis"
C 743	"Standard Test Method for Continuity of Porcelain Enamel Coatings"
C 756	"Standard Test Method for Cleanability of Surface Finishes"
C 774	"Standard Test Method for Yield Strength of Enameling Steels after Straining and Firing"
C 810	"Standard Test Method for Nickel on Steel for Porcelain Enameling by X-Ray Emission Spectrometry"
C 839	"Standard Test Method for Compressive Stress of Porcelain Enamels by Loaded-Beam Method"
C 872	"Standard Test Method for Lead and Cadmium Release from Porcelain Enamel Surface"
C 988	"Standard Test Method for Image Gloss of Porcelain Enamel Surfaces"

(a) This test, while withdrawn from the latest ASTM list because of inability to obtain the required equipment, continues to be used by laboratories that possess the equipment.

Adherence refers to the degree of attachment of enamel to the metal substrate. A number of tests regularly used in the industry provide adherence criteria, but none gives the force per unit area required to detach the enamel by tensile force normal to the interface.

ASTM C 313 for porcelain enamel on steel deforms the metal and measures the area from which the porcelain enamel is removed. The indicator of adherence is the adherence index, which is the ratio of the porcelain enamel remaining in the deformed area to that in the same measured area prior to deformation.

Enamels for cast iron pose a special problem because of the relatively greater thickness of the coating, the rigidity of the metal substrate, and the brittleness of the iron. Here, simple nonstandard impact tests are used.

Resistance to spalling, a defect characterized by separation of porcelain enamel from the base metal without apparent external cause, is the indicator used to measure adherence of porcelain enamel on aluminum. Spalling can result from the

use of improper alloys, improper enamel formulations, incorrect pretreatment of the base metal, faulty application, or unsatisfactory firing procedures. The most common test for spall resistance is ASTM C 703.

Thickness. A number of specifications for products and applications require a specific thickness for porcelain enamel coating. The procedure used to measure the thickness depends on the type of base metal used. For porcelain enamel products with a steel substrate, enamel thickness is measured according to ASTM D 1186. For porcelain enamel products with an aluminum substrate, enamel thickness is measured according to ASTM E 376. (Neither of these tests is listed in Table 16, because they are not under the jurisdiction of ASTM Porcelain Enamel Subcommittee B.08.12.) In some cases, such as laboratory investigations, enamel thickness is measured according to ASTM C 664.

Color and Gloss. Porcelain enamel finishes are produced in literally hundreds of colors and countless textures. The common method of specifying color is based on the capacity of the observed article to reflect light of different wavelengths and hence of different colors. A physical standard, such as a reference plaque of porcelain enameled steel, is provided as the color to be matched within stated limits. The difference in color between the control standard and the test specimen can be measured by a color difference meter, using the procedures specified in ASTM D 2244 (not under B.08.12 jurisdiction).

Gloss, which is defined in ASTM C 286 as "the shine or luster of porcelain enamel," is particularly desirable in some products, such as appliances, sanitary ware, and lighting reflectors. However, high gloss enamels capable of reflecting distinct images are not recommended for architectural porcelain enamel for exterior use. The most commonly used test to measure gloss of porcelain enamel is ASTM C 346. ASTM C 540 may also be used if the equipment is available.

Acid Resistance. Porcelain enamels can be formulated to exhibit high resistance to all acids except hydrofluoric or concentrated phosphoric. This resistance to food acids and certain chemical cleaners is of particular importance to manufacturers of ranges and other kitchen and household appliances, as well as plumbing fixtures and various industrial and chemical processing products.

The acid resistance of enamels under boiling conditions is important for certain uses, such as cookware. ASTM C 283 is used here. Similarly, acid resistance is a major consideration for predicting the weatherability of architectural porcelain enamel components. Extensive testing under controlled exposure conditions has shown a distinct correlation between acid resistance and weatherability. Here the test for determining acid resistance is ASTM C 282.

Alkali Resistance. Home laundry equipment, dishwashers, and similar applications normally exposed to an alkaline environment at elevated temperatures require an alkali-resistant coating. The standard test for alkali resistance is ASTM C 614.

Weather Resistance. Actual weathering performance of porcelain enamel panels has been documented in a series of onsite exposure tests carried out over periods up to 30 years in length by the National Bureau of Standards (now the National Institute of Standards and Technology) in cooperation with the Porcelain Enamel Institute. As mentioned above, acid resistance as measured by ASTM C 282 is important.

Weathering of porcelain enamel is evaluated in terms of the changes in gloss and color that occur during outside exposure. Multiyear weathering tests demonstrate that porcelain enamels have considerable inherent gloss and color stability. Tests that are used are ASTM C 346 and ASTM D 2244 (the latter is not under B.08.12 jurisdiction).

Spalling resistance of weathered porcelain enamel on aluminum is best ascertained through use of ASTM C 703.

Resistance to Organic Solvents. Porcelain enamels are inert to all common organic solvents; however, there is no standard procedure for determining this special performance characteristic.

Resistance to Chipping. Relatively thick layers of porcelain enamel are fractured when subjected to severe bending or other substrate deformation. However, thin coatings of 125 μm (5 mils) or less that are well bonded to a relatively thin metal substrate (for example, 26-gage 0.4546 mm, or 0.0179 in., or less) can withstand the bending of the substrate to radii of curvature within its elastic limit and return to the original shape with little or no apparent damage. Chipping of typical porcelain enamel on sheet iron occurs at about the strain required for permanent deformation of the metal base.

Torsion Resistance. In transit and during service, porcelain enameled products may be subjected to distortion through bending, twisting, or a combination of both. This can cause coating failures from fractures originating at the outer surface

and normal to the tensional stress. ASTM C 409 evaluates the relative resistance to torsion-induced failure of laboratory test specimens for steel substrate thicknesses ranging from 24 to 12 gage.

Abrasion Resistance. The resistance of porcelain enamel to various types of abrasion is measured by ASTM C 448, which consists of three parts. The first determines the resistance to surface abrasion of porcelain enamels for which the unabraded 45° specular gloss is more than 30 gloss units. The second determines the resistance to surface abrasion of porcelain enamels for which the unabraded 45° specular gloss is 30 gloss units or less. The third measures the resistance of porcelain enamels to subsurface abrasion.

Thermal shock resistance of a porcelain enamel surface varies inversely with the thickness of the enamel. It is also affected by the compressive stress present in the enamel at room temperature. Most porcelain enamels can be quenched in ice water from a temperature of 205 °C (400 °F) without thermal shock failure. Some porcelain enamels specifically designed for resistance to thermal shock will not fail when quenched in ice water from 650 °C (1200 °F). ASTM C 385 is the standard for evaluating the durability of porcelain enameled utensils when subjected to thermal shock.

Continuity of Coatings. Ensuring continuity of coating after manufacture is important in porcelain enamel ("glassed steel") applications where a prime purpose of the coating is to protect the substrate against corrosion. Test methods used to determine either discontinuity of coverage or potential discontinuity through too-thin coverage are ASTM C 536 and ASTM C 743. Both tests essentially involve the use of electrical probes of relatively high voltage to discern either discontinuities in the coating or insufficient coverage for coating integrity in service use.

Resistance to Hot Water. Federal specification W-H-196J, "Heater Water, Electric and Gas Fired, Residential," specifies a solubility test to determine the resistance of porcelain enamels to hot water.

Ceramic Coatings and Linings

Revised by Woodrow W. Carpenter, The Ceramic Coating Company

Introduction

CERAMIC COATINGS include glasses, with or without additions of refractory compounds; high-temperature coatings based on oxides, carbides, silicides, borides, or nitrides; cermets; and other inorganic materials. Ceramic coatings are applied to metals to protect them against oxidation and corrosion at room temperature and at elevated temperatures. Special coatings have been developed for specific uses, including wear resistance, chemical resistance, high reflectivity, electrical resistance, and prevention of hydrogen diffusion. Ceramic-coated metals are used for furnace components, heat treating equipment, chemical processing equipment, heat exchangers, rocket motor nozzles, exhaust manifolds, jet engine parts, and nuclear power plant components.

Selection Factors

Several factors must be considered when selecting a ceramic coating:

- Service environment to be encountered by the coated metal
- Mechanisms by which the coatings provide protection at elevated temperatures
- Compatibility of the coating with the substrate metal
- Method of applying the coating
- Quality control of the coating
- Ability of coating to be repaired

Service environment may involve a wide range of conditions. The intended operating life of a coated part may range from a few seconds to several hundred hours. Conditions may involve exposure to atmospheric gases at various mass flows with velocities up to, or even beyond, Mach 10. Components made of the refractory alloys may be subjected to very high stresses, or they may be used as heat shields or furnace windings, for which the only load is the mass of the component. Heating and cooling rates may be gradual or rapid, and one or more thermal cycles may be involved. For any specific service environment, the coating selected must protect the metal from oxidation and the effects of hydrogen

pickup by preventing or minimizing the diffusion of oxygen, nitrogen, and hydrogen from the atmosphere through the coating into the substrate.

Mechanisms of Protection. Ceramic coatings have two mechanisms to protect metals at elevated temperatures. One type of coating is applied as a layer of stable oxide on the surface of the metal, which prevents or delays contact between metal and atmosphere. The other type of ceramic coating is an intermetallic compound that forms a thin oxide film on its surface. The composition of the intermetallic is such that it provides the optimum combination of metallic elements for forming a stable and adherent protective oxide film on its surface and for healing the oxide film in the event the film is broken. Thus, this type of coating depends on the formation and preservation of the oxide film for protection of the substrate material.

Chemical and Mechanical Compatibility. Chemical compatibility of the ceramic coating with the substrate metal is important, especially when the coating is applied to refractory metals and nickel-base alloys for high-temperature service. The so-called stable oxide coatings, such as alumina, are not stable in the presence of some of the refractory metals, such as niobium (columbium) and tantalum, at temperatures above 1370 °C (2500 °F). Also, alumina reacts with metals such as titanium and zirconium, and the protective characteristics of the coating are soon exhausted.

The coating must also be mechanically compatible with the underlying metal, so that undesirable mechanical stresses are not induced in either material. Because most stable coatings are brittle at low temperatures, the coefficients of thermal expansion of the coating and substrate should not be greatly different; however, the coefficient of expansion of the coating should be somewhat less than that of the substrate, so that the coating will be in compression at low (room) temperature. The mismatch in expansion should be greater for parts subjected to thermal cycling. The system must be designed so the difference in the coefficients keeps the coating in compression at all temperatures below the softening point of the coating. if the coating is in tension at low temperature, it will crack. Conversely, if it is under too much compression, it will spall.

The effect of the coating on fatigue life and on the brittle transition temperature of the composite material should also be considered. In general, the coating is more brittle than the substrate metal, and cracks that form in the coating during service act as stress raisers on the substrate, thus reducing the low-temperature ductility and fatigue life.

Application Method. The method of applying the coating is restricted by the type of coating, the type of metal to be coated, and the size and configuration of the work. Many of the coating processes include heat treatment to promote bonding and sealing. The atmospheres used for spraying and heat treating must be closely controlled to prevent any deterioration in properties of the substrate metal.

Control of Coating Quality. It is important to ensure that the coating is capable of protecting the substrate. Thickness measurements and visual observations are two methods of determining coating quality. However, these methods are not satisfactory for coatings on complex shapes and internal passages that are difficult to see or reach. A preliminary oxidation test of a few minutes or hours in an oxidizing atmosphere at the operating temperature is also an acceptable method for determining quality of the coating.

Ability of coating to be repaired is an important consideration in coating selection. The ideal coating should be repairable if coverage is insufficient in the initial application or if the coating is damaged during handling or service. Repair procedures and their effectiveness differ for the various coatings, methods of application, substrate metals, and size and shape of work.

Coating Materials

The nonmetallic, inorganic materials used as ceramic coatings have several characteristics in common. Among these are relatively good chemical stability at elevated temperatures, hardness, brittle behavior under load, and mechanical continuity in thin cross section.

Silicate Glasses. Coatings prepared from glass powders, with or without additions of refractory compounds, have the greatest industrial usage of all ceramic coatings. Glass is typically manufactured by mixing specific proportions of minerals, heating the mixture to a molten or liquid state, and rapidly quenching. Quenching is normally accomplished by discharging the melt into cold water or by pouring it through water-cooled steel rolls. The former case results in small friable pieces of glass that can be ground into a powder with relative ease using a ball mill or other standard crushing equipment. These friable pieces are called *frit.* The word refers to the physical condition of the particle, not its

composition or properties. Quenching through water-cooled steel rolls results in flake-like particles, somewhat less friable than those produced by water quenching but with less environmental nuisance.

Glass coatings are used for such long-duration elevated-temperature applications as aircraft combustion chambers, turbines and exhaust manifolds, and heat exchangers. Variations in composition of the glass are virtually unlimited. They range from alkali-alumina borosilicate glasses, which are relatively soft, low melting, and highly fluxed, to barium crown glasses.

Crystallized glass coatings have been developed. In these coatings, crystallization of the glass is controlled by formulation and heat treatment and by the presence of nucleating agents added to the glass during melting.

Several different refractory materials may be combined with glass to produce satisfactory coatings for elevated-temperature service. The addition of a refractory material depends on service requirements and on the compatibility of the refractory material with the glass, other mill-added materials, and the substrate metal. Raw batch compositions of glasses, their melted compositions, and slips (mixtures of frit and additives ground to a smooth consistency) for high-temperature service coatings are indicated in Tables 1, 2, and 3, respectively.

Table 1 Compositions of unmelted frit batches for high-temperature service silicate-based coatings

Constituent	**Parts by weight for specific frits[a]**						
	UI-32	**UI-285**	**UI-346**	**UI-418**	**NBS-11**	**NBS-331**	**NBS-332**
Quartz	29.3	21.2	18.3	31.2	18.0	38.0	37.5
Feldspar	42.0	30.2	47.4	. . .	31.0	. . .	. . .
Hydrated borax	28.9	21.0	17.9	. . .	37.1	. . .	. . .
Sodium carbonate	7.7	5.3	6.1	. . .	5.9	. . .	. . .
Sodium nitrate	5.0	4.0	4.4	. . .	3.8	. . .	. . .
Fluorspar	4.5	3.2	2.8	. . .	3.0	. . .	. . .
Tricobalt tetroxide	0.6	. . .	0.4	. . .	0.5	. . .	. . .
Nickel oxide	0.6	. . .	0.4	. . .	0.6	. . .	. . .
Manganese dioxide	1.8	. . .	1.1	. . .	1.1	. . .	. . .
Barium carbonate	. . .	. . .	. . .	26.3	. . .	56.6	56.6
Zinc oxide	. . .	. . .	. . .	4.2	. . .	5.0	5.0
Whiting	. . .	. . .	. . .	7.5	. . .	7.1	6.3

Vanadium pentoxide	. . .	. . .	1.3	. . .	. . .	. . .	. . .
Aluminum hydrate	. . .	15.1	. . .	. . .	. . .	. . .	1.5
Boric acid	. . .	. . .	. . .	12.0	. . .	11.5	11.5
Cerium oxide	. . .	. . .	. . .	4.2	. . .	. . .	. . .
Titania	. . .	. . .	. . .	4.2	. . .	. . .	. . .
Bismuth nitrate	. . .	. . .	. . .	4.2	. . .	. . .	. . .
Bismuth oxide	. . .	. . .	. . .	6.2	. . .	. . .	. . .
Beryllia	. . .	. . .	. . .	. . .	. . .	2.5	. . .
Zirconia	. . .	. . .	. . .	. . .	. . .	. . .	2.5

(a) UI numbers designate frit compositions developed at the University of Illinois; NBS numbers, frits developed at the National Bureau of Standards (now the National Institute of Standards and Technology, NIST)

Table 2 Compositions of melted silicate frits for high-temperature service ceramic coatings

Constituent	**Percentage for specific frits**[(a)]						
	UI-32	**UI-285**	**UI-346**	**UI-418**	**NBS-11**	**NBS-331**	**NBS-332**
Silicon dioxide (SiO_2)	56.5	51.1	57.0	37.0	42.0	38.5	37.5
Aluminum oxide (Al_2O_3)	8.4	19.8	10.7	. . .	5.6	. . .	1.0
Boron oxide (B_2O_3)	10.6	9.5	8.0	8.0	25.8	6.5	6.5
Sodium monoxide (Na_2O)	12.0	10.9	10.8	. . .	17.9	. . .	. . .
Potassium monoxide (K_2O)	5.1	4.6	6.7	. . .	3.4	. . .	. . .
Calcium fluoride (CaF_2)	4.5	4.1	3.4	. . .	3.0	. . .	. . .
Cobalt oxide (CoO)	0.5	. . .	0.45	. . .	0.5	. . .	. . .

Nickel monoxide (NiO)	0.6	. . .	0.45	. . .	0.6	. . .	. . .
Manganese dioxide (MnO_2)	1.8	. . .	1.3	. . .	1.2	. . .	. . .
Vanadium pentoxide (V_2O_5)	. . .	. . .	1.2	. . .	. . .	. . .	. . .
Bismuth dioxide(BiO_2)	. . .	. . .	. . .	10.0	. . .	. . .	. . .
Calcium oxide (CaO)	. . .	. . .	. . .	5.0	. . .	3.5	3.5
Barium oxide (BaO)	. . .	. . .	. . .	25.0	. . .	44.0	44.0
Zinc oxide (ZnO)	. . .	. . .	. . .	5.0	. . .	5.0	5.0
Cerium dioxide (CeO_2)	. . .	. . .	. . .	5.0	. . .	. . .	. . .
Titanium dioxide (TiO_2)	. . .	. . .	. . .	5.0	. . .	. . .	. . .
Beryllium oxide (BeO)	. . .	. . .	. . .	. . .	. . .	2.5	. . .
Zirconium oxide (ZrO_2)	. . .	. . .	. . .	. . .	. . .	. . .	2.5

(a) UI numbers designate frit compositions developed at the University of Illinois; NBS numbers, frits developed at the National Bureau of Standards (now the National Institute of Standards and Technology, NIST)

Table 3 Compositions of slips for high-temperature service silicate-based ceramic coatings

Constituent	**Parts by weight for specific coatings**[(a)]										
	UI-32-22	**UI-32-53**	**UI-285-1**	**UI-346-2**	**UI-346-4**	**UI-418-1**	**UI-418-4**	**A-19H**	**A-418**	**A-417**	**A-520**
Frit[(b)]	88[(c)]	100[(c)]	100[(d)]	100[(e)]	100[(e)]	100[(f)]	100[(f)]	100[(g)]	70[(h)]	70[(i)]	90[(i)]
Diaspore	12	. . .	. . .	15	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Clay	7	10	7	7	10	7	6	10	5	5	6
Hydrated borax	0.75	0.5	0.75	0.75	0.5	0.75	. . .	. . .	. . .	. . .	. . .
Water	50	50	50	55	50	50	50	50	48	48	45

Sodium pyrophosphate	. . .	0.05	. . .	. . .	0.05	. . .	. . .	. . .	. . .	. . .	. . .
Calcined aluminum oxide	. . .	25	. . .	. . .	25	. . .	. . .	25	. . .	. . .	. . .
Tricobalt tetroxide	. . .	. . .	. . .	. . .	. . .	. . .	. . .	1	. . .	. . .	. . .
Citric acid	. . .	. . .	. . .	. . .	. . .	. . .	. . .	0.05	. . .	. . .	. . .
Chromic oxide	. . .	. . .	. . .	. . .	. . .	. . .	25	. . .	30	30	. . .
Copper oxide	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	10
Sodium nitrite	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	0.025

(a) UI numbers designate coatings developed at the University of Illinois; A numbers, coatings developed at the National Bureau of Standards (now the National Institute of Standards and Technology).

(b) See Tables 1 and 2 for batch and melted compositions of frits.

(c) UI-32 frit.

(d) UI-285 frit.

(e) UI-346 frit.

(f) UI-418 frit.

(g) NBS-11 frit.

(h) NBS-332 frit.

(i) NBS-331 frit

Glass coatings can be applied by spraying or air brushing (for which the material is atomized and carried by compressed air), dipping and draining (which may be followed by spraying), slushing and draining, filling and draining, and flow coating. Under certain conditions, electrostatic spraying also can be used.

Spraying is the most commonly used method, except when the configuration of the part prevents complete coverage or when production requirements are great enough so that a saving in material costs would be realized by the use of dipping or slushing. Dipping and draining is the most economical procedure for coating small parts with simple shapes. For larger parts with restricted areas, filling and draining may be the best coating method. Rotation or shaking of parts is often necessary when dipping or filling is used to distribute the coating and obtain uniform draining.

Glass coatings are brittle, but when applied at the usual thickness of 25 to 50 μm (1 to 2 mils), they will withstand considerable abuse, even at edges and unavoidable sharp corners. Mechanical roughening of the metal surface before applying the coating provides a greater surface area, affects the rate of oxidation, and frequently improves adherence. After application, coatings are dried at slightly elevated temperatures and are subsequently fired at higher temperatures to provide them with the desired performance and appearance characteristics.

Another type of coating for high-temperature service is a combination of glass and metal called *cermet.* A high proportion of metal powder (e.g., aluminum) is added after the glass has been made into a slip (see above). These coatings can be exposed to temperatures above the original firing temperature. Small steel sheets coated with this type of coating can be quenched red hot in water without chipping or blistering of the surface. Appropriate applications are heat exchangers, exhaust systems for internal combustion engines, marine service, structural members and panels for vehicular tunnels, and fire boxes of central heating boilers. Additional information is available in the section "Cermets" in this article.

Oxides. Coatings based on oxide materials provide underlying metals, except refractory metals, with protection against oxidation at elevated temperatures and with a high degree of thermal insulation. Flame-sprayed oxide coatings do not provide refractory metals with the necessary protection against oxygen because of their inherent porosity. Oxide coatings can be readily applied in thicknesses up to 6.4 mm (0.25 in.), but their resistance to thermal shock decreases with increasing thickness.

Alumina (Al_2O_3) and zirconia (ZrO_2) are the oxides most commonly used as coatings. Alumina coatings are hard and have excellent resistance to abrasion and good resistance to corrosion. Zirconia is widely used as a thermal barrier because of its low thermal conductivity.

Table 4 lists the principal oxides used for coatings and gives their melting points. Basic oxide is the major constituent of an oxide coating, usually being present in excess of 95 wt%. Other materials, such as calcium oxide (CaO), chromium oxide (Cr_2O_3), and magnesium oxide (MgO), are added in small percentages for stabilization, increase of as-sprayed density, modification of surface-emittance characteristics, and improvement of resistance to thermal shock. Physical properties for alumina and zirconia coatings flame sprayed from rod are given in Table 5.

Table 4 Melting points of principal oxides used in ceramic coatings

Oxide	Melting point	
	°C	°F
Aluminum oxide (Al_2O_3)	2070±28	3760±50
Aluminum titanate ($Al_2O_3TiO_2$)	1860	3380
Beryllium oxide (BeO)	2570±84	4660±150
Calcium zircanate ($CaZrO_3$)	2345	4250
Cerium oxide (CeO_2)	Over 2600	Over 4710
Chromium oxide (Cr_2O_3)	2265±110	4110±200
Cobalt oxide (CoO)	1805±56	3280±100
Forsterite ($2MgO\cdot SiO_2$)	1885	3425

Hafnium oxide (HfO_2)	2900±110	5250±200
Magnesium oxide (MgO)	2850±28	5165±50
Mullite ($3Al_2O_3{\cdot}SiO_2$)	1810	3290
Nickel oxide (NiO)	1980±110	3600±200
Silicon dioxide (SiO_2)	1720±14	3130±25
Spinel ($MgO{\cdot}Al_2O_3$)	2135	3875
Thorium oxide (ThO_2)	3220±56	5830±100
Titanium oxide (TiO_2)	1870±28	3400±50
Uranium oxide (UO_2)	2875±56	5210±100
Yttrium oxide (Y_2O_3)	2455±56	4455±100
Zircon ($ZrO_2{\cdot}SiO_2$)	1775±11	3225±20[(a)]
Zirconium oxide (ZrO_2)	2710±110	4910±200

(a) Decomposes

Table 5 Physical properties of alumina and zirconia flame sprayed from rod

Coating	Bulk density		Porosity, %	Color	Typical compressive strength		Thermal expansion[(a)]		Thermal conductivity[(b)]	
	g/cm^3	$lb/in.^3$			MPa	ksi	μm/m·K	μin./in.· °F	W/m·K	$Btu{\cdot}in./ft^2{\cdot}h{\cdot}°F$
Alumina	3.3	0.12	8-12	White	255	37	7.4	4.1	33	19

(a) 20 to 1230 °C (70 to 2250 °F).

(b) 540 to 1095 °C (1000 to 2000 °F)

Oxide coatings are usually applied by the flame or plasma-arc spraying methods. Before spraying by either method, the substrate surface should be clean and rough; abrasive blasting provides a satisfactory surface condition. Sprayed coatings usually range in thickness from 25 to 2500 μm (1 to 100 mils).

Flame spraying, using either oxyhydrogen or oxyacetylene systems, can deposit any refractory oxide whose melting point is below 2760 °C (5000 °F). However, certain refractory oxides, particularly silicon dioxide, do not spray well even though their melting points are considerably below 2760 °C (5000 °F).

An oxidation-resistant nickel chromium alloy often is applied to the substrate before an oxide coating is deposited by flame spraying. Without such a base coat, the adhesion of the oxide may be inadequate. Coating rates during flame spraying are slow, usually in the range of 16 to 410 cm^3/h (1 to 25 $in.^3$/h).

All oxides that can be flame sprayed and those with higher melting points can be applied by plasma spraying. In general, plasma spraying produces coatings of greater density (porosity of sprayed oxide coatings ranges from 5 to 15%, depending on method of application), greater hardness, and smoother finish than those obtained by flame spraying. Also, the temperature of the substrate remains lower, because deposition is faster. Because of the inert gases used during plasma spraying, oxidation of the substrate is minimized.

In addition to spraying, any of the oxides may be applied by troweling. Troweled coatings usually are thicker than sprayed coatings and are designed to provide maximum thermal protection to the underlying metal. A bonding medium, such as sodium silicate, calcium aluminate, phosphoric acid, or glass, is used for coatings applied by troweling. In addition, the use of expanded-metal reinforcements greatly improves troweled coatings.

Carbides as ceramic coatings are principally used for wear and seal applications, in which the high hardness of carbides is an advantage. These applications include jet engine seals, rubber-skiving knives, paper machine knives, and plug gages. Carbide coatings for wear resistance are applied by flame spraying or detonation-gun techniques. Table 6 gives the melting points of ten carbides.

Table 6 Melting points of carbides

Carbide	Melting point	
	°C	°F
Boron carbide (B_4C)	2470	4480
Chromium carbide (Cr_3C_2)	1900	3440
Niobium carbide (NbC)	3480	6295
Hafnium carbide (HfC)	3890	7030
Molybdenum carbide (Mo_2C)	2410	4375
Silicon carbide (SiC)	2540	4605
Tantalum carbide (TaC)	3980	7200
Titanium carbide (TiC)	2940	5325

Tungsten carbide (WC)	2790	5050
Zirconium carbide (ZrC)	3400	6150

Silicides are the most important coating materials for protecting refractory metals against oxidation. Silicide-based coatings protect by means of a thin coating of silica that forms on the coating surface when heated in an oxygen-containing atmosphere. To improve the self-healing, emittance, chemical stability, or adherence of this thin silica coating, other elements, such as chromium, niobium, boron, or aluminum, are added to the coating formula.

Table 7 lists and describes several silicide coatings. These materials are usually applied to a substrate by some variation of the vapor-deposition process. Deposition, diffusion, and reaction of silicon (and any other elements added in small quantities) with the substrate metal at a high temperature produce the silicide-based coating.

Table 7 Silicide coatings for protection of refractory metals against oxidation

Constituents of as-applied coating		Suitable substrate metal	Oxidation protection[(a)]			Application		
			Temperature		Life, h	Method	Thickness	
Silicide	Additives		°C	°F			μm	mils
Molybdenum silicide ($MoSi_2$)	None	Mo-0.5 Ti	1480	2700	10	Fluidized bed	25-50	1-2
	Nb	Mo-0.5 Ti	1540	2800	12	Pack cementation	75	3
	Cr, Al	Mo-0.5 Ti	1540	2800	8	Pack cementation[(b)]	60	2
	Cr	Mo-0.5 Ti	1480	2700	36[(c)]	Pack cementation	60	2
	Cr, Al, B, Nb, Mn	Mo	1540	2800	19-45	Pack cementation	60-100	2-4
Niobium silicide ($NbSi_2$)	None	Nb-33 Ta-0.8 Zr	1480	2700	3	Fluidized bed	25-50	1-2
		Nb-10 Ti-10-10 Mo	1425	2600	15-25	Pack cementation	50	2
	Cr, Ti	Nb-10 Ti-10 Mo	1370	2500	Over 100	Vacuum pack[(b)(d)]	100	4
	Cr, B	Nb-10 Ti-10 Mo	1370	2500[(e)]	Over 15[(e)]	Pack cementation[(b)]	50	2
Niobium silicide ($NbSi_2$),	. . .	Nb	1370	2500	396	Pack cementation	Over	Over

$(NbAl_3)$[f]							150	6
Tantalum silicide ($TaSi_2$), plus others[f]	. . .	Ta	1370	2500	275	Pack cementation	Over 150	Over 6

(a) Representative data only; can vary depending on test conditions.

(b) Multiple-cycle processing.

(c) 95% confidence.

(d) Variation of pack-cementation process; pack is elevated to remove residual air before heating.

(e) Life of coating system is at least 10 h at 1425 °C (2600 °F).

(f) Proprietary

Vapor-deposited and diffused silicide coatings are characterized by their superior adhesion to the substrate. Fairly precise control of coating thickness is obtained through this process. Uniform silicide coatings with a thickness of a few tenths of a mil to several mils are produced on both simple and complex shapes by either the pack-cementation or the fluidized-bed technique.

The slurry fusion process is the most commonly used method for the deposition of silicide coatings on refractory metals. A slurry of fine silicon powder with desired additives (iron, chromium, hafnium, or titanium) in an organic liquid is applied to the part by dipping, spraying, or brushing. The coated part is heated in a vacuum or inert atmosphere at 1300 to 1400 °C (2370 to 2550 °F) for 30 to 60 min. An excellent coating-to-substrate bond is developed.

Because they are more brittle than the substrate metals, silicide coatings are highly susceptible to crack formation, which can act as a stress raiser on the substrate. In general, silicide coatings have an adverse effect on all room-temperature mechanical properties of the substrate; the thicker the coating, the greater the effect. Silicide coatings generally embrittle the metals to which they are applied, but they do not necessarily impair the usefulness of the coated metals for structural applications.

Phosphate-Bonded Coatings. Phosphates for metal protective coating systems are formed by the chemical reaction of phosphoric acid and a metal oxide such as aluminum oxide, chromium oxide, hafnium oxide, zinc oxide, and zirconium oxide. The phosphate-bonded materials are used to protect metals against heat and to act as a binder in thin ceramic paint films. Thicker composites are troweled, rammed, or sprayed to the desired thickness. Phosphate-bonded coatings have low density, low thermal conductivity, and high refractoriness after curing in place at temperatures ranging from 21 to 425 °C (70 to 800 °F), and they can be applied in greater thicknesses than other ceramic coatings. Thus, a thick refractory composite can be used to protect lower-temperature-resistant metal systems. Phosphate-bonded composites, depending on composition, withstand temperatures up to 2425 °C (4400 °F) and have been applied in thicknesses up to 50 mm (2 in.).

Reinforcements, bonded or welded to the metal substrate, usually are used within phosphate-bonded coatings to facilitate bonding to the substrate and to provide resistance to vibration and impact. Reinforcements are corrugated metal screen, expanded metal, open metal strips, and metal and nonmetallic honeycomb.

When phosphate-bonded composites are prepared, one of the strongest bonds between the metal oxide particles is obtained with 85% orthophosphoric acid (H_3PO_4). However, composites bonded with orthophosphoric acid have lower

maximum service temperatures than composites formed by the reaction of metal oxide and fluorophosphoric acid (H_2PO_3F). The use of fluorophosphoric acid also permits the use of lower curing temperatures.

After preparation, the composites are aged for 24 h or more to permit reaction between the acid and the metal oxide. The aged composite is troweled either directly onto the substrate or over another protective coating. The coating is then cured with close control of time and temperature. Oxides bonded with orthophosphoric acid are cured for 1 h at each of the following temperatures successively: 93, 120, 150, 215, 315, and 425 °C (200, 250, 300, 420, 600, and 800 °F). Oxides bonded with fluorophosphoric acid are cured for 3 h at room temperature and then for 1 h at 120, 150, and 205 °C (250, 300, and 400 °F). Table 8 identifies several common phosphate-bonded coatings and gives their densities and maximum service temperatures.

Table 8 Characteristics of phosphate-bonded ceramic coatings

Type of phosphate	Constituents	Density		Maximum service temperature	
		kg/m³	lb/ft³	°C	°F
Aluminum	85% $H_3PO_4 + Al_2O_3$	3040-3600	190-225	1925	3500
	$H_2PO_3F + Al_2O_3$	3040-3600	190-225	1980	3600
Hafnium	85% $H_3PO_4 + HfO_2$	4490-4810	280-300	1925	3500
	$H_2PO_3F + HfO_2$	4490-4810	280-300	2205	4000
Zinc	85% $H_3PO_4 + ZnO$	. . .	. . .	1650	3000
Zirconium	85% $H_3PO_4 + ZrO_2$	3200-4650	200-290	1925	3500

A reaction between the acidic coating and the substrate may cause bloating or blistering upon deposition or after initial curing as the result of the release of hydrogen from the acid. The volatilization of phosphorus pentoxide (P2O5), a decomposition product of the acid, also can cause blistering.

Various compounds, such as chromic oxide, ammonia compounds, or ferric phosphate, are added to the coating materials to prevent phosphorus pentoxide from corroding the substrate. These additives increase the pH of the coating without affecting the bonding action. Chromic acid may also be added to improve heat emission of the coating. Coatings are usually thixotropic and appear to have a greater viscosity than is actual because slight agitation causes the material to flow.

Coatings are formulated to possess optimum physical and thermal properties. Particle size and filler-to-binder ratio have a great influence on the final properties, including shrinkage, resistance to thermal shock, bond strength, porosity, and thermal conductivity. The common range of particle size for phosphate-bonded coatings is -14 to -325 mesh.

Phosphate-bonded coatings are used primarily to prevent deterioration of the substrate metal during high-temperature service. Applications include combustion-chamber linings, re-entry leading edges, hot gas ducts, and high-temperature insulation repairs.

Cermets. Table 9 lists the constituents of electrodeposited coatings based on cermets and indicates thicknesses, service life at elevated temperatures, and suitable substrates for these materials. Electrodeposited cermet coatings currently have only a few commercial applications.

Table 9 Cermet electrodeposited coatings for high-temperature oxidation protection

Constituents of coating as applied	Suitable substrate metal	Service temperature		Service life, min	Thickness	
		°C	°F		μm	mils
Cr + ZrB_2	Mo-0.5Ti	2130	3865	20	75-150	3-6
	Tantalum	2130	3865	20	75-150	3-6
	Tungsten	2205	4000	10	75	3
Pt-Rh + ZrB_2	Tungsten	2870	5200	1	510-760	20-30

Cermet coatings, consisting of a mixture of metal and ceramic oxides, protect metallic substrates against oxidation and erosion. The electrodeposition process used for applying these coatings is a combination of electroplating (for metals) and electrophoresis (for ceramics). The amount of ceramic that can be deposited depends on particle size, density, and composition. Ceramic particles ranging in size from less than 1 μm to 44 μm (40 to 1730 μin.) can be plated. These particles are suspended in any common electroplating bath by agitation. With ordinary procedures, coatings containing about 20 wt% ceramic can be obtained in a deposit; with special procedures, this can be increased to 50 to 60 wt%. Because most cermet coatings are for erosion-resistance applications such as rocket nozzles, coatings are relatively thick (>75 μm or >3 mils). Thinner coatings can be obtained, however, and thickness can be controlled to 25 μm (1 mil).

Cermets applied by plasma spraying or detonation gun processes are the basis for increasing the wear resistance of metals and superalloys. The most important cermets are metal-bonded carbides and borides, especially tungsten carbide with 8 to 15% Co. At the lower cobalt content, high hardness and wear resistance are produced. Increasing the cobalt content increases the toughness necessary for wear plus impact service. Tungsten carbides wear well to about 590 °C (1000 °F) in air. At higher temperatures, chromium carbide and certain nickel-chromium alloys are used because of self-lubricating qualities. Coatings based on aluminum oxide, refractory carbides, and an oxidation-resistant metallic binder are in use at temperatures above 870 °C (1600 °F).

Coating Methods

Ceramic coatings may be applied by brushing, spraying, dipping, flow coating, combustion flame spraying, plasma-arc flame spraying, detonation gun spraying, pack cementation, fluidized-bed deposition, vapor streaming, troweling, and electrophoresis. Most of these methods have been used for coating production parts.

Selection of coating method depends on the following factors:

- Substrate metal
- Coating material (some materials are restricted as to method of application)
- Size and shape of the part to be coated
- Cost
- Service conditions (coating method can modify the properties of the coating)

Spraying and Dipping

Spraying and dipping are two methods of applying ceramic coatings in a slip or slurry form. Spraying and dipping methods are used to apply silicates and other coatings onto engine exhaust ducts, space heaters, radiators, and other high-production parts.

Spraying can be used when the shape of the work permits direct access to all surface areas to be coated. This method is usually used for applying a closely controlled thickness of coating to exterior surfaces only.

Dipping can be used for almost all parts. This includes riveted or spot welded assemblies, except those in which faying surfaces would be inadequately covered by the slurry. For a uniform coating thickness, a handling cycle must be established for each part to produce drainage of each surface at the proper angle.

Surface Preparation. Parts must be thoroughly cleaned before spraying or dipping. Oily spots prevent adherence of the coating and cause blistering or spalling during firing. When sand blasting is used, the abrasive must be free of contaminants. Sharp workpiece edges should be rounded because they are difficult to coat. If sharp edges are coated without being rounded off, the coating will often spall after firing.

The principal cleaning processes used are chemical and abrasive. Chemical cleaning methods for metals of low-alloy content are similar to those used before porcelain enameling. (Additional information can be found in the article "Porcelain Enameling" in this Volume.) For high-alloy materials, such as stainless steels and heat-resisting alloys, heat scaling or trichloroethylene-vapor degreasing, followed by grit blasting, is the preferred cleaning method, except for parts made of thin-gage material or with inaccessible areas. For these parts, chemical cleaning is required. Table 10 shows the sequence of chemical cleaning solutions and immersion times used for stainless steels and heat-resisting alloys. The use of chemical cleaning with alkaline solutions is limited to parts that permit good drainage. All cleaning solutions must be removed from the work by water rinsing before the coating is applied.

Table 10 Descaling of stainless steels and heat-resisting alloys before ceramic coating

Alloy	Immersion time, min			
	Solution 1 Sodium hydroxide[(a)]	Solution 2 Sodium hydride[(b)]	Solution 3 Nitric-hydrofluoric acid[(c)]	Solution 4 Nitric acid[(d)]
410, 430	1-2	10-30	None	5-15
321, 347, 316; 19-9 DL	1-2	10-30	10-30	5-15
Inconel; Nimonic 75, 80A	1-2	10-30	5 max	5-15

(a) Molten sodium hydroxide at 400 to 425 °C (750 to 800 °F).

(b) Molten sodium hydroxide containing 0.1 to 2 wt% sodium hydride; bath at 370 to 400 °C (700 to 750 °F).

(c) Aqueous solution containing 1 to 4 vol% 70% hydrofluoric acid and 15 to 25% nitric acid (1.41 sp gr); temperature, 60 to 82 °C (140 to 180 °F). Solution may be used at ambient temperature by increasing immersion time.

(d) Aqueous solution containing 12 to 20 vol% nitric acid (1.41 sp gr); temperature, 60 to 82 °C (140 to 180 °F)

Abrasive blast cleaning should be used on parts that will not be distorted by the blasting action and whose surfaces are accessible to the blasting medium. Abrasive cleaning is particularly applicable when an extremely strong mechanical bond between the coating and substrate is required. Silica sand, the most commonly used blasting medium, has low initial cost. However, its high breakdown rate and its highly detrimental effect on blasting equipment results in high equipment maintenance costs. Use of materials with a higher initial cost, such as steel grit or shot, aluminum oxide, garnet, and glass shot, often results in lower overall cost. For additional information about materials, equipment, and techniques used in abrasive blast cleaning, see the article "Mechanical Cleaning Systems" in this Volume.

Processing. Ceramic coating materials may be purchased as slips, in which form only the specific gravity requires adjustment by either adding or pouring off water before application. Coatings may also be obtained as frits. Frits are milled in porcelain-lined mills with water to which refractory oxides or other inert materials, clay, and setup agents are added to produce the required analysis.

Changes from the recommended composition and specific gravity of a slip may produce undesirable results. A low specific gravity causes limited coverage or running of the applied coating. A high specific gravity results in thick coatings that spall on firing. To obtain satisfactory results, test pieces, 25 by 75 mm (1 by 3 in.) and of the same composition and gage as the work material, should be used to check the dry film weight of the slip and the characteristics of the coating as fired. The slip should be checked at the beginning of each working period and whenever an adjustment is made or when a new batch is prepared.

Application of the slip to the work is also critical because of the coating thickness. For stainless steels and heat-resisting alloys, coating thickness ranges from 13 to 75 μm (0.5 to 3 mils). No specific tolerances for coating thickness exist. If the coating is too thin, it oxidizes during firing and loses its protective value; if too thick, it spalls.

Dipping is the preferred method of coating for production operations, although spraying is also extensively used. In some instances, manual debeading is necessary to remove excess coating from points of buildup to prevent spalling. Complex shapes must be sprayed, because dipping builds up excessive beads or fillets in inaccessible areas.

After being applied, the slip is dried in forced circulating air at 60 to 120 °C (140 to 250 °F) for 10 to 15 min. If the drying temperature is too low, waterlines appear on the coating; if too high, the coating tears. All free water must be removed, or the coating will blister during firing.

Firing is accomplished in a gas or electrically heated furnace. Firing temperature and time depend on the thickness of both the coating and the substrate. The temperature and furnace atmosphere are controlled to produce the required as-fired appearance of the coating with maximum adherence. Overfiring causes excessive oxidation of the substrate, resulting in poor adhesion or a decrease in coating properties. Underfired coatings have poor adhesion and strength and do not develop maximum coating protection.

Equipment for spraying ceramic coatings is available commercially. The spray gun should have a nozzle with an orifice diameter of 1.30 to 2.80 mm (0.050 to 0.110 in.). Efficient nozzles have a spraying capacity of 260,000 to 330,000 mm^3 (16 to 20 $in.^3$) of coating material per minute using an air pressure of 345 kPa (50 psi) to propel the coating material to the work surface. The compressed air supply should be filtered to remove dirt, rust, oil, and moisture. A reliable air pressure regulator should be used to permit accurate adjustment of pressures, particularly in the range of 205 to 550 kPa (30 to 80 psi).

For most dipping applications, the equipment consists of a tank such as that shown in Fig. 1. The tank should be large enough to permit complete submersion of the part into the slip. An easel or rack is required for draining. Dipping equipment can be elaborated to include temperature-controlled dip tanks and recirculating systems with screens and separators in the line for removing contaminants. Automatic equipment incorporating positioners for proper drainage is often used.

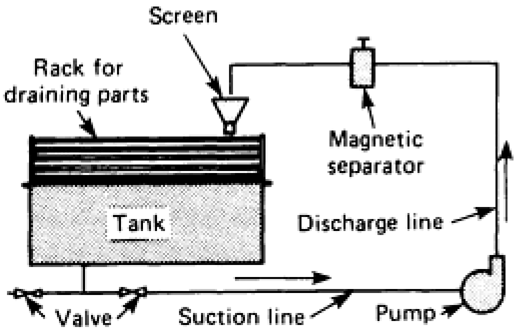


Fig. 1 Recirculating dip tank for the application of ceramic coatings

Flow coating is modified dipping and draining in which slip is flowed onto conveyorized parts. Slip flows from nozzles designed to flush all surfaces of the work, after which it drains into a catch basin and is recirculated.

Flame Spraying

Most ceramic coating materials used currently can be applied by flame spraying. Silicates, silicides, oxides, carbides, borides, and nitrides are among the principal materials deposited by this process. There are three methods of heating and propelling the particles in the plastic condition to the substrate surface: combustion flame spraying, plasma-arc flame spraying, and detonation gun spraying. The first two methods use coating materials in powder or rod form. Detonation gun spraying uses only powder materials.

Applicability. Flame-sprayed ceramic coatings can be applied to workpieces in a wide range of sizes and shapes. Practically all metals that can be adequately cleaned, textured by standard abrasive blasting equipment, and safely heated to 150 to 205 °C (300 to 400 °F) can be coated.

Spray equipment can be fitted with extensions having deflecting heads that can turn the spray direction up to 45°. Thus, any shape can be coated if the spray head can be placed within a few inches of the substrate and at an angle of ±45° to the surface.

From a practical standpoint, the maximum size limits for coating the outside and inside surfaces of workpieces depend only on the preparation and handling equipment. In general, the minimum size of the internal diameter is limited to 50 mm (2 in.), and the length should not exceed 3.7 m (12 ft) unless the diameter is large enough to accommodate the entire gun and the supply lines. The coating of curved passages is limited to sizes and shapes that permit approach of the gun at the angles and distances already prescribed. For example, satisfactory coatings have been applied to wires as small as 0.10 mm (0.004 in.) in diameter, to rocket nozzles with 6.4 mm (0.25 in.) throat diameter that were 13 mm (0.5 in.) in length, and to large ducting 2 m (6 ft) in diameter by 8.2 m (27 ft) long.

Combustion Flame Spraying

Processing variables of flame spraying that directly affect the serviceability of a coating are principally surface preparation, gun operation, spraying distance, temperature of the workpiece, and type of coating.

The serviceability of the coating depends on the surface preparation. If a surface is not absolutely clean or is not roughened sufficiently, bond strength may be reduced 50% or more.

Optimum adherence of the spray particles to each other (cohesion) depends on the fineness of the spray, uniformity of the spray pattern, correct adjustment of gas ratios and pressures, and proper material feed rate. These can be accomplished only by proper adjustment of the spray system.

The temperature and size of the spray particles must be closely controlled. If a rod gun periodically produces large spray particles, they are not sufficiently heated and are consequently less plastic, resulting in poor bonding to adjacent particles or to the substrate and creating a weak point or area in the coating.

Spray guns should be maintained at the prescribed distance from the substrate for the type of coating desired. If the gun is too close, the coating becomes crazed and has low thermal shock resistance. An excessive gun-to-work distance can result in soft, spongy deposits with low physical properties and decreased deposit efficiency.

Surface Preparation. Because flame-sprayed particles adhere to the substrate surface primarily by mechanical bonding, suitable methods of surface roughening are essential. These consist of undercutting, grooving, threading, knurling, abrasive blasting, and applying sprayed metal undercoats. Abrasive blasting and metal undercoats provide optimum surface conditions for ceramic coatings. When blasting is used, abrasives must be clean and sharp. Roughening should be uniform and should produce as many re-entrant angles and sharp peaks as possible.

Steel grit is one of the most satisfactory blasting abrasives. It disintegrates slowly and offers maximum life. The grit should be screened periodically to remove dirt and fines. Angular steel grit is available in many sizes. A G25 grit propelled by 275 kPa (40 psi) air pressure is used in many applications.

Fused-alumina grit may be used when surface contamination by a steel abrasive is objectionable. Optimum surface preparation is obtained with a No. 24 grit propelled at a pressure of 275 to 345 kPa (40 to 50 psi). This abrasive cuts faster than steel, but some breakdown of the grit occurs, and the fines should be removed before reuse. For light-gage materials, finer grit (No. 46) and lower blasting pressures are recommended to prevent distortion of the work. Silicon carbide also produces a satisfactory surface for ceramic coatings.

Sprayed metal coatings provide an anchoring base for flame-sprayed ceramics equal to that obtained by abrasive blasting. Sprayed molybdenum undercoatings are used as a bonding coat for subsequent application of ceramic coating to metal substrates that are too hard or too thin to receive adequate surface roughening through abrasive blasting.

Nickel-chromium or nickel-chromium-aluminum alloy sprayed undercoatings are used as an adherent base for flame-sprayed ceramic coatings that are repeatedly subjected to high temperatures. An undercoat in thicknesses of 50 to 330 μm (2 to 13 mils) develops an optimum bond for the ceramic coating. When the metal alloy is used, the substrate surface is first roughened by abrasive blasting. Areas that do not require coating can be protected with masking tape, rubber, or sheet metal, depending on the severity of the surface roughening operation.

Processing. After surface preparation, the spray gun is loaded with ceramic coating material of proper size, and the gun is ignited according to the procedure recommended by the manufacturer. Techniques used in flame spraying of ceramics are similar to those used in spraying paint. Successful application depends primarily on the skill of the operator.

Spraying distance and rate of gun traverse across the work should be held as nearly constant as possible. The distance and rate of traverse depend on the spraying equipment, composition of the coating material, substrate metal, and desired physical characteristics of the coating. Powder guns have a relatively long, bushy flame to heat the ceramic powder during its passage through the extensive heat zone. Consequently, powder guns may need to be placed 150 to 200 mm (6 to 8 in.) from the workpiece and traversed quite rapidly to minimize overheating. Rod guns using the same type of heating operate with a very short flame and heat zone, because heating of the ceramic always takes place at a fixed location at the end of the rod. For rod guns, the optimum spraying distance is about 75 mm (3 in.).

The gun should be moved continuously across a surface in such a manner that each pass slightly overlaps the preceding one. When the surface is completely coated, succeeding passes to increase thickness should be at right angles to those used for initial coverage.

When possible, the spraying angle should be 90° to the workpiece surface to produce the smoothest coating at the fastest rate. Spraying angles up to 45° from the preferred gun position can be tolerated if the slight reduction in physical characteristics of the coating is acceptable.

To obtain optimum coating properties, the workpiece temperature should be controlled. Adherence of the coating is greatly reduced if the substrate is heated over 260 °C (500 °F). Substrate temperatures can be measured on the reverse sides of panel specimens by applying temperature-sensitive paint or crayon that melts when a specific temperature is exceeded.

When a rod gun is used for coating flat surfaces, use the following practices to avoid overheating the substrate:

- Move the gun across the face of the work in a smooth motion and at a rate of about 0.3 m (1 ft) every 5

s.

- Maintain the proper distance between gun and work (about 75 mm or 3 in.) during spraying passes.
- If a workpiece is small, pause to the side of the work after a coating pass to permit the workpiece to cool slightly.

Overheating of substrates was overcome in one plant by fixturing the work and spraying for a limited time. The conditions of this operation are illustrated in Fig. 2. Combustion flame spray coating of the inside surface of the rocket combustion chamber shown in Fig. 2 caused melting or burning of the magnesium-alloy substrate when the zirconia coating was applied in a continuous operation. Destruction occurred before the required coating thickness of 890 to 1020 μm (35 to 40 mils) could be applied.

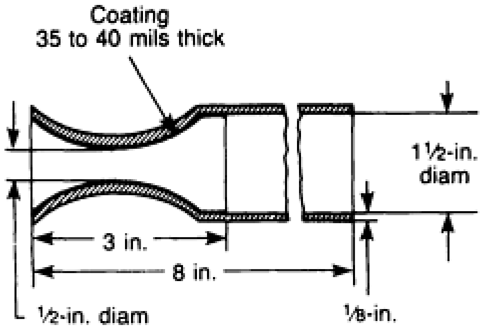


Fig. 2 Zirconia-coated magnesium-alloy rocket combustion chamber

This problem was solved by using a fixture comprised of three friction-loaded thin steel fingers that extended from a standard rotatable chuck. The fingers gripped the exterior of each combustion chamber with just enough force to hold the workpiece during rotation and to permit rapid interchange of the workpieces.

The coating operation consisted of rotating the workpiece at about 30 to 50 rev/min, spraying for not longer than 25 s, then removing the workpiece to permit cooling to room temperature, during which time uncoated or partly coated workpieces would be processed in the same manner. Each combustion chamber required eight or more cycles for producing a coating of the specified thickness.

Figure 3 illustrates a metal nozzle to which a coating of alumina and zirconia was applied 635 μm (25 mils) thick. The operating conditions were as follows: The total area coated on each nozzle was 7100 mm^2 (11 $in.^2$). The time required for preparation, sand blasting, coating, and handling is broken down as follows:

Conditions	Coating material	
	Alumina	Zirconia
Size of ceramic rod	4.8 by 610 mm ($\frac{3}{16}$ by 24 in.)	4.8 by 455 mm ($\frac{3}{16}$ by 18 in.)

Rods per nozzle coated	1	$1\frac{1}{2}$
Average feed rate	180 mm/min (7 in./min)	100 mm/min (4 in./min)

When large areas require coating, it may be more economical to use more than one spray gun. With the proper mechanical setup, one operator can operate four spray guns efficiently.

Process	**Cycle time, min**	
	Alumina	**Zirconia**
Fixturing	5	5
Masking	5	5
Sand blasting	1	1
Coating	3	6
Unpacking, repacking, transportation, paper work	6	6
Inspection, individual packaging	1	1

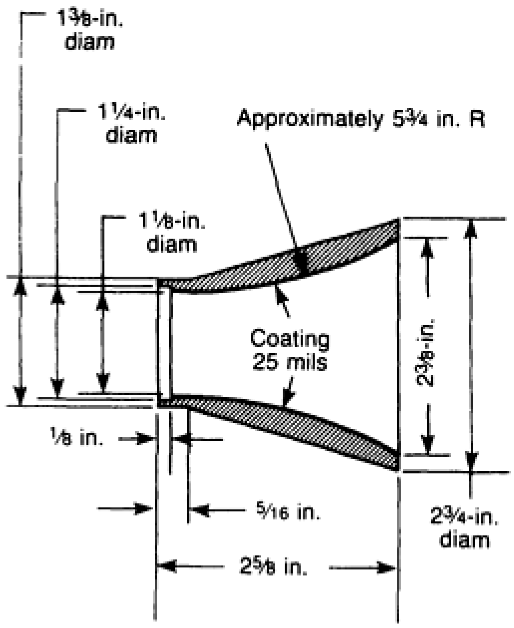


Fig. 3 Metal nozzle coated with alumina and zirconia

Equipment. Most parts require fixturing. For simple shapes that are hand coated, only a simple clamping device is needed for rigidly supporting the part within an exhaust hood during coating. Sheet metal is used for masking areas that do not require coating. A lathe is a suitable fixture for coating parts such as cylinders and nozzles. The chuck rotates the part, and the tool post carriage mechanically moves the spray gun. This setup requires a movable exhaust system for removal of the combustion products and excess spray material.

Gravity-feed or pressure-feed spray guns for powder, or electric-feed or air-motor-feed rod guns, are used in combustion flame spraying.

A typical gravity-feed powder spray installation consists of a fuel gas-control unit, including regulators, to provide a supply of oxygen and acetylene or hydrogen fuel gas; a meter for accurate measurement of aspirating gas flow; and a spray gun with a nozzle and a canister for containing powder. The principle of operation for this gun is illustrated in Fig. 4. Powder falls through a metering valve in the bottom of the canister into a stream of aspirating gas, which propels it to a stream of fuel gas that has been diverted through a valving system in the gun. The flow rate of the powder is controlled by the size of the metering valve and the amount of aspirating gas metered through the nozzle. This gun usually has a vibrator to maintain uniform powder flow.

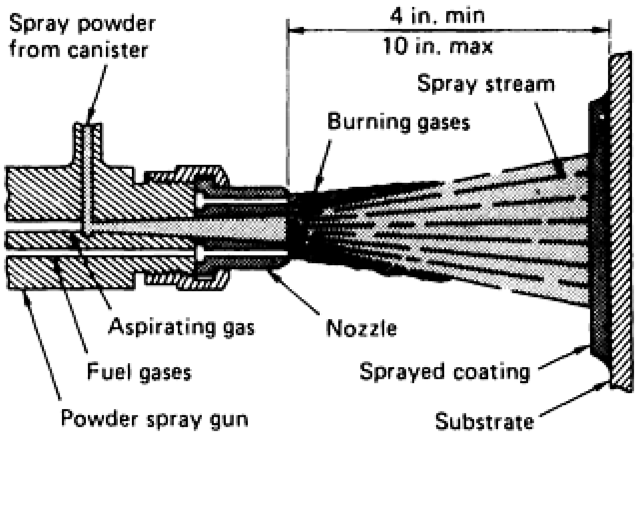


Fig. 4 Operational principle of a gravity-feed powder spray gun

In the pressure-feed system, the powder container is separated from the gun and connected by means of a hose through which powder and carrier gas flow. The carrier gas may be compressed air, fuel gas, or inert gas. Hydrogen is commonly used as both carrier and fuel gas.

Control of particle size is important in both gravity-feed and pressure-feed systems. However, the pressure-feed system requires less control of distribution of particle size because of the higher velocity of the carrier gas. Compared to rod spraying, powder spraying has lower initial equipment costs and greater flexibility of coating properties, as well as being adaptable to a wider variety of coating materials.

A typical rod spray installation is illustrated in Fig. 5. In addition to the auxiliary equipment required for the powder spray process, rod spraying requires a supply of compressed air, an air-control unit that includes a filter and a regulator, and an air flowmeter. A good grade of acetylene should be used, and at least two tanks should be manifolded so that withdrawal rates can be kept below a maximum of one-seventh of the volume of the tank capacity per hour to prevent acetone withdrawal. This is recommended because of the cooling effect that acetone vapor has on flame temperature.

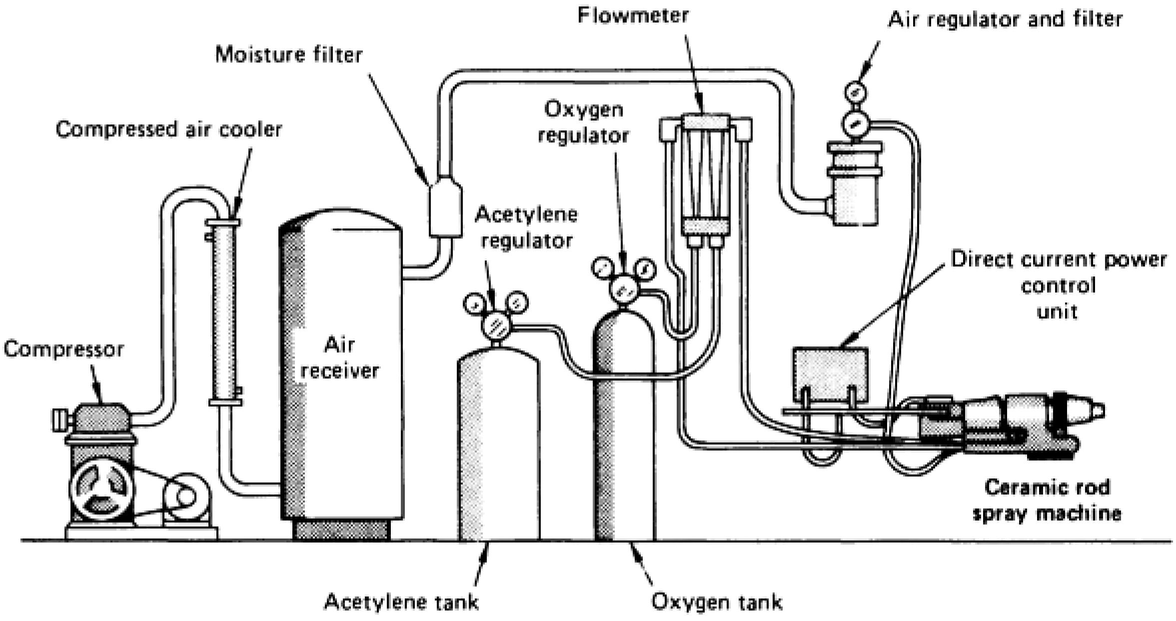


Fig. 5 Rod spray installation

The operation of a ceramic rod spray gun is shown in Fig. 6. The ceramic rod is fed through the center of the nozzle and atomized by the surrounding oxyacetylene flame and compressed air. Compressed air is used to cool the nozzle, increase the velocity of the sprayed material, and control the spray pattern. Control of the diameter and straightness of the rod is required to eliminate problems such as rod sticking and blowback. Control of rod speed is important for control of the density and surface characteristics of the coating. The rod and powder guns can be equipped with extensions and 45° angle air caps for coating inside diameters. The velocities of the sprayed particles from a rod gun and those from a powder gun are compared in Fig. 7.

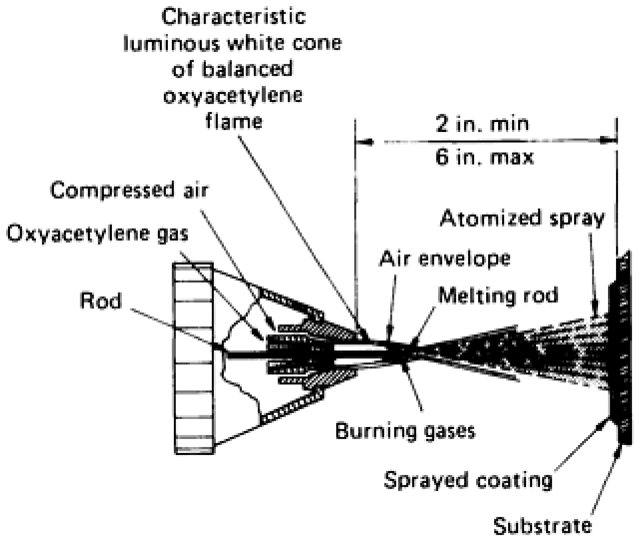


Fig. 6 Operational principle of rod gun

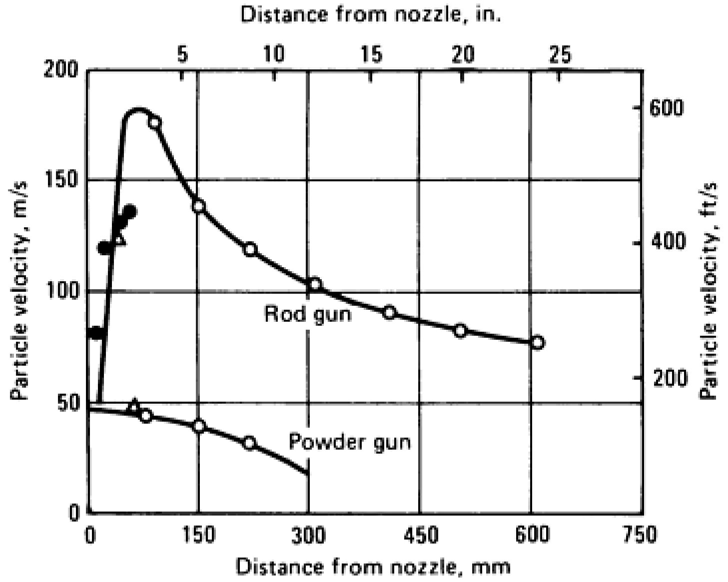


Fig. 7 Comparison of spray particle velocity from rod and powder guns. ○: Velocimeter; •: streak camera, fast particle; △: high-speed motion pictures

Rod spraying causes less heating of a workpiece than powder spraying, and it produces a coating with higher density and better bond between the coating and substrate.

Control of coating thickness is related directly to the method used for handling the workpiece and the spray gun. Hand-applied coatings can easily be held within a tolerance of ±50 μm (±2 mils). Mechanical systems for handling both workpiece and gun decrease this tolerance by 50% or more. The variation in coating thickness obtained by hand spraying alumina and zirconia on one side of steel test coupons (25 by 25 by 3.2 mm, or 1 by 1 by $\frac{1}{8}$ in.) with a rod gun is shown in Fig. 8.

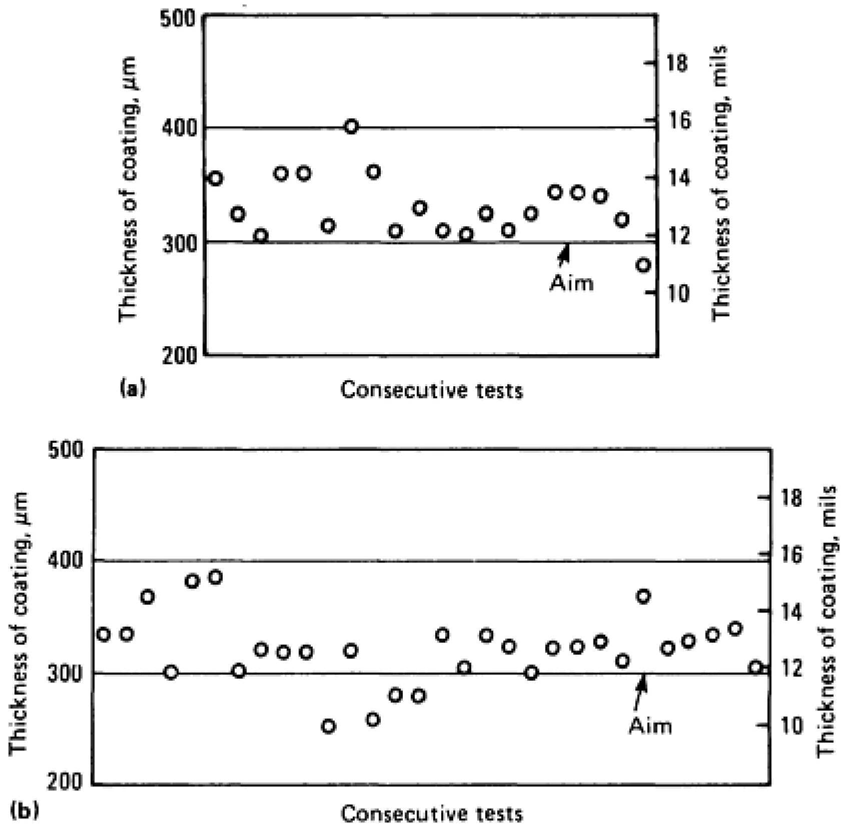


Fig. 8 Variation in thickness of hand-sprayed alumina and zirconia coatings on steel test coupons. Coatings flame sprayed from rod. (a) Alumina on steel, 20 tests. (b) Zirconia on steel, 30 tests

Flame-sprayed coatings are applied relatively slowly; therefore, after a uniform surface coverage system has been set up, control of the coating thickness depends on timing the duration of coating application with sufficient accuracy to achieve the desired tolerances. If closer tolerances or finer surface finishes are required, most flame-sprayed ceramic coatings can be ground by conventional grinding techniques.

Plasma-Arc Flame Spraying

In the plasma process, a gas or a mixture of gases, such as argon, hydrogen, or nitrogen, is fed into the arc chamber of the plasma generator and heated by an electric arc struck between an electrode and the nozzle. The gas is heated to temperatures as high as 8300 °C (15,000 °F) to form a plasma, or ionized gas, that is accelerated through the nozzle. The ceramic powder, carried by a gas stream, is injected into the plasma, where it is heated, melted, and propelled toward the workpiece.

The higher-temperature heat source of the plasma arc imparts an energy content to the ceramic particles that is different from that in the combustion flame process. This necessitates some modification of the gun position. When the plasma process is used, higher-melting ceramic materials, such as the refractory metal carbides, can be deposited with a greater deposition rate.

The processing operations for plasma-arc spraying are similar to those discussed in the section on combustion flame spraying in this article. For a more detailed discussion of plasma-arc spraying, see the article "Thermal Spray Coatings" in this Volume.

Thermal barrier coating is one current application using plasma-arc spraying. Applied to certain high-temperature components, such as the inside of combustion chambers or the first-stage vane or blade of a gas turbine engine, thermal barrier coatings act to insulate the metal substrate thermally. Coatings are designed to provide as much as a 110 °C (200 °F) drop in temperature at 980 to 1095 °C (1800 to 2000 °F), but they should be used in a temperature gradient, such as is provided by air cooling the substrate or metal side. A thermal barrier could be a 150 to 200 μm (6 to 8 mils) undercoat of

a high-temperature nickel-cobalt-chromium-aluminum-yttrium alloy, followed by 255 to 305 μm (10 to 12 mils) of yttria-stabilized zirconia or magnesium zirconate ($MgO \cdot ZrO_2$). If greater thickness for greater insulation is desired, thermal stresses resulting from application should be carefully considered. In laboratory applications, a thermal cycling test is used followed by a bench engine evaluation to qualify the coating and estimate service life.

Detonation Gun Flame Spraying

Detonation gun flame spraying is markedly different from other flame spraying processes and was developed specifically for the deposition of hard, wear-resistant materials, such as tungsten carbide. Detonation gun spraying uses controlled detonations of acetylene and oxygen to melt and propel the particles onto the substrate.

Powder materials sprayed by this process are carbides containing a small amount of metal binder, and oxides or oxide mixtures. Coatings are usually less than 255 μm (10 mils) thick and are used primarily in applications requiring wear resistance under extreme service conditions. Applications include aircraft jet engine seals (for protection against high-temperature dry rubbing wear) and aircraft compressor and turbine blades (for protection against fretting corrosion at medium to high temperatures).

Coating particles emerge from the gun at supersonic speeds, and only those areas that permit the particles sufficient access are plated uniformly. This limitation prevents the coating of narrow holes, blind cavities, and deep V-grooves. Internal diameters over 9.7 mm (0.38 in.) and open at both ends can be coated to a depth of $1\frac{1}{2}$ times the diameter.

Cementation Processes

Pack cementation, the fluidized-bed process, and vapor streaming are three types of cementation processes used in ceramic coating. These processes are used to produce impervious, oxidation-protective coatings for refractory metals and nickel-base, cobalt-base, and vanadium-base alloys. The principal types of coating applied by the cementation processes are silicides, carbides, and borides, usually of the base metal although frequently of codeposited or alternately deposited other metals such as chromium, niobium, molybdenum, and titanium.

Pack Cementation

Preparation of the substrate surface for application of a ceramic coating by pack cementation consists of removing burrs, rounding edges (0.125 mm, or 0.005 in. minimum radius to half the edge thickness, for foil), and rounding corners (preferably to a minimum radius of 3.2 mm or 0.125 in.). Edges and corners must be rounded to prevent cracking of the coating (Fig. 9). This can be accomplished by manual sanding with fine-mesh cloth or with a small motor-driven fine-mesh conical grinding wheel. Mass (barrel) finishing can be used for removing burrs and rounding edges and corners of small articles such as rivets.

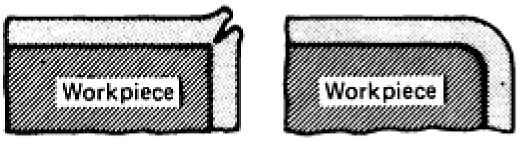


Fig. 9 Effect of sharp and round corners on the continuity of a ceramic coating

The next operation consists of cleaning the work by vapor degreasing followed by mechanical or chemical cleaning. Mechanical cleaning is usually preferable to chemical cleaning and may consist of wet blasting, abrasive blasting with 200-mesh alumina, or buffing. Parts that are buffed should be washed in acetone, and precautions should be taken to prevent adherence of the buffing compound. Chemical cleaning is used when the shape of the part is not suited to blasting or buffing. Parts must be rinsed and dried thoroughly after they are removed from chemical solutions, and precautions must be taken to avoid contamination of cleaned parts during subsequent handling.

Processing. After cleaning, parts are packed in a retort with the desired coating material. Parts should be placed about 25 mm (1 in.) from the retort walls; spacing may be from 3.2 to 13 mm ($\frac{1}{8}$ to $\frac{1}{2}$ in.) between parts, and from 6.4 to 25 mm ($\frac{1}{4}$ to 1 in.) between layers. Packing material must fill all cavities or areas that may entrap air. Sufficient packing material must be placed between the bottom of the retort and the first layer of parts, and over the top layer. The packed retort should not be handled roughly or be vibrated before or during the thermal process cycle.

An inert filler (aluminum oxide) is used to obtain the most efficient use of packing material when large assemblies or components are being coated. The filler should be no closer than 13 mm ($\frac{1}{2}$ in.) from the substrate surface. Figure 10 shows the use of a filler for filling space within the throat of a nozzle, the internal surfaces of which were being coated by the pack cementation process.

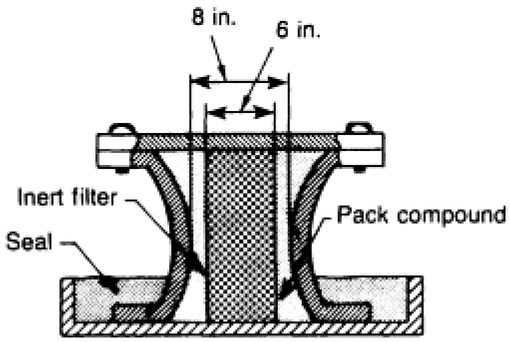


Fig. 10 Use of an inert filler during application of pack cementation coating to the internal surfaces of a nozzle

The packing material usually consists of coating materials (in elemental or combined form), a suitable activator or carrier-gas-producing compound, and inert filler material. A standard siliconizing packing material contains silicon powder (100- to 325-mesh), a halide salt (ammonium chloride, sodium fluoride, or potassium bromide), and an inert filler (aluminum oxide, 100- to 325-mesh). Occasionally, urea is incorporated in the pack material to purge entrapped air before the cementation reaction begins.

The processing temperatures used for pack cementation coating of refractory metals depend on the substrate metal and the desired coating characteristics. In general, temperature controls the rate of deposition, and time is varied to control the thickness of the coating. A low processing temperature results in a coarse, columnar structure and an uneven deposit. High processing temperatures result in deposits of uniform thickness and dense structure. The recrystallization temperature of molybdenum-base and tungsten-base substrates should not be exceeded because of resulting embrittlement. Table 11 gives time-temperature cycles adequate for applying oxidation-resistant coatings.

Table 11 Cycles for application of silicide and other oxidation-resistant ceramic coatings by pack cementation

Processing cycles suitable for depositing coatings of silicon, chromium, boron, aluminum, titanium, zirconium, vanadium, hafnium, and iron

Substrate metal	Processing cycle		
	Temperature[(a)]		Time, h[(b)]
	°C	°F	

Niobium alloys	1040-1260	1900-2300	4-16
Molybdenum alloys	1040-1150	1900-2100	4-16
Tantalum alloys	1040-1150	1900-2100	4-12
Tungsten alloys	1040-1370	1900-2500	3-16

(a) Tolerances: ±6 °C (±10 °F) at 1040 °C (1900 °F);±14 °C (±25 °F) at 1260 °C (2300 °F).

(b) Tolerance, ±10 min

After thermal treatment is completed, the retort may be cooled in the furnace or in air. The coated parts can be removed from the retort when they are cool enough to handle. Loose packing material is removed by washing the parts in warm water, bristle brushing, and spray rinsing. Water under pressure may be used to remove packing material from difficult-to-clean areas. If a second pack cementation operation is required for the addition of other coating elements, parts should be handled with clean gloves or plastic-tipped tongs. If contaminated, parts must be vapor degreased just before packing for the next coating cycle.

When a second coating cycle is not required, the coated parts may be subjected to a high temperature (about 1095 °C, or 2000 °F) to form a protective oxide surface. Normally, 15 to 30 min at this temperature is sufficient to form a protective film on refractory alloys.

Components of assemblies are coated individually, then assembled and packed for the second cycle to protect the joint areas. If assembling causes discontinuities or cracks in the coating, areas are wet blasted and dried or are lightly sand blasted before packing.

The optimum thickness of coating on refractory metals is from 25 to 100 μm (1 to 4 mils). In general, oxidation resistance increases with coating thickness; however, the sharp radii of foils do not permit a coating thickness of much over 25 μm (1 mil). The usual thickness of pack cementation coatings is 38 ± 13 μm (1.5 ± 0.5 mils) for machined components, formed parts, and sheet materials; for foils of 0.250 mm (0.010 in.) or less, the coating thickness is usually 25 ± 8 μm (1.0 ± 0.3 mils).

Equipment for pack cementation consists of a retort and a furnace of suitable size to accommodate the retort. Furnace atmosphere is not critical and may be air, endothermic, exothermic, or inert gas. When a specific atmosphere around the retort is essential, an atmosphere housing may be incorporated.

Retorts are either top-loaded or inverted and may be designed for shallow or deep sealing (Fig. 11). The type of material from which retorts are made depends on the operating temperature and furnace atmosphere. For operating temperatures between 980 to 1260 °C (1800 to 2300 °F), Inconel and types 310, 321, and 347 stainless steel provide satisfactory service. When the furnace atmosphere is oxidizing or carburizing, a stopoff slip ceramic coating on exposed areas of the retort prolongs its service life. Materials for sealing the retort may be sand, alumina, or garnet, with or without oxide scavengers such as silicon or titanium, or low-melting-point materials such as sodium orthosilicate.

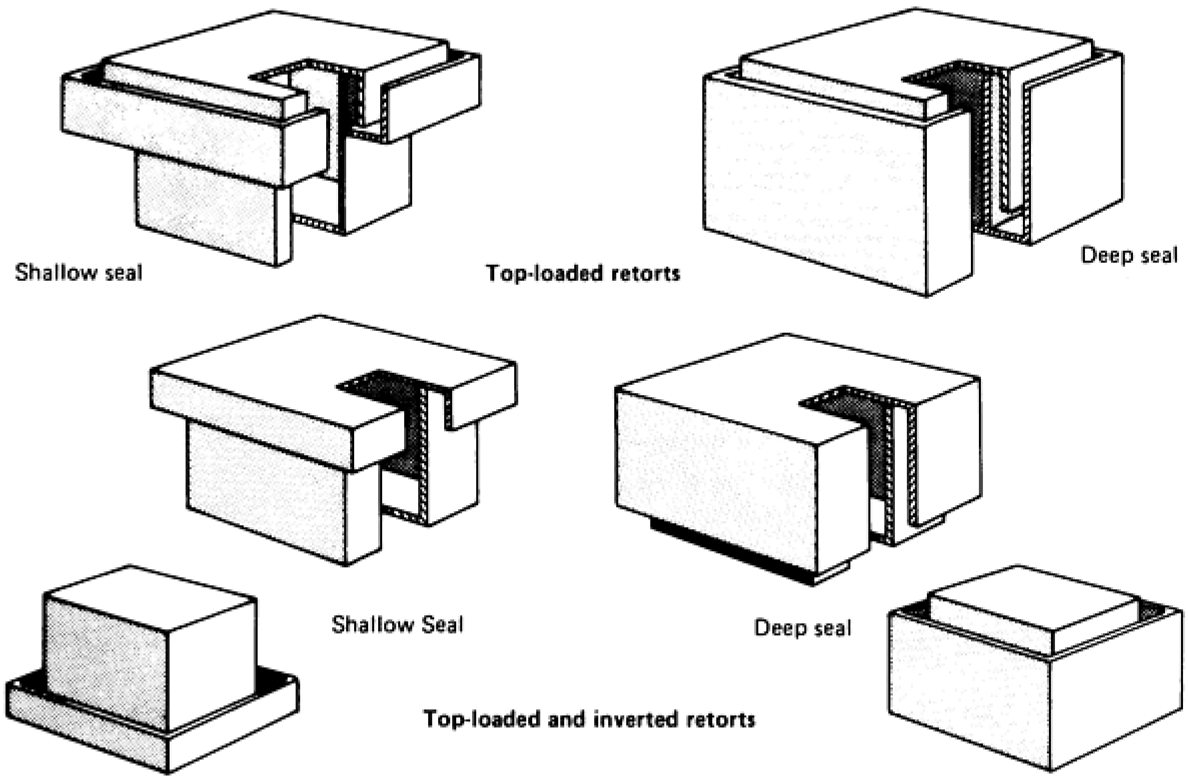


Fig. 11 Designs of retorts used in the pack cementation process

Fluidized-Bed Cementation Process

The fluidized-bed process for applying ceramic coatings involves:

- Thermal decomposition and displacement reactions of metal halides
- Presence of hydrogen to reduce the halides
- Diffusion of deposited materials into the substrate metal to produce an intermetallic compound, such as molybdenum disilicide

In this process, a bed of metal powder reactant and inert material is fluidized or floated at elevated temperature by an inert or reactive gas. The finely divided particles of reactant and inert material are constantly agitated by the fluidizing gas. Thus, the transfer of heat between the object to be coated, the coating material, and the gas is greatly increased by the diffusion of vapor and gas and by the relatively high flow rates. Vapors of coating material can be prepared within the fluidizing chamber by the reaction of particles in the bed with the gases, or they can be prepared and evaporated in a separate vessel. A schematic flow diagram of the fluidized-bed process is shown in Fig. 12.

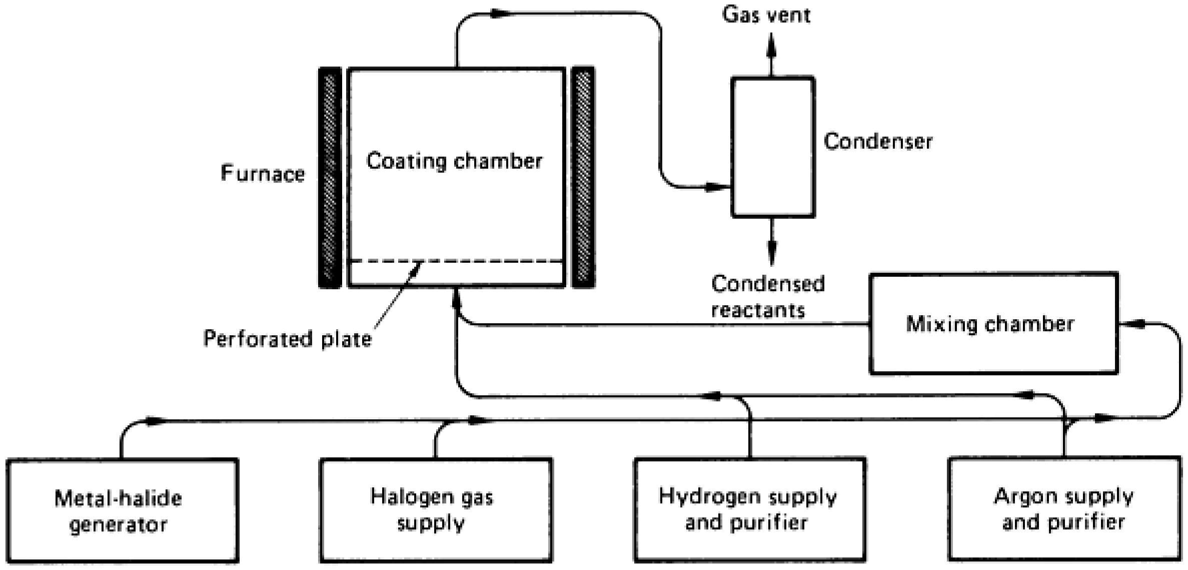


Fig. 12 Fluidized-bed cementation process

Processing. Preparation of the surface of the work consists of rounding the edges, buffing the surfaces and edges, and etching. The following etching procedure is used for molybdenum-base substrates:

- Dip in 80% nitric acid solution at room temperature for several seconds.
- Rinse in cold water (three rinses).
- Dip in 50% hydrochloric acid at room temperature for several seconds.
- Rinse in cold water (three rinses).
- Wash in acetone.

After etching, parts are placed into the fluidizing chamber and processed at 1065 °C (1950 °F) for 1 h. Coated parts are removed from the furnace when cool.

Effect of Process Variables on Coating Characteristics. The control of time, temperature, and carrier-compound concentration is important in the fluidized-bed process, because these variables control the thickness and uniformity of the coating, as well as the rates of deposition and diffusion. Temperature should be controlled to within ±14 °C (±25 °F).

Coating thickness as a result of time and temperature is shown in Fig. 13 for a silicide coating applied to Mo-0.5Ti alloy. The coating thickness represented by these data was calculated from the change in weight of the coated part, using the average density of molybdenum silicide ($MoSi_2$). Although data for operating temperatures below 925 °C (1700 °F) are included, coatings applied to refractory metals at these low temperatures have poor oxidation resistance.

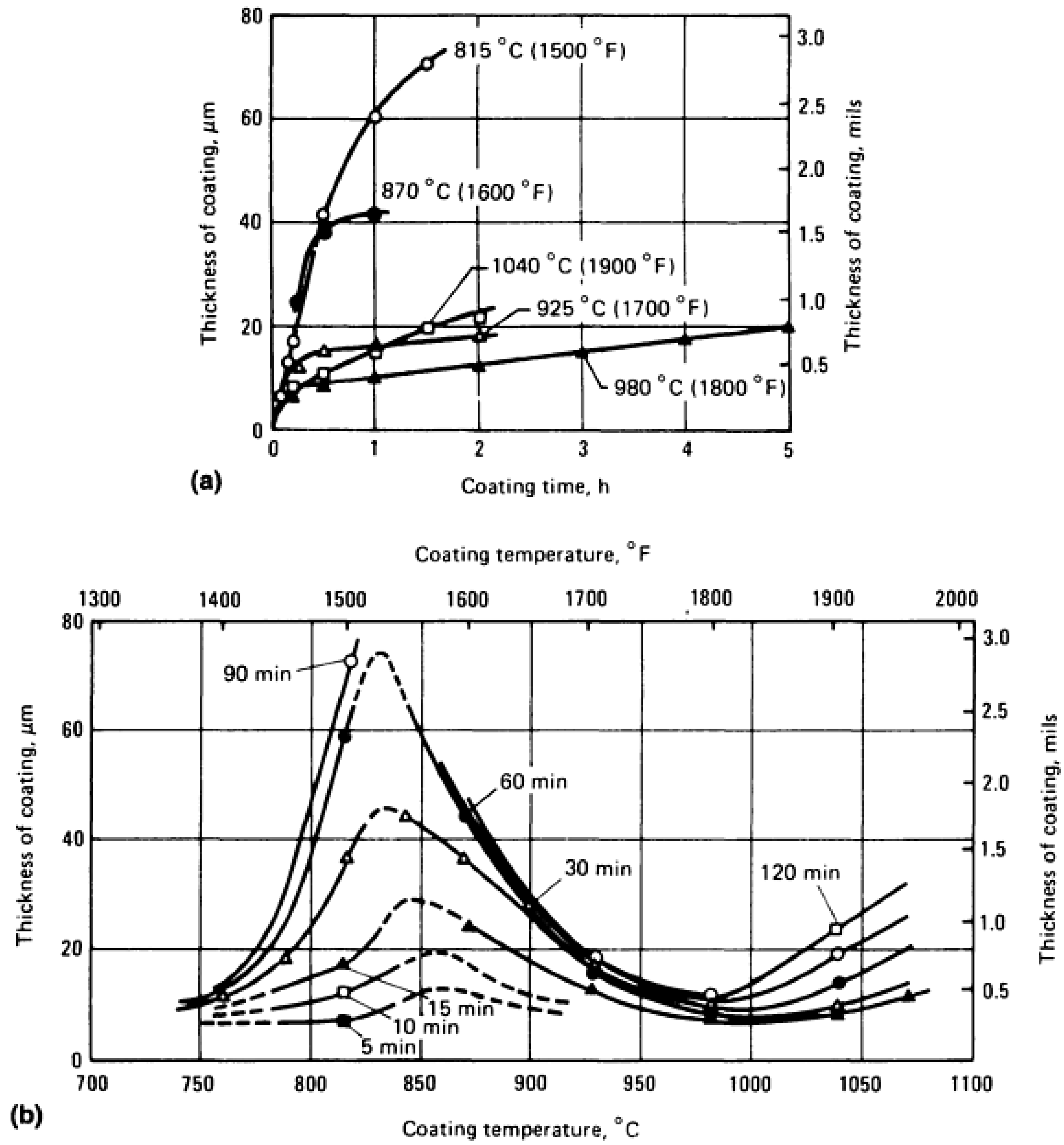


Fig. 13 Effects of (a) time and (b) temperature on the thickness of a silicide coating applied by the fluidized-bed process to Mo-0.5Ti alloy

Applicability. Complex shapes can be coated by the fluidized-bed process. With special techniques, inside surfaces of long small-diameter closed-end tubes can be coated. However, coatings will form only on edges with a radius of 0.125 mm (0.005 in.) or more.

Cracks around rivet heads and joints between sheets cannot be bridged by ceramic coating during elevated-temperature service. Therefore, double processing cycles are required, one before joining and one after assembly of the component parts.

Service life of a coating 50 to 75 μm (2 to 3 mils) thick on flat surfaces is about 1 to 2 h at 1650 °C (3000 °F). The effects of edges and corners combine to reduce this life, because coating thickness for satisfactory coverage is less at these locations.

Vapor-Streaming Cementation

Vapor streaming is a cementation process in which a vapor of the coating material is decomposed on the surface of a heated part. For example, silicide coatings are produced by passing silicon halide vapor in a hydrogen atmosphere over heated substrate. The silicon halide is reduced, and silicon deposits on the substrate and diffuses to form an intermetallic compound. Commercial application of this process has been insignificant.

Trowel Coating

Coatings applied by troweling are acid-bonded systems (phosphates and sulfates), hydraulic-setting cements (calcium aluminate and portland cement), soluble silicate-bonded systems (sodium, potassium, and lithium), and colloidal metal oxide-bonded ceramic oxides and carbides. Troweled coatings are used for furnace linings, hot gas ducts, and certain repair patches on other coatings for relatively short service exposure. The resistance to heat transfer of these coatings depends on the porosity, density, and thermal conductivity of the solid phase and on the thermal shorts caused by any reinforcement metal present. Coatings applied by troweling consist of filler, binder, carrier, and additives. Coating constituents are blended in a muller or other suitable mixer to a uniform consistency. Some materials, such as the acid-bonded coatings, require aging before application to permit reaction between constituents.

Surface Preparation. Surfaces to be coated must be free of contaminants such as oil and grease that may interfere with the wetting and bonding of these water-based coatings. Most coatings applied by troweling are chemically bonded or hydraulic-setting materials. Because these materials do not form a strong metallurgical bond with substrate metals, and because of the differences in coefficients of expansion, substrate surfaces must be roughened for maximum mechanical bonding and to minimize the effects of expansion, vibration, and impact during service. Surface roughening is accomplished by grit blasting or chemical cleaning, or by attaching mechanical reinforcements such as wire mesh, corrugated metal, angular clips, or honeycomb structures. Reinforcement is usually required for surfaces having a finish of less than 6.35 μm (250 μin.).

Processing. Application of coating material, in thicknesses ranging from 3 to 25 mm (0.1 in. to over 1 in.), is accomplished by standard troweling techniques. The material is worked under, around, and through the reinforcements. The smoothed thickness can be measured by a depth gage or with pre-fixed height gages. Vibration of the coating followed by retroweling produces a denser coating. Hydraulic-setting coatings must be applied immediately after mixing with water, because bonding occurs during dehydration.

After application, hydraulic-setting coatings may be cured at ambient temperature or by being heated at less than 100 °C (212 °F). If heat curing is used, the coated work should be raised to temperature at a slow rate to prevent the coating from blistering. The acid-bonded composites are cured at temperatures ranging from 20 to 425 °C (68 to 800 °F), depending on composition and thickness of the coating. Well-ventilated facilities must be used when working with acid-bonded coatings.

Soluble silicate materials are cured at temperatures from 21 to 425 °C (70 to 800 °F), depending on the system and special additives that produce air-drying properties. To remove entrapped moisture, chemical-setting materials are dried in air. Colloidal metal oxides require only the removal of excess water either by air drying or by heating to 100 °C (212 °F).

Electrophoresis

Electrophoresis is the migration of electrically charged particles suspended in a colloidal solution under the influence of an applied electric field. Deposition occurs at one of the electrodes where the charge on the particle is neutralized. The particles acquire a static charge during milling, or they can be charged artificially by absorption of certain additives or electrolytes. This coating process, now being used commercially with increasing frequency, is applicable to practically all substrates, including tool steels, stainless steels, superalloys, refractory metals, oxides, and graphite.

Coatings as applied are soft, and densification is sometimes required. Densification, if needed, may be accomplished by isostatic pressing, hot pressing, or a combination of these methods, depending on the substrate metal. The coating is sintered, usually in a controlled atmosphere.

During sintering, metal coatings are bonded to the substrate by diffusion; oxide coatings, by mechanical and electrochemical bonding. Coating thickness rarely exceeds 75 μm (3 mils), and the thermal expansivity of coating and substrate should be closely matched to prevent spalling. The electrophoresis coating process is simple and easily automated while providing better control of coating thickness and composition than is possible with the slurry and pack cementation processes.

Quality Control

No single nondestructive method is adequate for evaluating the quality of a ceramic coating. Although visual inspection or comparison is only of limited usefulness, many plants prepare samples of coating with surface defects that are known to be harmful to the protective value and service life of the coating and use these samples as visual comparators.

High-Temperature Test. The most reliable test procedure for determining coating continuity and oxidation resistance on complex structures made of refractory metals is to subject the structure to a high-temperature test environment under carefully controlled conditions. First, exposed surfaces are inspected visually under low-power magnification. The work is then heated to 1095 to 1205 °C (2000 to 2200 °F) in air. After a 15 min heating period, surfaces are examined while hot for evidence of evolution of an oxide gas (molybdenum trioxide when molybdenum is the substrate) or for the discoloration that accompanies oxidation of a niobium, tantalum, or tungsten substrate. If no evidence of oxidation is observed, the work is removed from the furnace, cooled, and examined under a magnification of 15 diameters; areas that may indicate oxidation of the substrate surface are examined at a magnification of 100 diameters. If no defects are observed, the work is reheated for an additional 45 min, cooled, and reexamined. Accessible defects observed after the 15 min heating period are repaired. Inaccessible defects, such as those on faying surfaces, may necessitate disassembly of the structure for reprocessing of the defective area.

Fluorescent-penetrant inspection is useful for detecting cracks, pits, and similar discontinuities in coating surfaces. The work is immersed in a penetrant, the excess penetrant is removed from the surfaces, and the surfaces are coated with a colloidal suspension known as a developer. Penetrant that has been entrapped by a defect seeps through the developer and reveals the outline of the defect when the surface is exposed to ultraviolet light. This is a sensitive test, and it frequently reveals very tight surface defects. When flexible-handle magnifying mirrors are used, this test method can be extended to the inspection of complex shapes and tubes.

Destructive tests can be performed on a workpiece or on specimens prepared and coated simultaneously with the workpieces. Standard test methods, such as for tensile strength, modulus of rupture, transverse bending, density, hardness, and metallographic and chemical analysis, can be used on specially prepared sections obtained from a thick section of the coating. An example is illustrated in Fig. 14(a). The tensile specimen of the coating is prepared as follows:

- Grind slots in coating with a cutoff wheel.
- Remove 13 mm ($\frac{1}{2}$ in.) wide sections of coating from the substrate and grind them flat to form 13 mm ($\frac{1}{2}$ in.) wide beam samples 0.125 mm (0.050 in.) in thickness. Beam samples may be tested in transverse rupture by a standard beam test. The coating can be removed by force when applied to a graphite substrate, because graphite has very low strength. A more widely used procedure is to use a substrate that can be chemically dissolved by a solvent that will not attack the coating.
- Grind samples to form a tensile specimen.

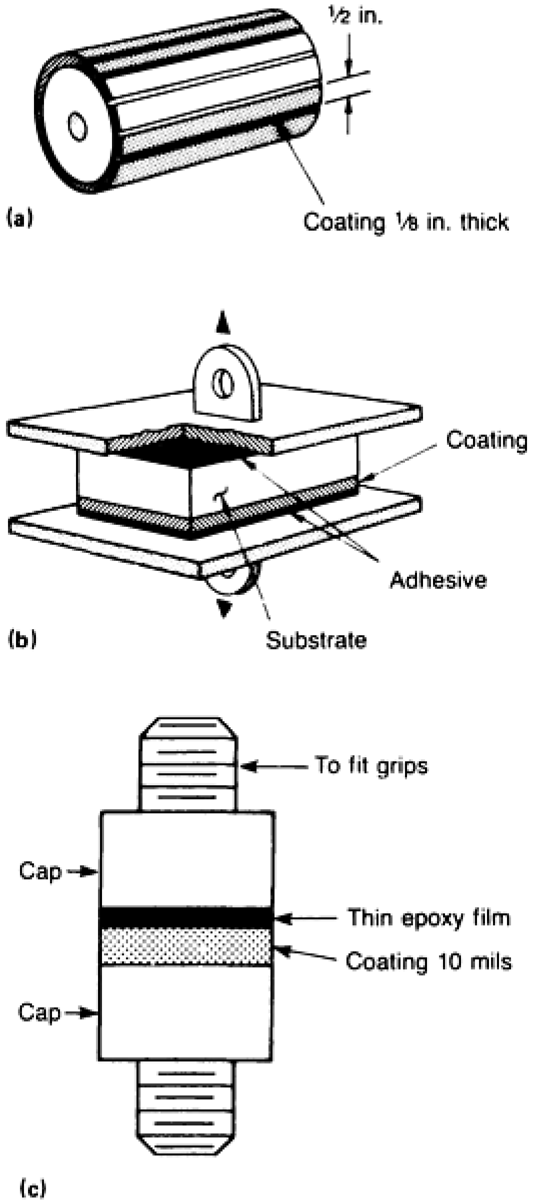


Fig. 14 Sectioning and testing of ceramic coatings. (a) Sectioning of 3 mm ($\frac{1}{8}$ in.) thick coating on a cylinder for preparation of specimens for determination of tensile strength, transverse bending, and other properties by standard test methods. (b) Testing the bond strength of coatings applied by plasma-arc or combustion flame spraying. (c) Testing bond strength of coatings applied by detonation gun process

Bond Strength. A simple test of the bond of a coating to a substrate is diagrammed in Fig. 14(b). This test, which makes use of an epoxy adhesive, is applicable to most coatings applied by plasma-arc or combustion flame spraying. A bond cap arrangement is illustrated in Fig. 14(c).

Impact Strength. Although conventional impact values can be obtained for a coating by an Izod or Charpy test on a specimen of the coating, a more useful impact test consists of projecting a pellet from an air gun with sufficient velocity to cause a measurable deformation of the substrate metal. The coating is then visually inspected for chipping and cracking. This test is best suited to coatings less than about 125 μm (5 mils) thick.

Wear Properties. In the dry-rubbing test, two specimens are mated and rubbed together with a load and relative surface speed selected on the basis of service severity. A similar setup can be used for determining wear properties at elevated temperatures, compatibility of the coating with lubricants or corrosives, and the effects of abrasives.

Structure and Hardness. The microscope is a useful tool for observing bond, binder, and metallic or oxide inclusions in a coating. Hardness testing provides a direct measurement of interparticle bond strength. For example, the true hardness of aluminum oxide usually ranges from 1800 to 2200 HV. Accepted Vickers hardness values of aluminum oxide deposited by various methods are 600 to 800 HV for flame-sprayed coatings, 700 to 1000 HV for plasma-sprayed coatings, and 1000 to 1200 HV for detonation gun-sprayed coatings. The maximum values represent the highest hardness obtained by these processes and thus the highest degree of interparticle bond. Accepted Vickers hardness values for three other ceramic coatings are indicated in Table 12. Hardness readings obtained with a Knoop indenter can be converted to Vickers for comparison.

Table 12 Hardness of three ceramic coatings deposited by three processes

Coating material	Hardness of coating, HV		
	Flame sprayed	Plasma sprayed	Detonation gun sprayed
Tungsten carbide + 8% cobalt	. . .	600-700	1200-1450
Tungsten carbide + 12% cobalt	. . .	600-700	1050-1200
Chromium oxide	900-1100	1200-1350	900-1150

Anodizing

Revised by Milton F. Stevenson, Jr., Anoplate Corporation

Introduction

IN GENERAL, anodizing refers to conversion coating of the surface of aluminum and its alloys to porous aluminum oxide. The process derives its name from the fact that the aluminum part to be coated becomes the anode in an electrolytic cell. This differentiates it from electroplating, in which the part is made the cathode. Whereas anodizing is typically associated with aluminum, similar processes are used for other base metals, including magnesium, titanium, and zinc; a brief discussion of anodizing of these materials is included at the end of this article. However, for the present, this discussion will be specific to aluminum and its alloys.

Anodizing aluminum can be accomplished in a wide variety of electrolytes, employing varying operating conditions including concentration and composition of the electrolyte, presence of any additives, temperature, voltage, and amperage. Several conventional anodizing processes and their resulting properties are shown in Table 1. As indicated in the table, depending on the process chosen, an anodizer can impart to the surface of the aluminum item specific properties as desired, depending on the end use. Some reasons for anodizing are outlined below:

- *Increase corrosion resistance:* Sealed anodic coatings of aluminum oxide are corrosion resistant and highly resistant to atmospheric and salt-water attack. The anodic coating protects the underlying metal by serving as a barrier to would-be corrosive agents. In order to achieve the optimum corrosion resistance, the amorphous aluminum oxide produced by anodizing is sealed by treating in slightly acidified hot water, boiling deionized water, a hot dichromate solution, or a nickel acetate solution. Sealing is discussed in a subsequent section of this article.
- *Improve decorative appearance:* All anodic coatings are lustrous and have relatively good abrasion resistance. Therefore, these coatings are used as the final finishing treatment when the natural appearance of the aluminum is desired or when a mechanically induced pattern is to be preserved. The degree of luster of anodic coatings depends on the condition of the base metal before anodizing. Dull etching decreases luster; bright etching, chemical or electrolytic brightening, and buffing increase luster, either diffuse or specular. Most of the aluminum used in architectural applications is anodized.
- *Increase abrasion resistance:* The hard anodizing processes produce coatings from 25 μm (1 mil) to more than

100 µm (4 mils) thick. These coatings, with the inherent hardness of aluminum oxide, are thick enough for use in applications involving rotating parts where abrasion resistance is required. Although all anodic films are harder than the substrate material, the coatings produced by chromic acid and some sulfuric acid baths are too thin or too soft to meet the requirements for abrasion resistance.

- *Increase paint adhesion:* The tightly adhering anodic coating offers a chemically active surface for most paint systems. Anodic films produced in sulfuric acid baths are colorless and offer a base for subsequent clear finishing systems. Aluminum-base materials that are painted for service in severe corrosive environments are anodized before being painted. A fully sealed anodize may result in interior adhesion.
- *Improve adhesive bonding:* A thin phosphoric acid or chromic acid anodize improves bond strength and durability. Such coatings are widely employed in the airframe structure of most modern aircraft.
- *Improve lubricity:* A combination of hand polishing and/or honing the hard anodizing to a smoother surface before applying a polytetrafluoroethylene coating is a perfect combination with the hard anodizing.
- *Provide unique, decorative colors:* Colored anodic coatings are produced by different methods. Organic dyes can be absorbed in the pores of the coatings to provide a whole spectrum of colored finishes. Certain mineral pigments can be precipitated within the pores to yield a limited range of stable colors. Integral color anodizing, depending on the alloy composition, is used to provide a range of stable earth-tone colors suitable for architectural applications. Electrolytic coloring is a two-step process involving conventional anodizing followed by electrodeposition of metallic pigments in the pores of the coating to achieve a range of stable colors useful in architecture. Coloring is discussed in a subsequent section of this article.
- *Provide electrical insulation:* Aluminum oxide is a dielectric. The breakdown voltage of the anodic film varies from a few volts to several thousand volts, depending on the alloy and on the nature and thickness of the film. The degree of seal also affects insulation properties.
- *Permit subsequent plating:* The inherent porosity of certain anodic films enhances electroplating. Usually, a phosphoric acid bath is used for anodizing prior to plating.
- *Detection of surface flaws:* A chromic acid anodizing solution can be used as an inspection medium for the detection of fine surface cracks. When a part containing a surface flaw is removed from the anodizing bath, then washed and dried quickly, chromic acid entrapped in the flaw seeps out and stains the anodized coating in the area adjacent to the flaw.
- *Increase emissivity:* Anodic films more than 0.8 µm (0.032 mil) thick increase the emissivity of the aluminum. When dyed black, the film has excellent heat absorption up to 230 °C (450 °F).
- *Permit application of photographic and lithographic emulsions:* The porosity of the anodic film offers a mechanical means of holding the emulsion.

Table 1 Conventional anodizing processes

Bath	Amount, wt%	Temperature		Duration, min	Voltage, V	Current density		Film thickness		Appearance properties	Other properties
		°C	°F			A/dm^2	A/ft^2	µm	mils		
Sulfuric acid bath											
Sulfuric acid	10	18	65	15-30	14-18	1-2	10-20	5-17	0.2-0.7	Colorless, transparent films	Hard, unsuitable for coloring, tensile strength design 250-370 Kgf/mm (2450-3630 N/mm)
Alumilite											
Sulfuric acid	15	21	70	10-60	12-16	1.3	13	4-23	0.1-0.9	Colorless, transparent films	Good protection against corrosion

Bath	Amount, wt%	Temperature		Duration, min	Voltage, V	Current density		Film thickness		Appearance properties	Other properties
		°C	°F			A/dm²	A/ft²	µm	mils		
Oxydal											
Sulfuric acid	20	18	65	30	12-16	1-2	10-20	15-20	0.6-0.8	Colorless, transparent films	Good protection against corrosion, suitable for variegated and golden coloring
Anodal and anoxal											
Sulfuric acid	20	18	65	50	12-16	1-2	10-20	20-30	0.8-1.5	Colorless, transparent films	For coloring to dark tones, bronze and black
Bengough-Stuart (original process)											
Chromic acid	3	40	105	60	0-50	0.3	3	5	0.2	Colorless to dark brown	Good chemical resistance, poor abrasion resistance; suitable for parts with narrow cavities, as residual electrolyte is not detrimental
Commercial chromic acid process											
Chromic acid	5-10	40	105	30-60	0 to increasing limit controlled by amperage	0.5-1.0	5-10	4-7	0.2-0.3	Gray to iridescent	God chemical resistance, poor abrasion resistance; suitable for parts with narrow cavities, as residual electrolyte is not detrimental
Eloxal GX											
Oxalic acid	2-10	20-80	68-175	30-80	20-80	0.5-30	5-300	5-60	0.2-2.4	Colorless to dark brown	Hard films, abrasion resistant, some self-coloring

Bath	Amount, wt%	Temperature		Duration, min	Voltage, V	Current density		Film thickness		Appearance properties	Other properties
		°C	°F			A/dm^2	A/ft^2	µm	mils		
											dependent on alloy, 450-480 Kgf/mm (4410-4710 N/mm) for tensile design
Oxal											
Oxalic acid	2-10	20-22	68-72	10-240	60	1.5	15	10-20 for 30 min 30-40 for 50 min	0.4-0.8 for 30 min 1.5-1.6 for 30 min	Colorless to dark brown	Hard films, abrasion resistant, some self-coloring dependent on alloy
Ematal											
Oxalic acid	1.2	50-70	120-160	30-40	120	3	30	12-17	0.5-0.7	Not transparent gray opaque enamel-like	Hard and dense type film possessing extreme abrasion resistance
Titanium salt ($TiOC_2O_4K_2 \cdot H_{20}$)	40										
Citric acid	1 g (28 oz)										
Boric acid	8 g (224 oz)										
Water	4 L (1 gal)										

Anodizing Processes

The three principal types of anodizing processes are chromic processes, in which the electrolyte is chromic acid; sulfuric processes, in which the electrolyte is sulfuric acid; and hard anodic processes that use sulfuric acid alone or with additives. Other processes, used less frequently or for special purposes, use sulfuric acid with oxalic acid, phosphoric acid, oxalic acid, boric acid, sulfosalicylic acid, sulfophthalic acid, or tartaric acid. Except for thicker coatings produced

by hard anodizing processes, most anodic coatings range in thickness from 5 to 18 μm (0.2 to 0.7 mil). Table 2 describes a few applications in which anodizing is used as a step in final finishing. The sequence of operations typically employed in anodizing from surface preparation through sealing is illustrated in Fig. 1.

Table 2 Typical products for which anodizing is used in final finishing

Product	Size		Alloy	Finishing before anodizing	Anodizing process	Post-treatment	Service requirements or environments
	mm	in.					
Auto head lamp	215 mm diam, 30	$8\frac{1}{2}$ in. diam, $1\frac{1}{4}$	5557-1125	Buff, chemical brighten	Sulfuric acid[(a)]	Seal	Atmospheric exposure
Canopy track	760 mm T-extrusion	30-in. T-extrusion	7075	Machine	Hard	None	Resist wear, sea air
Gelatin molds	150-205 mm overall	6-8 overall	1100-O	Chemical brighten as-drawn	Sulfuric acid	Dye, seal	Food
Landing gear	205 mm diam by 1.4 m	8 in. diam by $4\frac{1}{2}$ ft	7079-T6	[(b)]	Chromic acid	Paint	Corrosion resistance
Mullion	3.7 m by 180 mm by 100 mm[(c)]	12 ft by 7 by 4	6063-T6	[(d)]	Sulfuric acid[(e)]	Seal, lacquer[(f)]	Urban atmosphere
Name plates	Various sizes	Various sizes	3003-1114	[(g)]	Sulfuric acid	Dye, seal	Atmospheric exposure
Percolator shell	125 mm diam by 150	5 in. diam by 6	. . .	Buff, chemical brighten	Sulfuric acid	Seal	Coffee
Seaplane-hull skin	2850 by 1020	112 by 40	Clad 2014-T6	[(g)]	Chromic acid	None	Erosion; corrosion[(h)]
Seat-stanchion tube	50 mm diam by 610	2 in. diam by 24	7075-T6	Machine	Hard	None	Wear resistance
Signal-cartridge container	190 by 140 by 165	$7\frac{1}{2}$ by $5\frac{1}{2}$ by $6\frac{1}{2}$	3003-O	As drawn	Chromic acid	Prime, paint	Marine atmosphere

Tray, household	430 mm diam	17 in. diam	. . .	Butler	Sulfuric acid	Seal, buff	Food
Utensil covers	Up to 0.20 m^2 total area	Up to 2 ft^2 total area	1100	Buff, chemical brighten	Sulfuric acid[(i)]	Dye, seal	Steam, cooked foods[(j)]
Voice transmitter	50 mm diam	2 in. diam	5052-O	Burnish, alkaline etch	Sulfuric acid	Dye, seal[(k)]	Gas mask
Wheel pistons	Up to 5200 mm^2 area	Up to 8 $in.^2$ area	6151	Machine	Sulfuric acid[(l)]	Seal	Wear and corrosion[(m)]
Computer chip hat	160 by 160	6.2 by 6.2	6063-T6	Non-etch clean	Sulfuric acid	Deionized water seal	High dielectric, thermally conductive
Ice cream scoop	400 by 50	8 by 2	6061-T6	Light etch	Hard	Polytetrafluoroethylene seal	Food; good release

(a) Anodic coating 8 µm (0.3 mil) thick.

(b) Partially machine, clean with nonetching cleaner, and remove surface oxide.

(c) 5 mm (0.2 in.) thick.

(d) Lined finish (180-mesh grit) on 100-mm (4-in.) face; other surfaces alkaline etched.

(e) Anodized for 80 min; minimum coating thickness, 30 µm (1.2 mils).

(f) Sealed for 20 to 30 min. Methacrylate lacquer, 8 µm (0.3 mil) minimum.

(g) Clean with nonetching cleaner; remove surface oxide.

(h) Maximum resistance required.

(i) Anodic coating 5 µm (0.2 mil) thick.

(j) Must not discolor during service.

(k) Sealed in dichromate solution.

(l) Anodized in sulfuric acid solution (30% H_2SO_4) at 21 °C (70 °F) for 70 min at 2.5 A/dm^2 (25 A/ft^2).

(m) In presence of hydraulic brake fluids

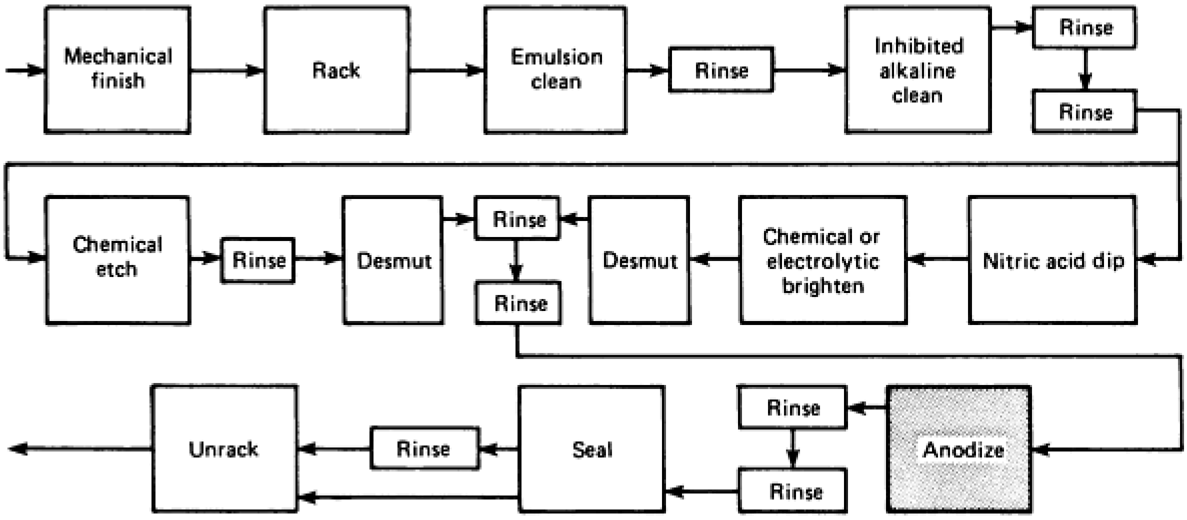


Fig. 1 Typical process sequence for anodizing operations

Surface Preparation. A chemically clean surface (free of all grease and oil, corrosion products, and the naturally occurring aluminum oxide found on even the cleanest-appearing aluminum) is a basic requirement for successful anodizing. The cleaning method is selected on the basis of the type of soils or contaminants that must be removed and the dimensional tolerance. Traditionally the first step employed was vapor degreasing; however, due to restrictions on ozone-depleting compounds, many of these degreasing solvents, such as trichloroethylene, are no longer in wide use. Alternatives to vapor degreasing, such as solvent wiping or alkaline soak cleaning, are now predominantly used for removing the major organic contaminants. The main function of this cleaning stage is to provide a chemically clean aluminum surface so that subsequent acid pickles or caustic etches can react uniformly over the entire surface.

After cleaning, the work is etched, pickled, or otherwise deoxidized to remove surface oxides. When specular surfaces are required, the work is treated in a brightening solution. After etching or brightening, desmutting usually is required for the removal of heavy metal deposits resulting from the preceding operations.

In order to treat precision-machined aluminum components, anodize pretreatment procedures that require neither etching nor pickling have been developed and are now widely employed.

Chromic Acid Process. The sequence of operations used in this process depends on the type of part, the alloy to be anodized, and the principal objective for anodizing. Due to the corrosive nature of sulfuric acid, chromic acid anodizing is the preferred process on components such as riveted or welded assemblies where it is difficult or impossible to remove all of the anodizing solution. This process yields a yellow to dark-olive finish, depending on the anodic film thickness. Color is gray on high-copper alloys. Table 3 gives a typical sequence of operations that meets the requirements of military specification MIL-A-8625.

Table 3 Sequence of operations for chromic acid anodizing

Operation	Solution	Solution temperature		Treatment time, min
		°C	°F	

Vapor degrease	Suitable solvent	. . .	. . .	. . .
Alkaline clean	Alkaline cleaner	(a)	(a)	(a)
Rinse(b)	Water	Ambient	Ambient	1
Desmut(c)	HNO_3, 10-25 vol%	Ambient	Ambient	As required
Rinse(b)	Water	Ambient	Ambient	1
Anodize	CrO_3, 46 g/L ($5\frac{1}{4}$ oz/gal)(d)	32-35	90-95	30(e)
Rinse(b)	Water	Ambient	Ambient	1
Seal(f)	Water(g)	90-100	190-210	10-15
Air dry	. . .	105 max(h)	225 max(h)	As required

(a) According to individual specifications.

(b) Running water or spray.

(c) Generally used in conjunction with alkaline-etch type of cleaning.

(d) pH 0.5.

(e) Approximate; time may be increased to produce maximum coating weight desired.

(f) Dependent on application.

(g) Water may be slightly acidulated with chromic acid, to a pH of 4 to 6.

(h) Drying at elevated temperature is optional.

Chromic acid anodizing solutions contain from 3 to 10 wt% CrO_3. A solution is made up by filling the tank about half full of water, dissolving the acid in water, and then adding water to adjust to the desired operating level.

A chromic acid anodizing solution should not be used unless:

- pH is between 0.5 and 1.0.

- The concentration of chlorides (as sodium chloride) is less than 0.02%.
- The concentration of sulfates (as sulfuric acid) is less than 0.05%.
- The total chromic acid content, as determined by pH and Baumé readings, is less than 10%. When this percentage is exceeded, part of the bath is withdrawn and is replaced with fresh solution.

Figure 2 shows the amount of chromic acid that is required for reducing the pH from the observed value to an operating value of 0.5.

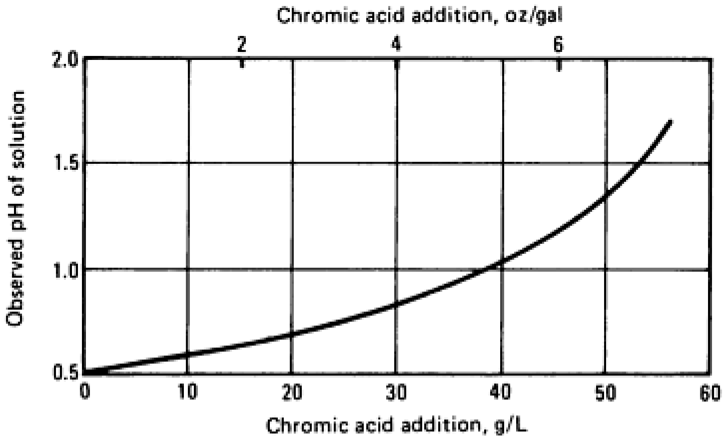


Fig. 2 Control of pH of chromic acid anodizing solutions. The graph shows the amount of chromic acid required to reduce pH to 0.5 from observed pH.

When anodizing is started, the voltage is controlled so that it will increase from 0 to 40 V within 5 to 8 min. The voltage is regulated to produce a current density of not less than 0.1 A/dm^2 (1.0 A/ft^2), and anodizing is continued for the required time, generally 30 to 40 min. Certain alloys, typically those in the 7*xxx* series, such as 7075, fail to develop a coating at 40 V, but running the process at 22 V produces acceptable results. Casting alloys should also be processed at 22 ± 2 V, as specified in military specification MIL-A-8625, type 18. Because of the porous structure of the casting alloys, processing them at higher voltages can cause excessive current densities that can be extremely damaging to the components. When the 22 V process is employed, times should be lengthened to 40 to 60 min. At the end of the cycle the current is gradually reduced to zero, and the parts are removed from the bath within 15 s, rinsed, and sealed.

According to MIL-A-8625, revision F, the coating weight should be checked prior to sealing, and depending on the type of alloy, the minimum coating weight should be 200 mg/ft^2. Measuring coating weight prior to sealing will allow the parts to be put back in the chromic anodizing tank so that anodizing can continue, if needed, and subsequent stripping can be avoided.

Sulfuric Acid Process. The basic operations for the sulfuric acid process are the same as for the chromic acid process. Parts or assemblies that contain joints or recesses that could entrap the electrolyte should not be anodized in the sulfuric acid bath. The concentration of sulfuric acid (1.84 sp gr) in the anodizing solution is 12 to 20 wt%. A solution containing 36 L (9.5 gal) of H_2SO_4 per 380 L (100 gal) of solution is capable of producing an anodic coating that when sealed meets the requirements of MIL-A-8625.

A sulfuric acid anodizing solution should not be used unless:

- The concentration of chlorides (as sodium chloride) is less than 0.02%.
- The aluminum concentration is less than 20 g/L (2.7 oz/gal), or less than 15 g/L (2 oz/gal) for dyed work.
- The sulfuric acid content is between 165 and 200 g/L (22 to 27 oz/gal).

At the start of the anodizing operation, the voltage is adjusted to produce a current density of 0.9 to 1.5 A/dm^2 (9 to 15 A/ft^2). Figure 3 shows the voltage required to anodize at two different temperatures with current density of 1.2 A/dm^2 (12 A/ft^2). The voltage will increase slightly as the aluminum content of the bath increases. The approximate voltages required for anodizing various wrought and cast aluminum alloys in a sulfuric acid bath at 1.2 A/dm^2 (12 A/ft^2) are:

Alloy	**Volts**
Wrought alloys	
1100	15.0
2011	20.0
2014	21.0
2017	21.0
2024	21.0
2117	16.5
3003	16.0
3004	15.0
5005	15.0
5050	15.0
5052	14.5
5056	16.0
5357	15.0
6053	15.5
6061	15.0
6063	15.0

6151	15.0
7075	16.0
Casting alloys	
413.0	26.0
443.0	18.0
242.0	13.0
295.0	21.0
514.0[(a)]	10.0
518.0[(a)]	10.0
319.0	23.0
355.0	17.0
356.0	19.0
380.0	23.0

(a) Current density, 0.9 A/dm^2 (9 A/ft^2)

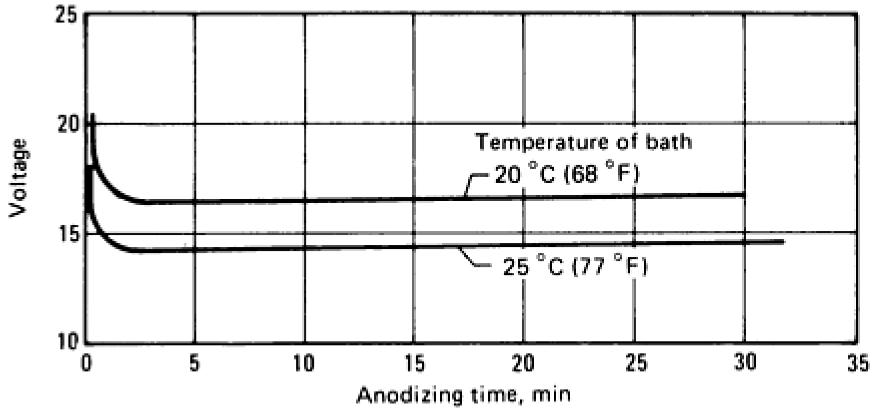


Fig. 3 Voltages required during sulfuric acid anodizing. To maintain a current density of 1.2 A/dm^2 (12 A/ft^2), a bath temperature of between 20 and 25 °C (68 and 77 °F) must be maintained.

When a current density of 1.2 A/dm^2 (12 A/ft^2) is attained, the anodizing process is continued until the specified weight of coating is produced, after which the flow of current is stopped and the parts are withdrawn immediately from the solution and rinsed. Figure 4 shows the effect of time on the weight of the coating developed on automotive trim anodized in 15% sulfuric acid solutions at 20 and 25 °C (68 and 77 °F), operated at a current density of 1.2 A/dm^2 (12 A/ft^2).

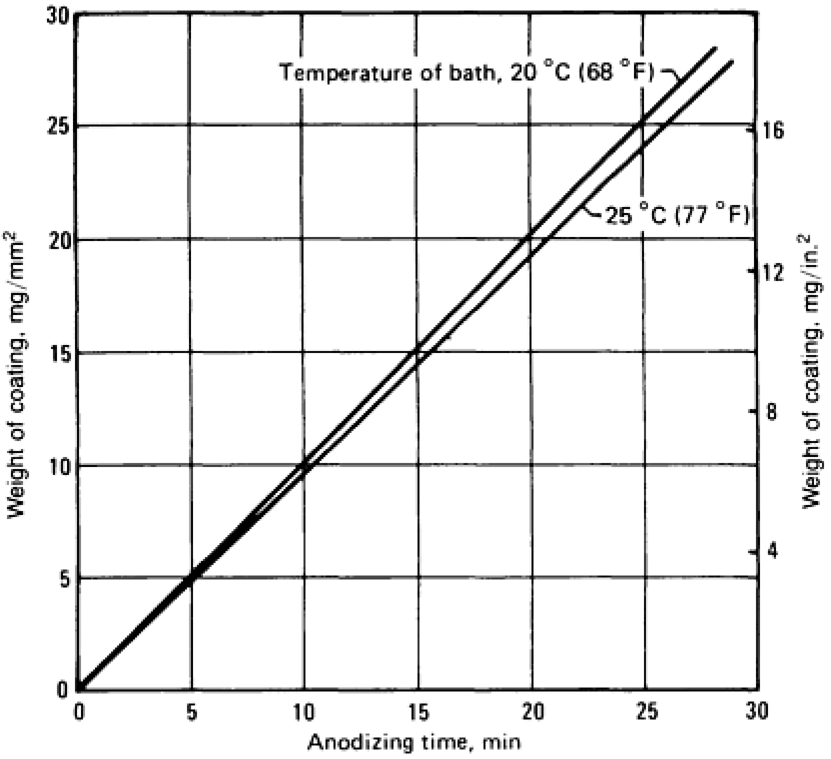
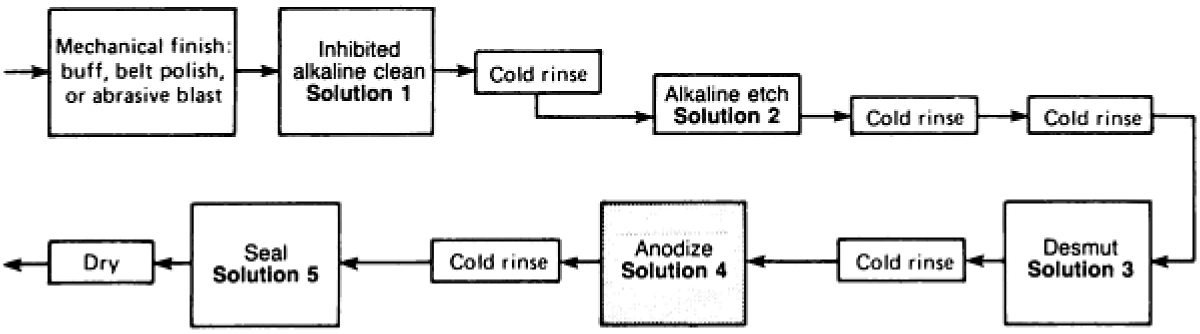


Fig. 4 Effect of anodizing time on weight of anodic coating. Data were derived from aluminum-alloy automotive trim anodized in 15% sulfuric acid solutions at 20 and 25 °C (68 and 77 °F) and at 1.2 A/dm^2 (12 A/ft^2).

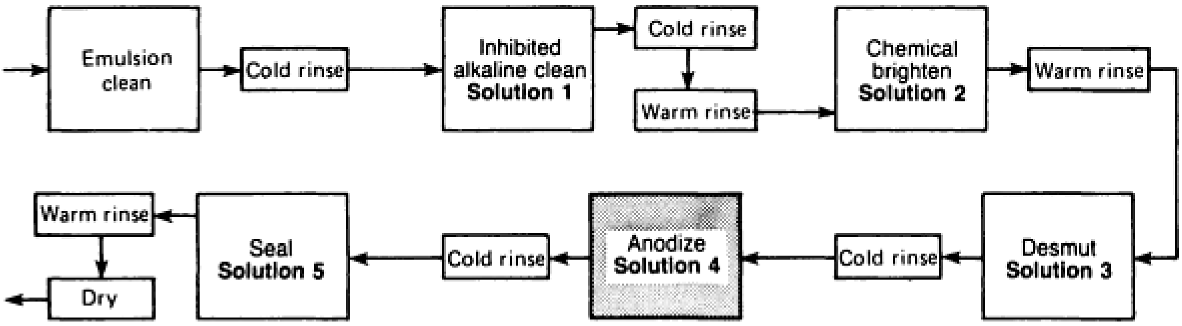
A flow chart and a table of operating conditions for operations typically used in anodizing architectural parts by the sulfuric acid process are presented in Fig. 5; similar information, for the anodizing of automotive bright trim, is given in Fig. 6.



Solution No.	Type of solution	Composition	Operating temperature	Cycle time, min

			°C	°F	min
1	Alkaline cleaning	Alkali, inhibited	60-71	140-160	2-4
2	Alkaline etching	NaOH, 5 wt%	50-71	120-160	2-20
3	Desmutting	HNO_3, 25-35 vol%	Room	Room	2
4	Anodizing	H_2SO_4, 15 wt%	21-25	70-75	5-60
5	Sealing	Water (pH 5.5-6.5)	100	212	5-20

Fig. 5 Operations sequence in sulfuric acid anodizing of architectural parts



Solution No.	Type of solution	Composition	Operating temperature		Cycle time, min
			°C	°F	
1	Alkaline cleaning	Alkali, inhibited	60-71	140-160	2-4
2	Chemical brightening	H_3PO_4 and HNO_3	88-110	190-230	$\frac{1}{2}$-5
3	Desmutting	HNO_3, 25-35 vol%	Room	Room	2
4	Anodizing	H_2SO_4, 15 wt%	21-25	70-75	5-60

Fig. 6 Operations sequence in sulfuric acid anodizing of automotive bright trim

Hard Anodizing. The primary differences between the sulfuric acid and hard anodizing processes are the operating temperature, the use of addition agents, and the voltage and current density at which anodizing is accomplished. Hard anodizing, also referred to as hardcoat or type III anodizing, produces a considerably heavier coating then conventional sulfuric acid anodizing in a given length of time. Coating weights obtained as a function of time are compared for the two processes in Fig. 7.

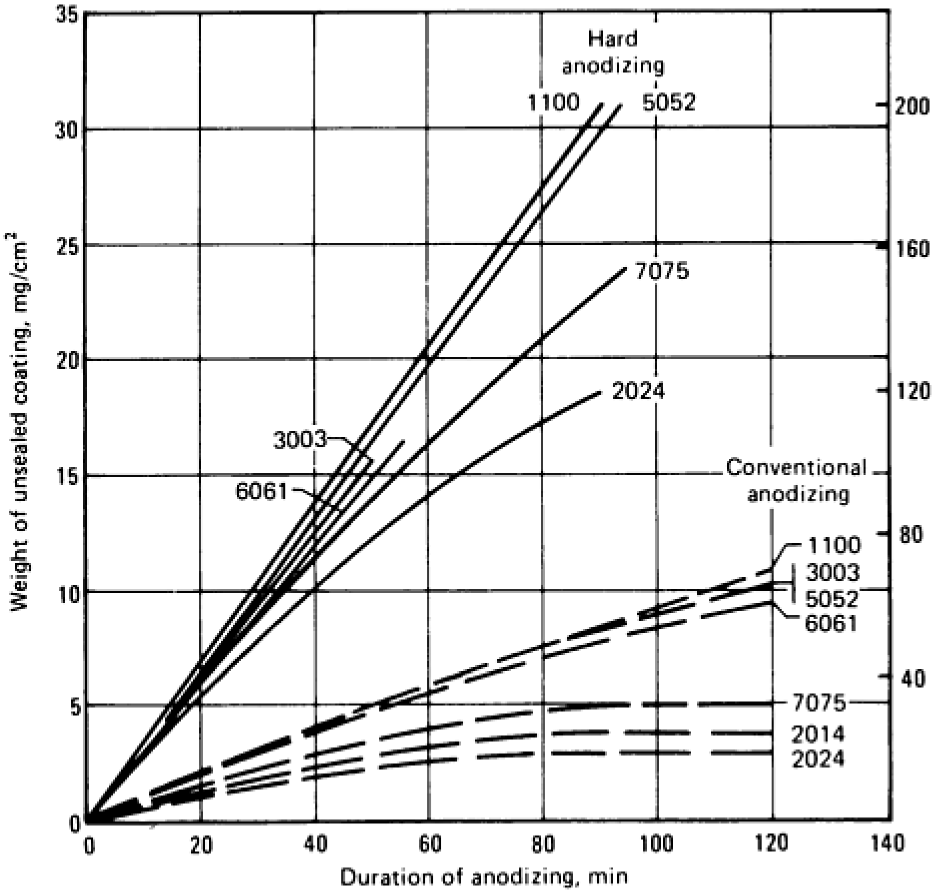


Fig. 7 Effect of anodizing time on weight of hard and conventional anodic coatings. The hard anodizing solution contained (by weight) 12% H_2SO_4 and 1% $H_2C_2O_4$ and was operated at 10 °C (50 °F) and 3.6 A/dm^2 (36 A/ft^2). The conventional anodizing solution contained 1% (by weight) H_2SO_4 and was operated at 20 °C (70 °F) and 1.2 A/dm^2 (12 A/ft^2).

The hard anodizing process uses a sulfuric acid bath containing 10 to 20 wt% acid, with or without additives. Typical operating temperatures of the bath range from 0 to 10 °C (32 to 50 °F), and current density ranges between 2 and 3.6 A/dm^2 (20 and 36 A/ft^2). With the use of particular additives and modified power, hard anodizing processes can operate at temperatures in excess of room temperature. However, some hard anodizing processes operated at high temperature may result in the formation of soft and more porous outer layers of the anodic coating. This change in coating characteristics reduces wear resistance significantly and tends to limit coating thickness. Without use of specific additives and/or modified power, such as superimposed alternating current over direct current or pulsed current, excessive operating temperatures result in dissolution of coating and can burn and damage the work.

Proprietary processes are commonly used. One of the more common of these processes uses a solution containing 120 to 160 g (16 to 21 oz) of sulfuric acid and 12 to 20 g (1.6 to 2.8 oz) of oxalic acid ($H_2C_2O_4$) per 3.8 L (1 gal) of water. This solution is operated at 10 ± 1 °C (50 ± 2 °F) and a current density of 2.5 to 3.6 A/dm^2 (25 to 36 A/ft^2) (voltage is

increased gradually from zero to between 40 and 60 V); treatment time is 25 min/25 μm (1 mil) of coating thickness. Additional proprietary processes for hard anodizing are listed in Table 4.

Table 4 Process and conditions for hard anodizing

Process	Bath	Temperature		Duration min	Voltage V	Current density		Film thickness		Appearance	Remarks
		°C	°F			A/dm^2	A/ft^2	μm	mils		
Martin Hard Coat (MHC)	15 wt% sulfuric acid, 85 wt% water	-4 to 0	25-32	45[(b)]	20-75	2.7	29	50	2	Light to dark gray or bronze	Very hard, wear resistant
Alumilite 225 and 226	12 wt% sulfuric acid, 1 wt% oxalic acid, water	10	50	20,40	10-75	2.8[(b)]	30[(b)]	25,50	1,2	light to dark gray or bronze	Very hard, wear resistant, allows a higher operating temperature over MHC
Alcanodox	Oxalic acid in water	2-20	36-68	[(a)]	[(a)]	[(a)]	[(a)]	20-35	0.8-1.4	Golden to bronze	. . .
Hardas	6 wt% oxalic water, 94 wt% water	4	39	[(a)]	60 dc plus ac override	2.0	22	. . .	. . .	Light yellow to brown	. . .
Sanford	Sulfuric acid with organic additive	0-15	32-58	[(a)]	15-150 dc	1.2-1.5	13-16	. . .	. . .	Light to dark gray or bronze	. . .
Kalcolor	7-15 wt% sulfosalicylic acid, 0.3-4 wt% sulfuric acid, water	18-24	64-75	. . .	. . .	1.5-4	16-43	15-35	0.6-1.4	Light yellow to brown to black	A self-coloring process, colors are dependent on alloy chosen, the colors produced are light fast
Lasser	0.75 wt% oxalic acid, 99.25 wt% water	1-7	35-44	to 20	From 50-500 rising ramp	Voltage controlled	Voltage controlled	700	28	Colorless	Hard, thick coatings produced with special cooling

(a) Proprietary information available to licensees only. Also, the entire Toro process is proprietary information available to licensees only.

(b) Changes from 9th edition, *Metals Handbook*

A recent development in hard anodizing uses an intermittent pulse current that reduces tank time and makes it possible to use a 20 vol% sulfuric acid solution as the electrolyte.

Special Anodizing Processes. Table 5 gives the operating conditions for anodizing baths that are used to produce an anodic coating with a hardness and porosity suitable for electroplating, or to produce anodic coatings of hardness or thickness intermediate to those obtainable from chromic acid, sulfuric acid, and hard anodizing baths.

Table 5 Compositions and operating conditions of solutions for special anodizing processes

Type of solution	Composition	Current density		Temperature		Treatment, time, min	Use of solution
		A/dm^2	A/ft^2	°C	°F		
Sulfuric-oxalic	15-20 wt% H_2SO_4 and 5 wt% $H_2C_2O_4$	1.2	12	29-35	85-95	30	Thicker coating[(a)]
Phosphoric	20-60 vol% H_3PO_4	0.3-1.2[(b)]	3-12[(b)]	27-35	80-95	5-15	Preparation for plating
Phosphoric, Boeing process	10-12 wt%	0.5-0.8[(c)]	5-8[(c)]	21-24	70-75	20-25	Adhesive bonding preparation
Oxalic	3 wt% $H_2C_2O_4$	1.2	12	22-	72-	15-60[(d)]	Harder coating[(e)]

(a) Coating is intermediate in thickness between the coating produced by sulfuric acid anodizing and the coating produced by hard anodizing.

(b) Potential, 5 to 30 V.

(c) Potential, 10 to 15 V.

(d) Depends on coating thickness desired.

(e) Hardness greater than by other processes except hard anodizing

Process Limitations

Composition of the aluminum alloy, surface finish, prior processing, temper or heat treatment, and the use of inserts influence the quality of anodic coatings. The limitations imposed by each of these variables on the various anodizing processes are described below.

Alloy Composition. The chromic acid process should not be used to anodize aluminum casting alloys containing more than 5% Cu or more than 7.5% total alloying elements, because excessive pitting, commonly referred to as burning, may result. The sulfuric acid process can be used for any of the commercially available alloys, whereas the hard anodizing process is usually limited to alloys containing less than 5% Cu and 7% Si. Choice of alloys is important when maximum corrosion and/or abrasion resistance is required. Alloys such as 6061 are superior to the copper and copper-magnesium alloys in their ability to produce a hard, corrosion-resistant coating.

A recent development permitting hard anodizing of any aluminum alloy, including such newly released alloys as aluminum-lithium alloys, is ion vapor deposition of a thin layer of pure aluminum over the difficult alloy followed by subsequent anodizing. The newly deposited aluminum is entirely incorporated into the anodic layer without interference of troublesome alloying elements. This method is also useful in repairing expensive aluminum components undersized as a result of overcleaning or overetching.

Two or more different alloys can be anodizing at the same time in the same bath if the anodizing voltage requirements are identical. However, simultaneous anodizing of two different alloys is not normally recommended. This condition is more difficult for the sulfuric acid process than for the chromic acid process.

Surface Finish. Anodic films accentuate any irregularities present in the original surface. However, surface irregularities are emphasized more by the chromic acid bath than by the sulfuric acid bath. Additionally, the sulfuric acid anodizing process should be used instead of the chromic acid process where optimum corrosion- and/or abrasion-resistant surfaces are required. Clad sheet should be handled with care to prevent mechanical abrasion or exposure of the core material. Anodizing magnifies scratches, and if the core material is exposed, it will anodize with a color different from that of the cladding.

Anodizing grade must be specified for extruded products so that mill operations are controlled to minimize longitudinal die marks and other surface blemishes. Surface irregularities must be removed from forgings, and the surfaces of the forgings must be cleaned by a process that removes trapped and burned-in die lubricants. Special attention is required when polishing the flash line if this area is to appear similar to other areas of the forging after anodizing.

Castings can be anodized provided their composition is within the process limits described under alloy composition. From the standpoint of uniform appearance, however, anodizing usually is undesirable for castings because of their nonuniform surface composition and their porosity.

The cosmetic concerns surrounding anodizing of castings, especially dyed anodic processes, can be overcome by vacuum impregnation of the casting. Using this process, exposed casting porosity is filled with an impregnant such as a thermosetting epoxy polyester. In sealing this porosity, the corrosion resistance of the anodized casting is also improved. Improved results may also be obtained by soaking castings in boiling water after cleaning and before anodizing. This treatment, however, merely attempts to fill surface voids with water, so that voids do not entrap anodizing solution.

Usually, permanent mold castings have the best appearance after anodizing, then die castings, and finally sand castings. Permanent mold castings should be specified if an anodic coating of uniform appearance is required. Anodizing usually reveals the metal flow lines inherent in the die-casting process, and this condition is objectionable if uniform appearance is desired. In general, solution heat treatment prior to anodizing is beneficial for producing the most uniform and bright anodized finish obtainable on castings.

To facilitate better cleaning of a casting prior to anodizing, aggressive cleaning with fluorides (in the case of castings high in silicon) can be accomplished prior to final machining. Following aggressive cleaning, the part is returned to the customer for final machining and returned to the finisher for anodizing. However, if close machining tolerances are involved, removal of metal with aggressive cleaning may not be permissible.

Regardless of the product form, rough finishing should be avoided when maximum corrosion resistance or uniformity of appearance of the anodic coating is desired. Rough surfaces, such as those produced by sawing, sand blasting, and shearing, are difficult to anodize and should be strongly etched prior to anodizing to ensure even minimal results. The machined areas of castings or forgings may have an appearance different from that of the unmachined surfaces.

Prior Processing. Because of their effect on surface finish, welding, brazing, and soldering affect the appearance of the anodic coating, for the reasons discussed above. In addition, the compositions of solders usually are not suited to anodizing. Spot, ultrasonic pressure, or other types of welding processes where there is no introduction of foreign metal,

fluxes, or other contaminants do not affect the appearance of the anodic coating. However, the sulfuric acid anodizing process should not be used for coating spot-welded assemblies or other parts that cannot be rinsed to remove the electrolyte from lap joints.

Temper or Heat Treatment. Identification of not only the alloy that is being used but also the temper to which the alloy has been heat treated is extremely important. For alloy 2024, for example, the voltage required to produce a given film thickness can vary by 25%, depending on whether the T-3 treatment or T-4 treatment was used. Failure to recognize the difference in heat treatment can be catastrophic, most notably in hard anodizing.

Differences in temper of non-heat-treatable alloys have no marked effect on the uniform appearance of the anodic coating. The microstructural location of the alloying elements in heat-treatable alloys affects the appearance of anodic coatings. Alloying elements in solution have little effect, but the effect is greater when the elements are precipitated from solid solution. The annealed condition should be avoided when maximum clarity of the anodic film is desired.

Inserts or attachments made of metals other than aluminum must be masked off, both electrically and chemically, to prevent burning and corrosion in surrounding areas. The masking must completely seal the faying surface between the insert and parent metal, to prevent adsorption of solution, which may result in corrosion and staining. Therefore, it is desirable to install inserts after anodizing.

Anodizing Equipment and Process Control

Chromic Acid Anodizing. Low-carbon steel tanks are satisfactory for chromic acid baths. It is common practice to line up to half of the tank with an insulating material, such as glass, to limit the cathode area with respect to the expected anode area (a 1-to-1 ratio is normal). The cathode area need only be 5% of the maximum anode area. In nonconducting tanks, suitable cathode area is provided by the immersion of individual lead cathodes; however, these require the installation of additional busbars to the tanks for suspension of individual cathodes. Provision must be made for heating the anodizing solution to 32 to 35 °C (90 to 95 °F); electric or steam immersion heaters are satisfactory for this purpose. Electric heaters are preferred, because they are easy to operate and do not contaminate the bath.

The anodizing process generates heat; therefore, agitation is required to prevent overheating of the bath and especially of the electrolyte immediately adjacent to the aluminum parts being anodized. Exhaust facilities must be adequate to trap the effluent fumes of chromic acid and steam.

Sulfuric Acid Anodizing. Tanks for sulfuric acid anodizing may be made of low-carbon steel lined throughout with plasticized polyvinyl chloride and coated on the outside with corrosion-resistant synthetic-rubber paint. Other suitable materials for tank linings are lead, rubber, and acid-proof brick. Tanks made of special sulfuric acid-resistant stainless steel containing copper and molybdenum, or made entirely of an organic material, may be used. As with chromic acid anodizing, individual lead cathodes or lead-lined tanks may be used for sulfuric acid anodizing. Alternatively, aluminum cathodes have been used, resulting in energy savings because they have higher conductivity than lead. The fact that lead effluent results from lead cathodes is another reason to prefer aluminum cathodes.

The tank should have controls for maintaining temperatures at between 20 to 30 °C (68 to 85 °F). Requirements for agitation and ventilation are the same as for chromic acid solutions. The surface of the floor under the tank should be acid resistant. The bottom of the tank should be about 150 mm (6 in.) above the floor on acid-resistant and moisture-repellent supports.

A separate heat exchanger and acid make-up tank should be provided for sulfuric acid anodizing installations. Tanks have been made of lead-lined steel. Lead may be preferred over plastic for the lining because lead withstands the heat generated when sulfuric acid is added. Polyvinyl chloride pipes are recommended for air agitation of the solution and for the acid-return lines between the two tanks. Cooling coils have also been made of chemical lead or antimonial lead pipe.

Hard Anodizing. Most of the hard anodizing formulations are variations of the sulfuric acid bath. The requirements for hard anodizing tanks are substantially the same as those for sulfuric acid anodizing tanks, except that cooling, rather than heating, maintains the operating temperature at 0 to 10 °C (32 to 50 °F).

Temperature-control equipment for all anodizing processes must regulate the overall operating temperature of the bath and maintain the proper temperature of the interface of the work surface and electrolyte. The operating temperature

for most anodizing baths is controlled within ±1 °C (±2 °F). This degree of control makes it necessary for the temperature-sensing mechanism and heat lag of the heating units to be balanced.

When electric immersion heaters are used, it is common practice to have high and low heat selection so that the bath can be heated rapidly to the operating temperature and then controlled more accurately on the low heat setting. Standard thermistor thermostats are used for sensing the temperature within the bath and activating the heating elements.

In steam-heated systems, it is advantageous to have a throttling valve to prevent overheating. An intermediate heat exchanger is used in some installations to prevent contamination of the electrolyte and the steam system by a broken steam line within the anodizing bath.

Agitation may be accomplished by stirring with electrically driven impellers, by recirculation through externally located pumps, or by air. In some installations, the anode busbars are oscillated horizontally, thus imparting a stirring action to the work.

The two primary requirements of an agitation system are that it is adequate and that it does not introduce foreign materials into the solution. With air agitation, filters must be used in the line to keep oil and dirt out of the solution. In the case of hard anodizing, attention to proper agitation is critical to correct processing. Agitation that is not uniform or not adequate will be instrumental in burning.

Power requirements for the principal anodizing processes are as follows:

Process	Voltage	Current density	
		A/dm^2	A/ft^2
Chromic	42	0.1-0.3	1-3
Sulfuric	24	0.6-2.4	6-24

(a) Alloys prone to burning (i.e., high-copper alloys) may demand lower current density (down to 2 A/dm^2, or 20 A/ft^2) rather than the lower limit of 2.5 A/dm^2 (25 A/ft^2).

Direct current is required for all processes. Some hard anodizing procedures also require a superimposed alternating current or a pulsed current. At present, most power sources for anodizing use selenium or silicon rectifiers. Compared to motor generators, the selenium rectifiers have greater reliability, are lower in initial cost and maintenance cost, and have satisfactory service life.

Voltage drop between the rectifier and the work must be held to a minimum. This is accomplished by using adequate busbars or power-transmission cables. Automatic equipment to program the current during the entire cycle is preferred. Manual controls can be used, but they necessitate frequent adjustments of voltage. The presence of a recording voltmeter in the circuit ensures that the time-voltage program specified for the particular installation is being adhered to by operating personnel. Current-recording devices also are advantageous.

Masking. When selective anodizing is required, masking is necessary for areas to be kept free of the anodic coating. Masking during anodizing may also be required for postanodizing operations such as welding, for making an electrical connection to the base metal, or for producing multicolor effects with dye coloring techniques.

Masking materials are usually pressure-sensitive tapes, stop-off lacquers, or plastic or rubber plugs. Various tape materials, including polyvinyl chloride, Mylar, or Kapton, may be used. One type of tape may adhere better or be easier to remove after anodizing than another. For instance, while more expensive than other tapes, tapes with silicone adhesive hold up best during chromic acid anodizing, generally considered by anodizers to be the toughest anodize process to mask for. Metallic aluminum foil tape may also be used.

Stop-off lacquers provide satisfactory masking, but they are labor-intensive to apply and thus costly. Secondly, they are difficult to remove, often requiring the use of organic thinners or solvents. Rubber plugs, such as tapered laboratory stoppers, are effective for masking holes. They are widely available in various configurations and are known to anodizers by such names as "pull plugs," "dunce caps," and "mouse tails." In addition, where volumes and lead times are warranted, customized plugs may be molded from plastisol (unplasticized polyvinyl chloride) or another acid-resistant material.

Lastly, anodize itself may be used as a maskant. For example, on a precision-machined aluminum aerospace component requiring one small area to be abrasion resistant, the part might be chromic acid anodized all over, then machined in the area required to be abrasion resistant and subsequently hard anodized. The key to such an approach is to seal the initially applied chromic anodize. In such cases, nickel acetate sealing is highly preferable. Care must also be exercised by the machinist not to damage the chromic anodize layer in areas where hard anodize is undesirable.

Racks for Anodizing

Anodizing racks or fixtures should be designed for efficiency in loading and unloading of workpieces. Important features that must be included in every properly designed rack are:

- *Current-carrying capacity:* The rack must be large enough to carry the correct amount of current to each part attached to he rack. If the spline of the rack is too slender for the number of parts that are attached to the rack, the anodic coating will be of inadequate thickness, or it will be burned or soft as the result of overheating.
- *Positioning of parts:* The rack should enable proper positioning of the parts to permit good drainage, minimum gassing effects and air entrapment, and good current distribution.
- *Service life:* The rack must have adequate strength, and sufficient resistance to corrosion and heat, to withstand the environment of each phase of the anodizing cycle.

The use of bolt and screw contacts, rather than spring or tension contacts, is a feature of racks designed for anodizing with the integral color processes. These processes require high current densities and accurate positioning of workpieces in the tank. Bolted contacts are used also on racks for conventional hard anodizing. However, bolting requires more loading and unloading time than tension contacts.

Materials for Racks. Aluminum and commercially pure titanium are the materials most commonly used for anodizing racks. Aluminum alloys used for racks should contain not more than 5% Cu and 7% Si. Alloys such as 3003, 2024, and 6061 are satisfactory. Contacts must be of aluminum or titanium. Racks made of aluminum have the disadvantage of being anodized with the parts. The anodic coating must be removed from the rack, or at least from contacts, before the rack can be reused. A 5% solution of sodium hydroxide at 38 to 65 °C (100 to 150 °F), or an aqueous solution of chromic and phosphoric acids (40 g or 5 $\frac{1}{3}$ oz CrO_3 and 40 mL or 5 $\frac{1}{3}$ fluid oz of H_3PO_4 per liter or per gallon of water) at 77 to 88 °C (170 to 190 °F) can be used to strip the film from the rack. The chromic-phosphoric acid solution does not continue to attack the aluminum rack after the anodic film is removed.

Caustic etching prior to anodizing attacks aluminum spring or tension contacts, causing a gradual decrease in their strength for holding the parts securely. This condition, coupled with vibration in the anodizing tank, especially from agitation, results in movement and burning of workpieces.

On many racks, aluminum is used for splines, crosspieces, and other large members, and titanium is used for the contact tips. The tips may be replaceable or nonreplaceable. Although replaceable titanium tips offer versatility in racking, the aluminum portions of the rack must be protected with an insulating coating. However, if the anodizing electrolyte penetrates the coating, the aluminum portion of the rack may become anodized and thus become electrically insulated from the replaceable titanium contact. A more satisfactory rack design uses nonreplaceable titanium contacts on aluminum splines that are coated with a protective coating. Titanium contacts that are welded to replaceable titanium crossbars offer a solution to many racking problems created by the variety of parts to be anodized. These crossbar members can be rapidly connected to the spline.

Titanium should not be used in solutions containing hydrofluoric acid or any solution bearing any fluoride species. Titanium has the disadvantage that it has less than half the current-carrying capacity of aluminum, which can handle 650 A per square inch of cross-sectional area. However, recent rack designs employing cores of titanium-clad copper have offset this disadvantage.

Plastisol is used as a protective coating for anodizing racks. This material has good resistance to chemical attack by the solutions in the normal anodizing cycle; however, it should not be used continuously in a vapor degreasing operation or in chemical bright dip solutions. Furthermore, if the coating becomes loose and entraps processing solution, the solution may bleed out and drip on the workpieces, causing staining or spotting. Entrapment of bright dip solution containing phosphates can be a "silent killer" of sealing solutions. Phosphates in very small quantities that are subsequently released in the seal bath will prevent sealing from occurring.

Bulk Processing. Small parts that are difficult to rack are bulk anodized in perforated cylindrical containers made of fiber, plastic, or titanium. Each container has a stationary bottom, a threaded spindle centrally traversing its entire length, and a removable top that fits on the spindle to hold the parts in firm contact with each other. While bulk processing is more economical in that parts do not have to be individually racked, the drawbacks are that it results in random unanodized contact marks on the exterior of the part, and that it is usable only on parts without flat sections or blind holes. It is usually used on relatively small parts.

Anodizing Problems

Causes and the means adopted for correction of several specific problems in anodizing aluminum are detailed in the following examples.

Example 1:

Anodic coatings were dark and blotchy on 80 to 85% of a production run of construction workers' helmets made of alloy 2024. After drawing, these helmets had been heat treated in stacks, water quenched, artificially aged, alkaline etched with sodium hydroxide solution, anodized in sulfuric acid solution, sealed, and dried. The dark areas centered at the crowns of the helmets and radiated outward in an irregular pattern. Examination disclosed the presence of precipitated constituents and lower hardness in the dark areas. The condition proved to be the result of restricted circulation of the quench water when the helmets were stacked, which permitted precipitation of constituents because of a slower cooling rate in the affected areas. The problem was solved by separating the helmets with at least 75 mm (3 in.) of space during heating and quenching.

Example 2:

Pieces of interior trim made from alloy 5005 sheet varied in color from light to dark gray after anodizing. Rejection was excessive, because color matching was required. Investigation proved that the anodizing process itself was not at fault; the color variation occurred because the workpieces had been made of cutoffs from sheet stock obtained from two different sources. To prevent further difficulty, two recommendations were made:

- All sheet metal of a given alloy should be purchased from one primary producer, or each job should be made of material from one source. In the latter instance, all cutoffs should be kept segregated.
- More rigid specifications should be established for the desired quality of finish. Most producers can supply a clad material on certain alloys that gives better uniformity in finishing.

Example 3:

The problem was to improve the appearance of bright anodized automotive parts made of alloy 5357-H32. Deburring was the only treatment preceding anodizing. An acceptable finish was obtained by changing to an H25 temper. The H25 had a better grain structure for maintaining a mirror-bright finish during anodizing.

Example 4:

After alkaline etching, web-shape extrusions made of alloy 6063-T6 exhibited black spots that persisted through the anodizing cycle. These extrusions were 3 m (11 ft) long and had cross-sectional dimensions of 100 by 190 mm (4 by 7 $\frac{1}{2}$ in.) and a web thickness of 5 mm ($\frac{3}{16}$ in.). Cleaning had consisted of treatment for 1 to 4 min in 15% sulfuric acid at 85 °C (185 °F) and etching for 8 min in a sodium hydroxide solution (40 g/L or 5 oz/gal) at 60 °C (140 °F). The spots occurred only on the outer faces of the web. Affected areas showed subnormal hardness and electrical conductivity. Metallographic examination revealed precipitation of magnesium silicide there.

The defects were found to have occurred in areas where cooling from the extrusion temperature was retarded by the presence of insulating air pockets created by poor joints between the carbon blocks that lined the runout table. The extrusion had only to remain stationary on the runout table (end of extrusion cycle, flipped on side for sawing) for as little as 1 min for $MgSi_2$ to precipitate at locations where cooling was retarded. This type of defect is not limited to a particular shape; it can result from a critical combination of size and shape of the extrusion, or from extrusion conditions and cooling rate.

The solution to the problem was to provide uniform cooling of the extrusion on the runout table; this was accomplished by modifying the table and employing forced-air cooling.

Sealing of Anodic Coatings

When properly done, sealing in boiling deionized water for 15 to 30 min partially converts the as-anodized alumina of an anodic coating to an aluminum monohydroxide known as Boehmite. It is also common practice to seal in hot aqueous solution containing nickel acetate. Precipitation of nickel hydroxide helps in plugging the pores.

The corrosion resistance of anodized aluminum depends largely on the effectiveness of the sealing operation. Sealing will be ineffective, however, unless the anodic coating is continuous, smooth, adherent, uniform in appearance, and free of surface blemishes and powdery areas. After sealing, the stain resistance of the anodic coating also is improved. For this reason, it is desirable to seal parts subject to staining during service.

Tanks made of stainless steel or lined low-carbon steel and incorporating adequate agitation and suitable temperature controls are used for sealing solutions.

Chromic acid anodized parts are sealed in slightly acidified hot water. One specific sealing solution contains 1 g of chromic acid in 100 L of solution (0.1 oz in 100 gal). The sealing procedure consists of immersing the freshly anodized and rinsed part in the sealing solution at 79 ± 1 °C (175 ± 2 °F) for 5 min. The pH of this solution is maintained within a range of 4 to 6. The solution is discarded when there is a buildup of sediment in the tank or when contaminants float freely on the surface.

Sulfuric acid anodized parts may also be sealed in slightly acidified water (pH 5.5 to 6.5), at about 93 to 100 °C (200 to 212 °F). At temperatures below 88 °C (190 °F), the change in the crystalline form of the coating is not satisfactorily accomplished within a reasonable time.

Dual sealing treatments are often used, particularly for clear anodized trim parts. A typical process involves a short-time immersion in hot nickel acetate 0.5 g/L (0.06 oz/gal) solution followed by rinsing and immersion in a hot, dilute dichromate solution. Advantages of dual sealing are less sealing smudge formed, greater tolerance for contaminants in the baths, and improved corrosion resistance of the sealed parts in accelerated tests (e.g., the CASS test, ASTM B 368).

One specific sealing solution contains 5 to 10 wt% potassium dichromate and sufficient sodium hydroxide to maintain the pH at 5.0 to 6.0. This solution is prepared by adding potassium dichromate to the partly filled operating tank and stirring until the dichromate is completely dissolved. The tank is then filled with water to the operating level and heated to the operating temperature, after which the pH is adjusted by adding sodium hydroxide (which gives a yellow color to the bath).

For sealing, the freshly anodized and rinsed part is immersed in the solution at 100 ± 1 °C (210 ± 2 °F) for 10 to 15 min. After sealing, the part is air dried at a temperature no higher than 105 °C (225 °F). The dichromate seal imparts a yellow coloration to the anodic coating.

Control of this solution consists of maintaining the correct pH and operating temperature. The solution is discarded when excessive sediment builds up in the tank or when the surface is contaminated with foreign material. Sealing is not done on parts that have received any of the hard anodized coatings unless properties other than abrasion resistance are required. If the parts are to be used in a corrosive environment, sealing would be a requirement after hard anodizing. Another application where sealing would be a requirement would be to increase electrical resistance. Sealing will reduce abrasion resistance by 30%. Some other sealing processes are given in Table 6.

Table 6 Sealing processes for anodic coatings

Process	Bath	Temperature		Duration, min	Appearance, properties	Remarks
		°C	°F			
Nickel-cobalt	0.5 kg (1.1 lb) nickel acetate, 0.1 kg (0.2 lb) cobalt acetate, 0.8 kg (1.8 lb) boric acid, 100 L (380 gal) water	98-100	208-212	15-30	Colorless	Provides good corrosion resistance for a colorless seal after anodizing bath buffered to pH of 5.5 to 6.5 with small amounts of acetic acid sodium acetate
Dichromate	5 wt% sodium dichromate, 95 wt% water	98-100	208-212	30	Yellow color	Cannot be used for decorative and colored coatings where the yellow color is objectionable
Glauber salt	20 wt% sodium sulfate, 80 wt% water	98-100	208-212	30	Colorless	. . .
Lacquer seal	Lacquer and varnishes for interior and exterior exposure	. . .	. . .	. . .	Colorless to yellow or brown	Can provide good corrosion resistance provided that the correct formulation is selected. Formulations for exterior exposure use acrylic, epoxy, silicone-alkyds resins and for interior exposure the previously mentioned

Water for sealing solutions can significantly affect the quality of the results obtained from the sealing treatment, as evidenced in the following example.

Strips for automotive exterior trim that were press formed from 5457-H25 sheet were found to have poor corrosion resistance after anodizing, even though appearance was acceptable. The strips had been finished in a continuous automatic anodizing line incorporating the usual steps of cleaning, chemical brightening, desmutting, and anodizing in a 15% sulfuric acid electrolyte to a coating thickness of 8 μm (0.3 mil). They had been sealed in deionized water at a pH of 6.0 and then warm air dried. Rinses after each step had been adequate, and all processing conditions had appeared normal.

Investigation eliminated metallurgical factors as a possible cause but directed suspicion to the sealing operation, because test strips sealed in distilled water showed satisfactory corrosion resistance. Although the deionized water used in processing had better-than-average electrical resistance (1,000,000 Ω· cm or 10,000 Ω· m), analysis of the water showed that it contained a high concentration of oxidizable organic material. This was traced to residues resulting from the leaching of ion-exchange resins from the deionization column. The difficulty was remedied by the use of more stable resins in the deionization column.

When the resin is approaching full absorption rate, the silicons (silicates) are one of the first elements to come across as

Color Anodizing

Dyeing consists of impregnating the pores of the anodic coating, before sealing, with an organic or inorganic (e.g., ferric ammonium oxalate) coloring material. The depth of dye adsorption depends on the thickness and porosity of the anodic coating. The dyed coating is transparent, and its appearance is affected by the basic reflectivity characteristics of the aluminum. For this reason, the colors of dyed aluminum articles should not be expected to match paints, enamel, printed fabrics, or other opaque colors.

Shade matching of color anodized work is difficult to obtain. Single-source colors usually are more uniform than colors made by mixing two or more dye materials together. Maximum uniformity of dyeing is obtained by reducing all variables of the anodizing process to a minimum and then maintaining stringent control of the dye bath.

Mineral pigmentation involves precipitation of a pigment in the pores of the anodic coating before sealing. An example is precipitation of iron oxide from an aqueous solution of ferric ammonium oxalate to produce gold-colored coatings.

Integral color anodizing is a single-step process in which the color is produced during anodizing. Pigmentation is caused by the occlusion of microparticles in the coating, resulting from the anodic reaction of the electrolyte with the microconstituents and matrix of the aluminum alloy. Thus, alloy composition and temper strongly affect the color produced. For example, aluminum alloys containing copper and chromium will color to a yellow or green when anodized in sulfuric or oxalic acid baths, whereas manganese and silicon alloys will have a gray to black appearance. Anodizing conditions such as electrolyte composition, voltage, and temperature are important and must be controlled to obtain shade matching. One electrolyte frequently used consists of 90 g/L (10 oz/gal) sulfophthalic acid plus 5 g/L (0.6 oz/gal) sulfuric acid.

Another method for coloring anodic coatings is the two-step (electrolytic) coloring process. After conventional anodizing in sulfuric acid electrolyte, the parts are rinsed and transferred to an acidic electrolyte containing a dissolved metal salt. Using alternating current, a metallic pigment is electrodeposited in the pores of the anodic coating. There are various proprietary electrolytic coloring processes. Usually tin, nickel, or cobalt is deposited, and the colors are bronzes and black. The stable colors produced are useful in architectural applications.

Evaluation of Anodic Coatings

Coating Thickness. In the metallographic method, the evaluator measures coating thickness perpendicular to the surface of a perpendicular cross section of the anodized specimen, using a microscope with a calibrated eyepiece. This is the most accurate method for determining the thickness of coatings of at least 2.5 μm (0.1 mil). This method is used to calibrate standards for other methods and is the reference method in cases of dispute. Because of variations in the coating thickness, multiple measurements must be made and the results averaged.

In the micrometer method, the evaluator determines coating thickness of 2.5 μm (0.1 mil) or more by micrometrically measuring the thickness of a coated specimen, stripping the coating using the solution described in ASTM B 137, micrometrically measuring the thickness of the stripped specimen, and subtracting the second measurement from the first.

Effectiveness of Sealing. The sulfur dioxide method comprises exposure of the anodic coating for 24 h to attack by moist air (95 to 100% relative humidity) containing 0.5 to 2 vol% sulfur dioxide, in a special test cabinet. The method is very discriminative. Coatings that are incompletely or poorly sealed develop a white bloom.

Abrasion Resistance. In the Taber abrasion method, the evaluator determines abrasion resistance by an instrument that, by means of weighted abrasive wheels, abrades test specimens mounted on a revolving turntable. Abrasion resistance is measured in terms of either weight loss of the test specimen for a definite number of cycles or the number of cycles required for penetration of the coating. These procedures are covered by Method 6192 in Federal Test Method Standard 141. Weight (thickness) loss (see Method 6192-4.1.3 in Federal Test Methods Standard 141) is measured using eddy current as a check, because milligram weight loss in checking abrasion resistance is difficult to duplicate. Penetration testing can take more than 30 h. Although described in Method 6192, it is rarely used for hard anodizing.

Lightfastness. The fade-O-meter method is a modification of the artificial-weathering method, in that the cycle is conducted without the use of water. Staining and corrosion products thus cannot interfere with interpretation of results. A further modification entails the use of a high-intensity ultra-violet mercury-arc lamp and the reduction of exposure to a

period of 24 to 48 h. Table 7 lists the various ASTM and ISO methods that can be used to evaluate the quality of anodic coatings.

Table 7 ASTM and ISO test methods for anodic coatings

Method	ASTM	ISO
Coating thickness		
Eddy current	B244	2360
Metallographic	B487	. . .
Light section microscope	B681	2128
Coating weight	B137	2106
Sealing		
Dye stain	B136[(a)]	2143
Acid dissolution	B680	3210
Impedance/admittance	B457	2931
Voltage breakdown	B110	2376
Corrosion resistance		
Salt spray	B117	. . .
Cooper-accelerated, acetic acid salt-spray	B368	. . .

(a) ASTM B 136 shows extremely poor sealing and is not considered a true sealing test. It is better classified as a test for staining by dyes.

Effects of Anodic Coatings on Surface and Mechanical Properties

As the thickness of an anodic coating increases, light reflectance, both total and specular, decreases. This decrease is only slight for pure aluminum surfaces, but it becomes more pronounced as the content of alloying elements other than magnesium, which has little effect, increases. The decrease in reflectance values is not strictly linear with increasing thickness of anodic coating; the decrease in total reflectance levels off when the thickness of the coating on super-purity and high-purity aluminum is greater than about 2.5 μm (0.1 mil).

Data comparing the reflectance values of chemically brightened and anodized aluminum materials with those of other decorative materials are given in "Anodic Oxidation of Aluminium and Its Alloys," Bulletin 14 of the Aluminium Development Association (now the Aluminium Federation), London, England, 1949.

Table 8 shows the effect of anodized coatings 2 to 20 μm (0.08 to 0.8 mil) thick on the reflectance values of electrobrightened aluminum of three degrees of purity. This table also includes specular reflectance values for surfaces after removal of the anodic coating. These data show that the degree of roughening by the anodizing treatment increases as the purity of the aluminum decreases. The reflectance values of the anodized surfaces are influenced by the inclusion of foreign constituents or their oxides in the anodic coating.

Table 8 Effect of anodizing on reflectance values of electrobrightened aluminum

Thickness of anodic coating		Specular reflectance, %			Total reflectance after anodizing, %
μm	mil	Electro-brightened	Electro-brightened and anodized	After removal, of anodic coating[(a)]	
Aluminum, 99.99%					
2	0.08	90	87	88	90
5	0.2	90	87	88	90
10	0.4	90	86	88	89
15	0.6	90	85	88	88
20	0.8	90	84	88	88
Aluminum, 99.8%					
2	0.08	88	68	83	89
5	0.2	88	63	85	88
10	0.4	88	58	85	87
15	0.6	88	53	85	86
20	0.8	88	57	85	84
Aluminum, 99.5%					
2	0.08	75	50	70	86
5	0.2	75	36	64	84

10	0.4	75	26	61	81
15	0.6	75	21	57	77
20	0.8	75	15	53	73

Source: Aluminum Development Council

(a) Anodic coating removed in chromic-phosphoric acid.

Metallurgical factors have a significant influence on the effect of anodizing on reflectance. For minimum reduction in reflectance, the conversion of metal to oxide must be uniform in depth and composition. Particles of different composition do not react uniformly. They produce a nonuniform anodic coating and roughen the interface between the metal and the oxide coating.

Anodizing Conditions. The composition and operating conditions of the anodizing electrolyte also influence the light reflectance and other properties of the polished surface. Figure 8 shows the effect of sulfuric acid concentration, temperature of bath, and current density on the specular reflectance of chemically brightened aluminum alloy 5457. These data show that a particular level of specular reflectance can be produced by varying operating conditions.

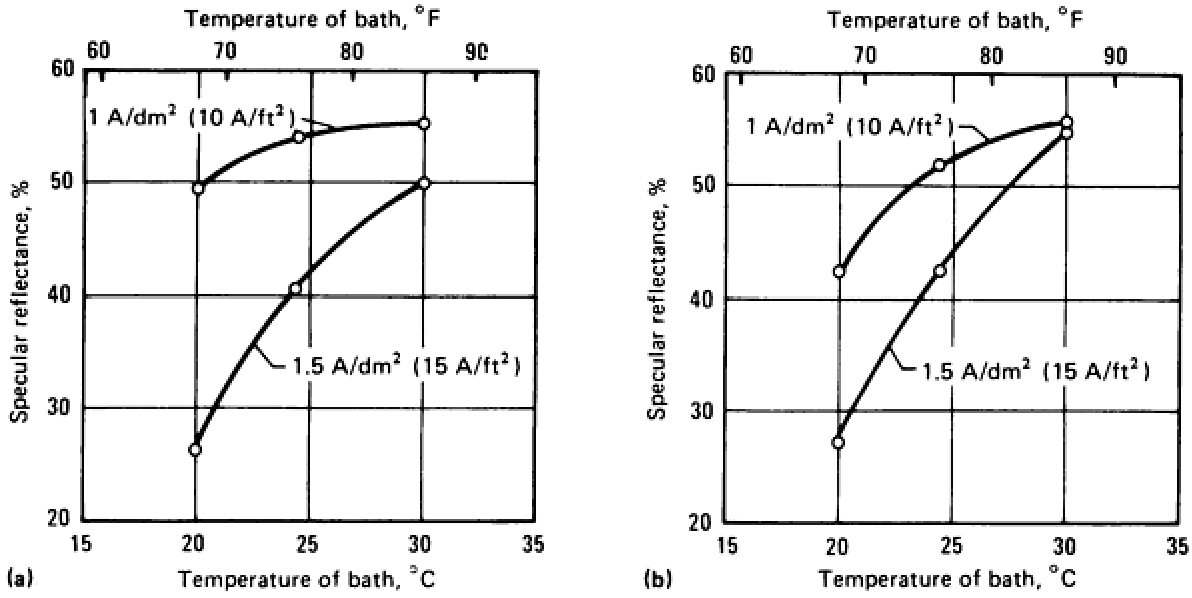


Fig. 8 Effect of anodizing conditions on specular reflectance of chemically brightened aluminum. Data are for a 5 μm (0.2 mil) anodic coating on 5457 alloy. (a) 17 wt% H_2SO_4. (b) 8.8 wt% H_2SO_4

Thermal Radiation. The reflectance of aluminum for infrared radiation also decreases with increasing thickness of the anodic coating, as shown in Fig. 9. These data indicate that the difference in purity of the aluminum is of minor significance. Figure 10 compares anodized aluminum surfaces and polished aluminum surfaces at 21 °C (70 °F) with respect to absorptance when exposed to blackbody radiation from sources of different temperatures. Although anodized aluminum is a better absorber of low-temperature radiation, as-polished aluminum is a more effective absorber of blackbody radiation from sources at temperatures exceeding 3300 °R (1850 K).

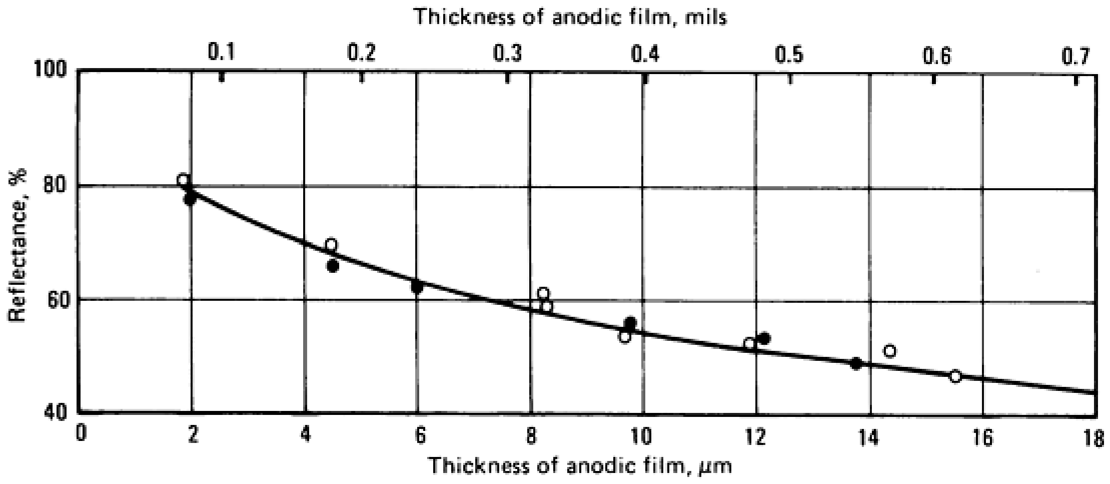


Fig. 9 Effect of anodic coating thickness on reflectance of infrared radiation. Temperature of infrared radiation source, 900 °C (1650 °F). ○: 99.99% Al. •: 99.50% Al. Courtesy of Aluminum Development Council

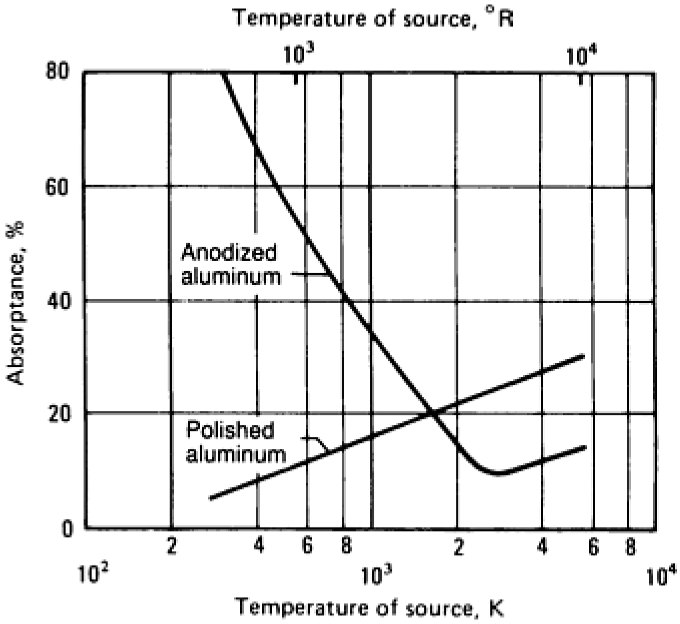


Fig. 10 Comparison of absorptance of blackbody radiation by anodized aluminum and polished aluminum. Temperature of aluminum surface. 530 °R (21 °C, or 70 °F)

Fatigue Strength. Anodic coatings are hard and brittle, and they will crack readily under mechanical deformation. This is true for thin as well as thick coatings, even though cracks in thin coatings may be less easily visible. Cracks that develop in the coating act as stress raisers and are potential sources of fatigue failure of the substrate metal. Typical fatigue-strength values for aluminum alloys before and after application of a hard anodic coating 50 to 100 μm (2 to 4 mils) thick are given in Table 9.

Table 9 Effect of anodizing on fatigue strength of aluminum alloys

Alloy	Fatigue strength at 1,000,000 cycles

	Not anodized		Anodized	
	MPa	ksi	MPa	ksi
Wrought alloys				
2024 (bare)	130	19	105	15
2024 (clad)	75	11	50	7.5
6061 (bare)	105	15	40	6
7075 (bare)	150	22	60	9
7075 (clad)	85	12	70	10
Casting alloys				
220	50	7.5	52	7.5
356	55	8	55	8

Note: Values are for sulfuric acid hard coatings 50 to 100 μm (2 to 4 mils) thick applied using 15% sulfuric acid solution at -4 to 0 °C (25 to 32 °F) and 10 to 75 V dc.

Source: F.J. Gillig, WADC Technical Report 53-151, P.B. 111320, 1953

Anodizing Non-Aluminum Substrates

Magnesium Anodizing. Three methods of anodizing magnesium are widely employed by industry. One uses only internal voltage generated as a result of a galvanic couple, and two use an external power source. The first method, often referred to as galvanic anodize or the Dow 9 process, uses a steel cathode electrically coupled to the magnesium component to be anodized. Dow 9 coatings have no appreciable thickness and impart little added corrosion resistance. However, the resulting coating is dark brown to black, which makes it useful for optical components and for heat sinks in electronic applications. This coating also serves as an excellent paint base.

The other anodizing processes, known as the HAE and Dow 17 processes, use an external power source. Both processes deposit an anodic layer about 50 μm (2 mils) thick, but they differ in that the solution used for Dow 17 coatings is acidic, a combination of ammonium bifluoride, sodium dichromate, and phosphoric acid, whereas the HAE process employs an alkaline bath. Details for both processes may be found by consulting military specification MIL-M-45202.

Titanium Anodizing. While extremely corrosion resistant in itself, titanium and its alloys are often anodized to impart properties other than corrosion resistance. For instance, in wear situations, titanium components are very prone to galling. In order to overcome its tendency to gall, titanium is often anodized in a caustic electrolyte. This application is detailed in the SAE specification AMS 2488.

Decorative colored coatings on titanium can be achieved by anodizing in slightly acidified solutions of phosphoric or sulfuric acid. By controlling the terminal voltage, vivid colors from magenta to cobalt blue can be obtained. Such

decorative uses have been widely utilized by the jewelry industry for years, and these coatings are now finding functional use for medical implants and dental instruments.

Zinc Anodizing. Zinc can be anodically treated in a wide range of electrolytes using either alternating or direct current to form decorative, yet protective, coatings. Anodic coatings on zinc and zinc alloys are covered in military specification MIL-A-81801. The zinc to be anodized may be wrought or die cast zinc parts or zinc coatings obtained by electroplating, mechanical deposition, thermal spraying, or galvanizing.

Electrolytes are formulated from such materials as phosphates, silicates, or aluminates to which are added chromates, vanadates, molybdates, and/or tungstates. Solutions are typically heated to 65 °C (150 °F), and anodize times vary from 5 to 10 min. The resulting coatings are 30 to 40 μm (1.2 to 1.6 mils) thick and are either green, gray, or brown, depending on the electrolyte used. For optimum corrosion resistance, anodic zinc coatings should be sealed using a material such as sodium silicate or an organic lacquer or enamel.

Thermal Spray Coatings

Robert C. Tucker, Jr., Praxair Surface Technologies, Inc.

Introduction

THERMAL SPRAY is a generic term for a group of processes in which metallic, ceramic, cermet, and some polymeric materials in the form of powder, wire, or rod are fed to a torch or gun with which they are heated to near or somewhat above their melting point. The resulting molten or nearly molten droplets of material are accelerated in a gas stream and projected against the surface to be coated (i.e., the substrate). On impact, the droplets flow into thin lamellar particles adhering to the surface, overlapping and interlocking as they solidify. The total coating thickness is usually generated in multiple passes of the coating device.

The invention of the first thermal spray process is generally attributed to M.U. Schoop of Switzerland in 1911 and is now known as flame spraying. Other major thermal spray processes include wire spraying, detonation gun deposition (invented by R.M. Poorman, H.B. Sargent, and H. Lamprey and patented in 1955), plasma spray (invented by R.M. Gage, O.H. Nestor, and D.M. Yenni and patented in 1962), and high velocity oxyfuel (invented by G.H. Smith, J.F. Pelton, and R.C. Eschenbach and patented in 1958). A variant of plasma spraying uses a transferred arc to heat the surface being coated. It is considered by some to be a welding process akin to hard facing rather than a true thermal spray process, because the surface of the substrate becomes momentarily molten immediately beneath the torch.

A major advantage of the thermal spray processes is the extremely wide variety of materials that can be used to make a coating. Virtually any material that melts without decomposing can be used. A second major advantage is the ability of most of the thermal spray processes to apply a coating to a substrate without significantly heating it. Thus, materials with very high melting points can be applied to finally machined, fully heat-treated parts without changing the properties of the part and without thermal distortion of the part. A third advantage is the ability, in most cases, to strip and recoat worn or damaged coatings without changing the properties or dimensions of the part. A major disadvantage is the line-of-sight nature of these deposition processes. They can only coat what the torch or gun can "see." Of course, there are also size limitations prohibiting the coating of small, deep cavities into which a torch or gun will not fit.

Figure 1 shows an example of the variety of shapes taken by the molten droplets as they impact, flow, and solidify on the surface. The mechanism of bonding of the particles to the surface is not well understood but is thought to be largely due to mechanical interlocking of the solidifying and shrinking particles, with asperities on the surface being coated unless supplemental fusion or diffusion heat treatment is used. Indeed, most thermal spray coatings require a roughened substrate surface for adequate bonding. Some interdiffusion or localized fusion of as-deposited coatings with the substrate has been observed in a few instances with unique combinations of coatings and substrates. There is evidence of chemical bonding in some coating/substrate systems, not unreasonable when the high-velocity impact of particles might be expected to rupture any films on either the powder particles or the substrate. In addition, van der Waals forces may play a role if the substrate is extremely clean and no significant oxidation occurs during deposition.

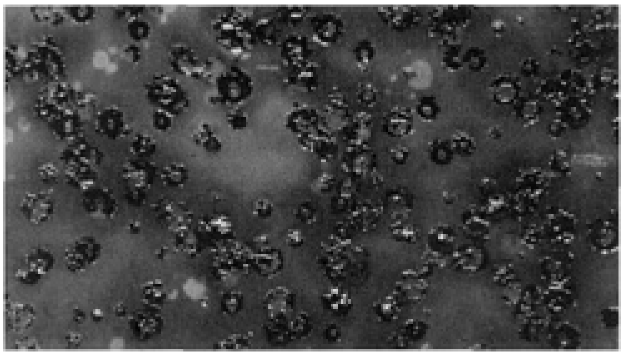


Fig. 1 Deformation of molten or semimolten particles resulting from spray impacting on a substrate

Thermal spray coatings are usually formed by multiple passes of a torch or gun over the surface. Typical cross sections of several examples of thermal spray coatings are shown in Fig. 2, illustrating the lamellar nature of the coatings. A coating can be made of virtually any material that can be melted without decomposing. Moreover, the deposition process itself can substantially alter the composition as well as the structure of the material. As a result, the microstructure and properties of the coatings can be extremely varied. Specification of a coating, therefore, must often involve more than simply stating the composition of the starting powder or wire and the general type of process to be used.

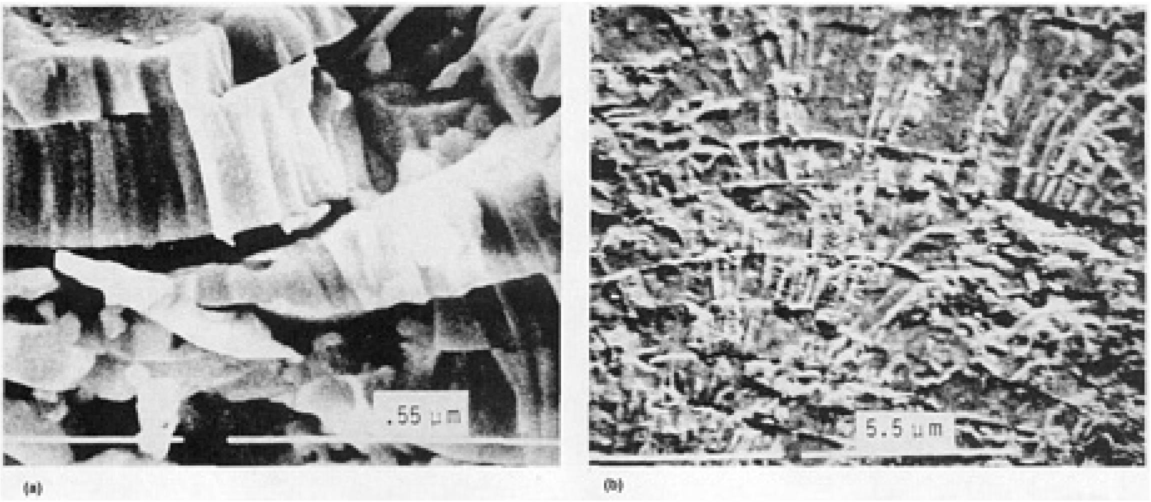


Fig. 2 Typical microstructure of a plasma-sprayed tungsten metal coating showing the splat structure and the fine crystalline structure within the splats. (a) Scanning electron micrograph of a fracture surface. (b) Light micrograph of the same coating. Courtesy of Praxair Surface Technologies, Inc.

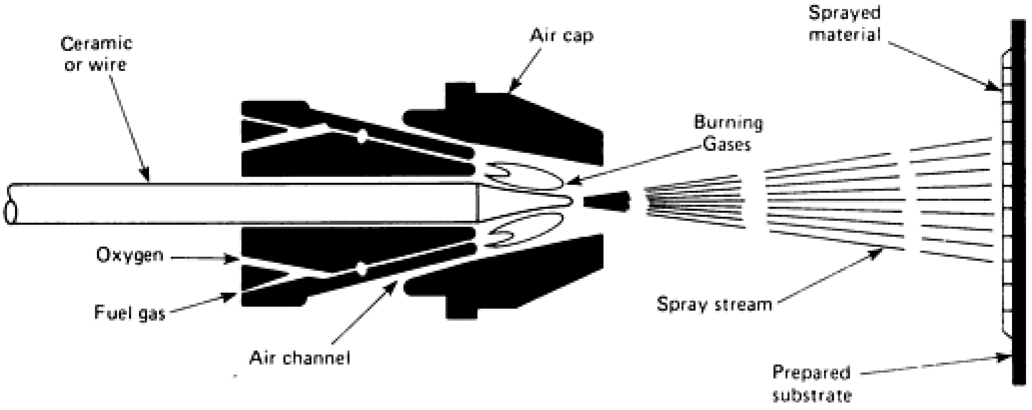
The applications of thermal spray coatings are extremely varied, but the largest categories of use are to enhance the wear and/or corrosion resistance of a surface. Other applications include their use for dimensional restoration, as thermal barriers, as thermal conductors, as electrical conductors or resistors, for electromagnetic shielding, and to enhance or retard radiation. They are used in virtually every industry, including aerospace, agricultural implements, automotive, primary metals, mining, paper, oil and gas production, chemicals and plastics, and biomedical. Some specific examples are given in the section "Uses of Thermal Spray Coatings" in this article.

Acknowledgements

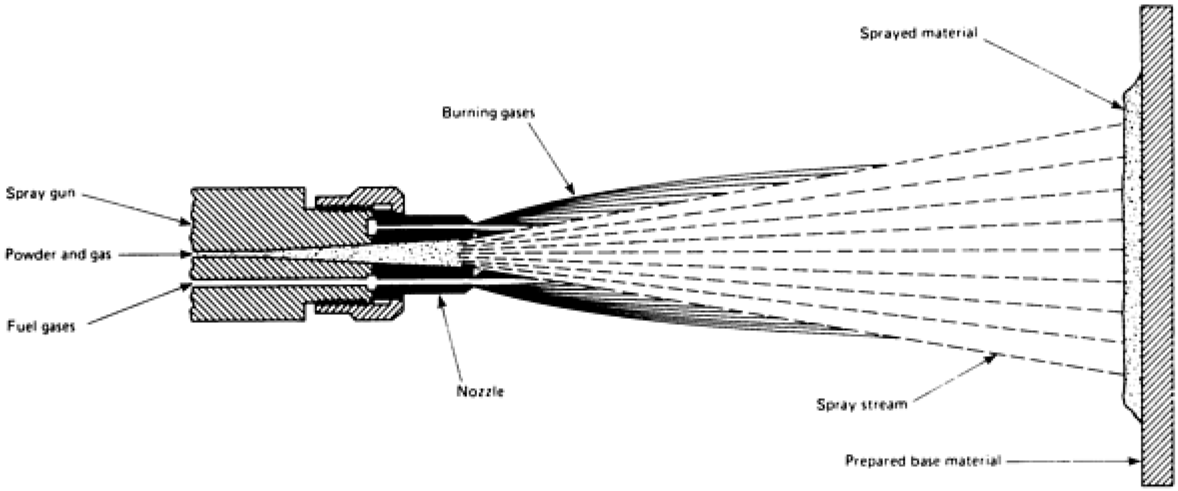
The author recognizes the contributions of James H. Clare and Daryl E. Crawmer, authors of the article "Thermal Spray Coatings" in *Metals Handbook,* 9th ed., Vol 5. In particular, the sections on flame spray, flame spray and fuse, and electric wire-arc spray, as well as several of the figures, were substantially adapted from the earlier edition.

Processes

Flame spray uses combustible gas as a heat source to melt the coating material (Fig. 3). Flame spray guns are available to spray materials in either rod, wire, or powder form. Most flame spray guns can be adapted to use several combinations of gases to balance operating cost and coating properties. Acetylene, propane, methyl-acetylene-propadiene (MAPP) gas, and hydrogen, along with oxygen, are commonly used flame spray gases. In general, changing the nozzle and/or air cap is all that is required to adapt the gun to different alloys, wire sizes, or gases. Figures 3(a) and 3(b) depict powder and wire flame spray guns. For all practical purposes, the rod and wire guns are similar.



(a)



(b)

Fig. 3 Cross sections of typical flame spray guns. (a) Wire or rod. (b) Powder

Flame temperatures and characteristics depend on the oxygen-to-fuel gas ratio and pressure. The approximate temperatures for stoichiometric combustion at 1 atm for some oxyfuel combinations are shown in Table 1. The flame spray process is characterized by low capital investment, high deposition rates and efficiencies, and relative ease of operation and cost of equipment maintenance. In general, as-deposited (or cold spray) flame-sprayed coatings exhibit lower bond strengths, higher porosity, a narrower working temperature range, and higher heat transmittal to the substrate than most other thermal spray processes. The flame spray process is widely used for the reclamation of worn or out-of-tolerance parts, frequently using nickel-base alloys. Bronze alloys may be used for some bearings and seal areas. Blends of tungsten carbide and nickel-base alloys may be used for wear resistance. Zinc is commonly applied for corrosion resistance on bridges and other structures.

Table 1 Maximum temperature of heat sources

Heat source	Approximate temperature (stoichiometric combustion)

Propane-oxygen	2526 °C (4579 °F)
Natural gas-oxygen	2538 °C (4600 °F)
Hydrogen-oxygen	2660 °C (4820 °F)
Propylene-oxygen	2843 °C (5240 °F)
Methylacetylene/propadiene-oxygen	2927 °C (5301 °F)
Acetylene-oxygen	3087 °C (5589 °F)
Plasma arc	2200 to 28,000 °C (4000 to 50,000 °F)

Source: Adapted Publication 1G191, National Association of Corrosion Engineers

Flame spray and fuse is a modification of the cold spray method. The materials used for coating are self-fluxing (i.e., they contain elements that react with oxygen or oxides to form low-density oxides that float to the surface, thus improving density, bonding, etc. They have relatively low melting points and require postspray heat treatment. In general, these are nickel- or cobalt-base alloys that use boron, phosphorus, or silicon, either singly or in combination, as melting-point depressants and fluxing agents. In practice, parts are prepared and coated as in other thermal spray processes and then fused. There are two variants: Spray and fuse, and spray-fuse. In spray and fuse, the fusion is done after deposition using one of several techniques, such as flame or torch, induction, or vacuum, inert, or hydrogen furnaces. In spray-fuse, the deposition and fusion are done simultaneously.

The alloys used generally fuse between 1010 to 1175 °C (1850 to 2150 °F), depending on composition. Reducing atmosphere flames should be used to ensure a clean, well-bonded coating. In vacuum and hydrogen furnaces, the coating may have a tendency to wick or run onto adjacent areas. Several brushable stopoff materials are commercially available to confine the coating. It is recommended that test parts be coated and fused whenever the shape, coating alloy, or lot of material is changed, to establish the minimum and maximum fusing temperatures. Fusing temperature is known to vary slightly between lots of spray material. On vertical surfaces, coating material may sag or run off if the fusing temperature is exceeded by more than a few degrees. These coatings are fully dense and exhibit metallurgical bonds. Excessive porosity and nonuniform bonding are usually indicative of insufficient heating.

Spray-and-fuse coatings are widely used in applications where excessive wear combined with high stresses on the coating/substrate (shear or impact) is a problem. These alloys generally exhibit good resistance to wear and have been successfully used in the oil industry for sucker rods and in agriculture for plowshares. In many applications, these coatings make possible the use of less expensive substrate materials. Coating hardnesses can be as high as 65 HRC. Some powder manufacturers offer these alloys blended with tungsten carbide or chromium carbide particles to increase resistance to wear from abrasion, fretting, and erosion. Grinding is usually necessary for machining a fused coating because of the high hardness. Use of spray-and-fuse coatings is limited to substrate materials that can tolerate the 1010 to 1175 °C (1850 to 2150 °F) fusing temperatures. Fusing temperatures may alter the heat-treated properties of some alloys. However, the coating will usually withstand additional heat treatment of the substrate. Slower cooling rates may be required to reduce cracking where greater thicknesses are needed or where there is a substantial difference in the thermal expansion coefficients between the coatings and the substrate.

The electric-arc (wire-arc) spray process uses metal in wire form. This process differs from the other thermal spray processes in that there is no external heat source such as gas flame or electrically induced plasma. Heating and melting occur when two electrically opposed charged wires, comprising the spray material, are fed together in such a manner that a controlled arc occurs at the intersection. The molten metal on the wire tips is atomized and propelled onto a prepared substrate by a stream of compressed air or other gas (Fig. 4).

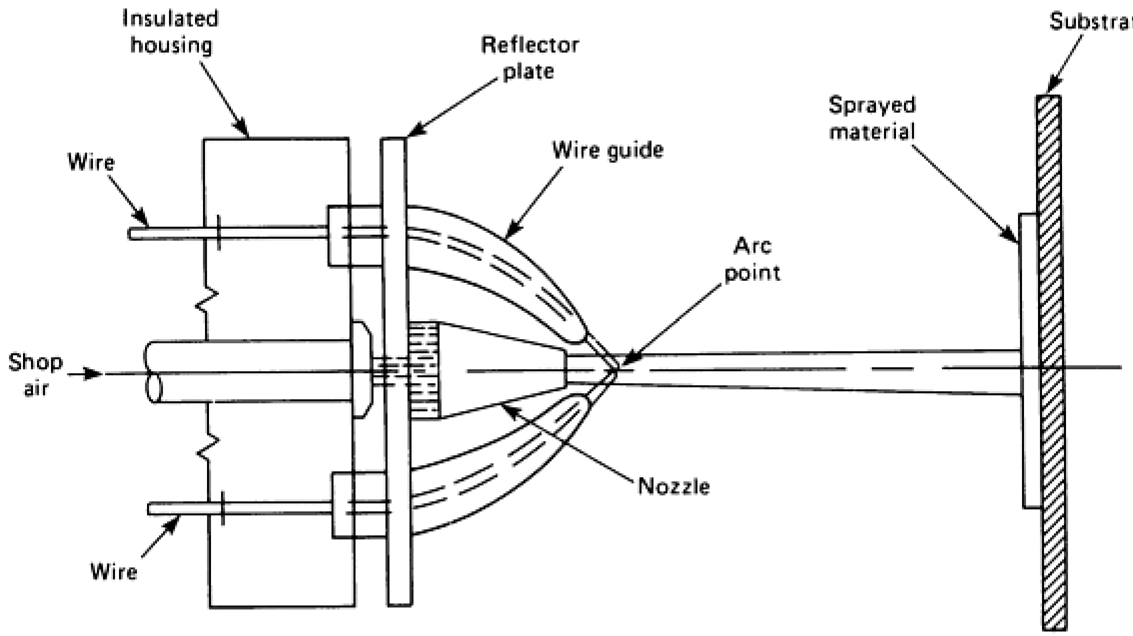


Fig. 4 Typical electric-arc spray device

Electric-arc spray offers advantages over flame spray processes. In general, it exhibits higher bond strengths, in excess of 69 MPa (10,000 psi) for some materials. Deposition rates of up to 55 kg/h (120 lb/h) have been achieved for some nickel-base alloys. Substrate heating is lower than in flame spray processes due primarily to the absence of a flame touching the substrate. The electric-arc process is in most instances less expensive to operate than the other processes. Electrical power requirements are low, and, with few exceptions, no expensive gas such as argon is necessary. The electric-arc process most commonly uses relatively ductile, electrically conductive wire about 1.5 mm (0.060 in.) in diameter. Electric-arc spray coatings of carbides, nitrides, and oxides are therefore not currently practical; however, the recent development of cored wires permits the deposition of some composite coatings containing carbides or oxides. By using dissimilar wires, it is possible to deposit pseudoalloys. A less expensive wear surface can be deposited using this technique. One wire, or 50% of the coating matrix, can be an inexpensive filler material.

Electric-arc coatings are widely used in high-volume, low-cost applications such as application of zinc corrosion-resistant coatings. In a more unusual application, metal-face molds can be made using a fine spray attachment available from some manufacturers. Molds made in this way can duplicate extremely fine detail, such as the relief lettering on a printed page.

Plasma Spray. A plasma spray torch is shown schematically in Fig. 5. A gas, usually argon, but occasionally including nitrogen, hydrogen, or helium, is allowed to flow between a tungsten cathode and a water-cooled copper anode. An electric arc is initiated between the two electrodes using a high-frequency discharge and then sustained using dc power. The arc ionizes the gas, creating a high-pressure gas plasma. The resulting increase in gas temperature, which may exceed 30,000 °C, in turn increases the volume of the gas and, hence, its pressure and velocity as it exits the nozzle. (Gas velocities, which may be supersonic, should not be confused with particle velocities.) Power levels in plasma spray torches are usually in the range of 30 to 80 kW, but they can be as high as 120 kW. Argon is usually chosen as the base gas because it is chemically inert and because of its ionization characteristics. The enthalpy of the gas can be increased by adding the diatomic gases, hydrogen or nitrogen.

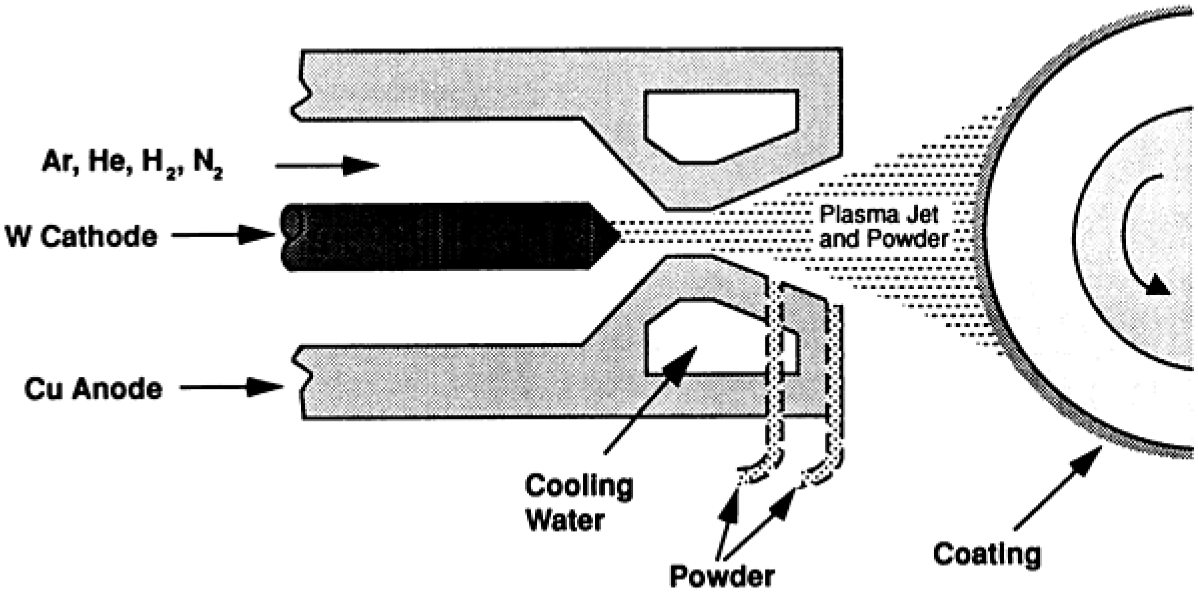


Fig. 5 Plasma spray process. Courtesy of Praxair Surface Technologies, Inc.

Powder is usually introduced into the gas stream either just outside the torch or in the diverging exit region of the nozzle (anode). It is both heated and accelerated by the high-temperature, high-velocity plasma gas stream. Torch design and operating parameters are critical in determining the temperature and velocity achieved by the powder particles. The operating parameters include not only the gas flows, power levels, powder feed rate, and carrier gas flow, but also the distance from the torch to from the substrate (standoff) and the angle of deposition. Standoff is of substantial importance because adequate distance must be provided for heating and accelerating the powder, but too great a distance will allow the powder to cool and lose velocity, because the gas stream is rapidly expanding, cooling, and slowing. The size and morphology of powder particles strongly influence their rate of heating and acceleration and, hence, the efficiency of deposition and quality of the coating. Frequently, a somewhat higher price paid for a powder with a tighter size distribution is more than compensated for by improved deposition efficiency.

The powder velocities usually achieved in plasma spray deposition range from about 300 to 550 m/s. Temperatures are usually at or slightly above the melting point. Generally, higher particle velocities and temperatures above the melting point, but without excessive superheating, yield coatings with the highest densities and bond strengths. The density of plasma spray coatings is usually much higher than that of flame spray coatings and is typically in the range of 80 to 95% of theoretical. Coating thickness usually ranges from about 0.05 to 0.50 mm (0.002 to 0.020 in.) but may be much thicker for some applications (e.g., dimensional restoration or thermal barriers). Bond strengths vary from less than 34 MPa (5000 psi) to greater than 69 MPa (10,000 psi).

In addition to powder temperature and velocity, a third very important factor is the extent of reaction of the powder particles with process gases or surrounding environmental gases (e.g., air) during the deposition process. With normal plasma spraying in air, the extent of oxidation of the powder particles is a function of the specific torch design, operating parameters, and standoff. Extensive oxidation of metallic and carbide powders can result in drastic reduction in coating density, cohesive strength, and bond strength with concomitant changes in performance. Such oxidation can be virtually eliminated by either effective gas shrouding of the effluent or spraying in a reduced-pressure, inert gas chamber.

Thermal spray done in an inert atmosphere and/or low-pressure chamber has become a widely accepted practice, particularly in the aircraft engine industry. Inert-atmosphere, low-pressure plasma spray systems have proven to be an effective means for applying complex, hot corrosion-resistant coatings of the Ni-Co-Cr-Al-Y type to high-temperature aircraft engine components without oxidation of the highly reactive constituents. Simple inert-atmosphere chamber spraying can also be used to confine hazardous materials. Hazardous materials are grouped into two categories: toxic and pyrophoric. Toxic materials include beryllium and its alloys. Pyrophoric materials include magnesium, titanium, lithium, sodium, and zirconium, which tend to burn readily when in a finely divided form or when purified by the plasma process.

A simple inert-atmosphere chamber spray system may include a jacketed, water-cooled chamber, an air lock, a plasma system, workpiece handling equipment, glove ports, a vacuum pumping system, and an inert gas backfill manifold. Usually, the chamber is pumped down to a pressure of 0.001 to 0.01 Pa (10^{-4} to 10^{-5} torr), then backfilled with high-purity dry argon. In any good inert-gas chamber, oxygen levels can be easily maintained below 30 ppm. Some metal powders tend to "clean up" when sprayed in an inert-gas chamber by the reduction of surface oxides. By the same mechanism, some oxide powders tend to be partially reduced when sprayed in an inert-gas chamber.

Inert-atmosphere spraying in a low-pressure chamber offers several unique advantages over conventional plasma spraying in an inert atmosphere at atmospheric pressure. Because of the lower pressure, the plasma gas stream temperature and velocity profiles are extended to greater distances, so the coating properties are less sensitive to standoff. In addition, the substrate can be preheated without oxidation. This allows better control of residual stress and better bond strengths. Deposition efficiency can be increased because of increased particle dwell time in the longer heating zone of the plasma and higher substrate temperature. The closed system also minimizes environmental problems such as dust and noise.

Figure 6 shows a typical inert-atmosphere and/or low-pressure plasma chamber. Normal operating procedures require that the spray chamber be pumped down to quite low pressures, as noted above, or be repeatedly cycled after pumping to approximately 55 Pa (0.4 torr) and then be backfilled with inert gas to about 40 kPa (300 torr). Once the system has been sufficiently purged to achieve an acceptable inert atmosphere, the plasma spray operation is activated and the chamber pressure is adjusted to the desired level for spraying. The entire spray operation is accomplished in a soft vacuum of approximately 6700 Pa (50 torr). The optimum spray condition exists when the plasma temperature at the substrate approximates the melting point of the powder particles; however, the optimum spraying conditions will vary with the chemistry and particle size of each spray material. These variables are similar to those of conventional plasma spraying. Because of the complexity of low-pressure spraying, the entire process is best controlled by computer to ensure complete reproducibility and uniformity throughout the coating. Productivity can be increased by using load/lock prepumping and venting chambers and robotics.

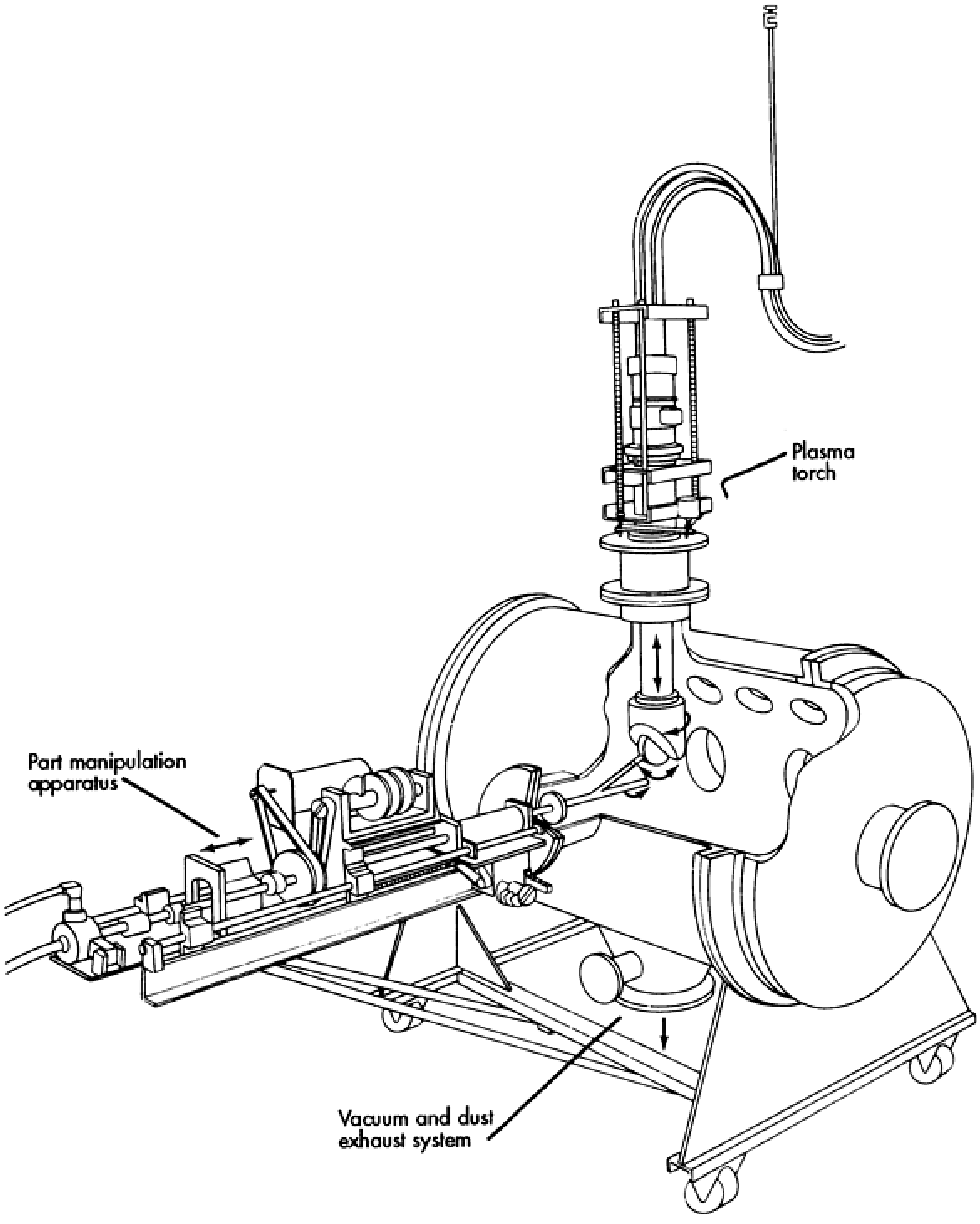


Fig. 6 Typical inert-atmosphere and/or low-pressure plasma chamber. Courtesy of Metco, Inc.

The complex low-pressure plasma spraying process is not required for all applications. Plasma spray using an inert-gas shroud around the plasma gas effluent can be just as effective in preventing oxidation during deposition as spraying in an inert-gas, low-pressure chamber. It has been used extensively to spray Ni-Co-Cr-Al-Y alloys on turbine blades, vanes, and outer air seals, and thermal barriers as an undercoat. Compared to chamber spraying, it has much lower capital costs but greater sensitivity to standoff. It is difficult to preheat the substrate to high temperatures without oxidizing the substrate, a technique used with low-pressure chamber spray to control the residual stress in some high-temperature, oxidation-resistant coatings. However, residual stress in these coatings can nonetheless be controlled when using inert-gas shrouding through control of deposition rates, auxiliary cooling, and so forth.

Plasma spray can be used to produce coatings of virtually any metallic, cermet, or ceramic material. The coatings are used for most of the types of applications described in a subsequent section.

The transferred plasma-arc process adds to plasma spray the capability of substrate surface heating and melting. Figure 7 is a schematic representation of the process. A secondary arc current is established through the plasma and substrate that controls surface melting and depth of penetration. Several advantages result from this direct heating: metallurgical bonding, high-density coatings, high deposition rates, and high thicknesses per pass. Coating thicknesses of 0.50 to 6.35 mm (0.020 to 0.250 in.) and widths up to 32 mm (1.25 in.) can be made in a single pass at powder feed rates of 9 kg/h (20 lb/h). In addition, less electrical power is required than with nontransferred arc processes. For example, for an 88% tungsten carbide, 12% Co material, plasma spray deposition 0.30 mm (0.012 in.) thick and 9.50 mm (0.375 in.) in width might require 24 passes at 40 to 60 kW to achieve maximum coating properties. This same material can be applied, using the transferred plasma-arc process, in one pass at approximately 2.5 kW.

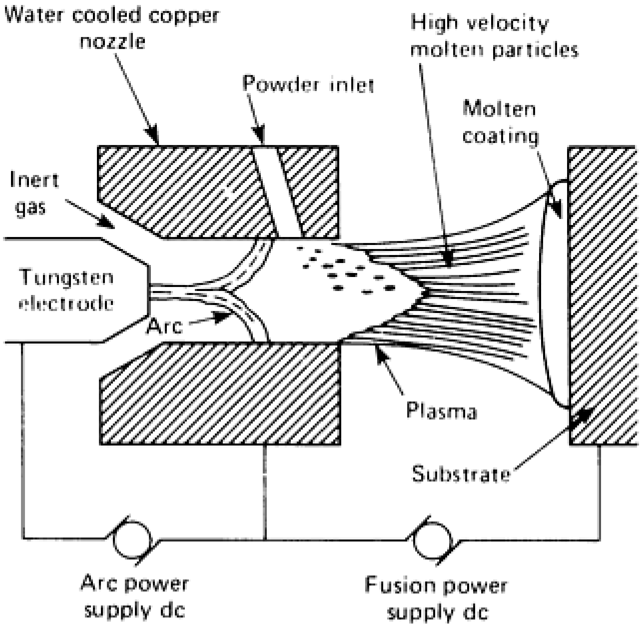


Fig. 7 Transferred plasma-arc spraying

The method of heating and heat transfer in the transferred plasma-arc process eliminates many of the problems related to using powders with wide particle size distributions or large particle sizes. Larger-particle-size powders, for example in the 50-mesh range, tend to be less expensive than closely classified 325-mesh powders.

Some limitations of the process should be considered for any potential application. Because substrate heating is a part of the process, some alteration of its microstructure is inevitable. Applications are also limited to substrates that are electrically conductive and can withstand some melting. The transferred plasma-arc process is used in hardfacing applications such as valve seats, plowshares, oil field components, and mining machinery.

High-Velocity Oxyfuel. A schematic of a high-velocity oxyfuel (HVOF) device is shown in Fig. 8. Fuel, usually propane, propylene, MAPP, or hydrogen, is mixed with oxygen and burned in a chamber. In other cases, liquid kerosene may be used as a fuel and air as the oxidizer. The products of the combustion are allowed to expand through a nozzle where the gas velocities may become supersonic. Powder is introduced, usually axially, in the nozzle and is heated and accelerated. The powder is usually fully or partially melted and achieves velocities of up to about 550 m/s. Because the powder is exposed to the products of combustion, they may be melted in either an oxidizing or reducing environment, and significant oxidation of metallics and carbides is possible.

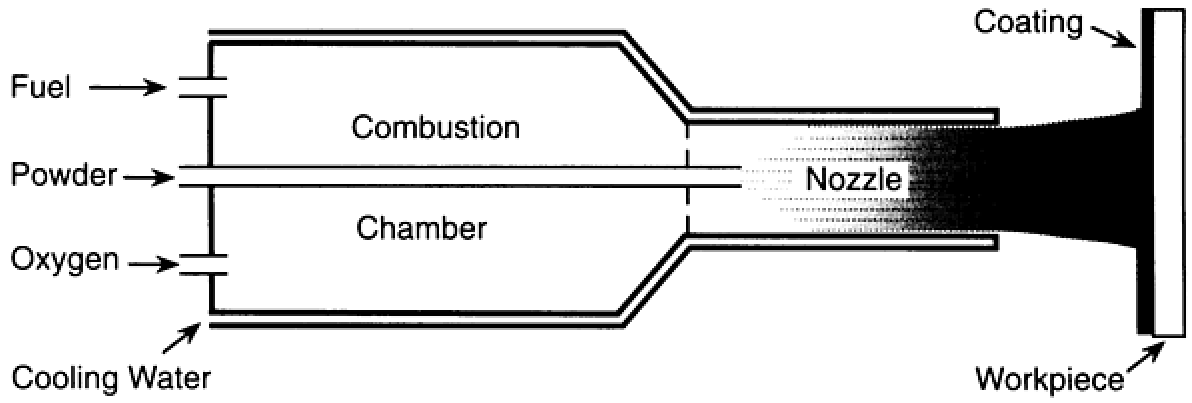


Fig. 8 High-velocity oxyfuel process. Courtesy of Praxair Surface Technologies, Inc.

With appropriate equipment, operating parameters, and choice of powder, coatings with high density and with bond strengths frequently exceeding 69 MPa (10,000 psi) can be achieved. Coating thicknesses are usually in the range of 0.05 to 0.50 mm (0.002 to 0.020 in.), but substantially thicker coatings can occasionally be used when necessary with some materials.

HVOF processes can produce coatings of virtually any metallic or cermet material and, for some HVOF processes, most ceramics. Those few HVOF systems that use acetylene as a fuel are necessary to apply the highest-melting-point ceramics such as zirconia or some carbides. HVOF coatings have primarily been used for wear resistance to date, but their field of applications is expanding.

Detonation Gun. In the detonation gun process, shown schematically in Fig. 9, a mixture of oxygen and acetylene, along with a pulse of powder, is introduced into a barrel and detonated using a spark. The high-temperature, high-pressure detonation wave moving down the barrel heats the powder particles to their melting points or above and accelerates them to a velocity of about 750 m/s. By changing the fuel gas and some other parameters, the Super D-Gun process achieves velocities of about 1000 m/s. This is a cyclic process, and after each detonation the barrel is purged with nitrogen and the process is repeated at up to about 10 times per second. Instead of a continuous swath of coating as in the other thermal spray processes, a circle of coating about 25 mm (1 in.) in diameter and a few micrometers thick is deposited with each detonation. A uniform coating thickness on the part is achieved by precisely overlapping the circles of coating in many layers. Typical coating thicknesses are in the range of 0.05 to 0.50 mm (0.002 to 0.02 in.), but thinner and much thicker coatings can be used.

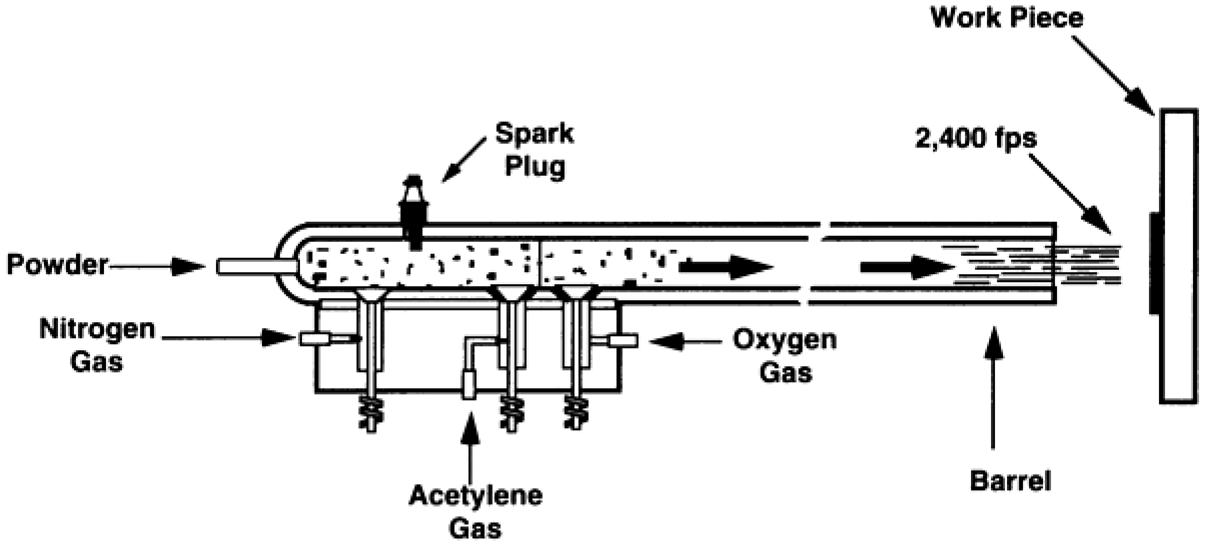


Fig. 9 Detonation gun process. Courtesy of Praxair Surface Technologies, Inc.

The detonation gun coatings have some of the highest bond strengths (usually exceeding the epoxy strength of the test, that is, 69 MPa) and lowest porosities (usually less than 2% when measured metallographically) of the thermal spray coatings. They have been the benchmark against which the other coatings have been measured for years. Careful control of the gases used generally results in little oxidation of metallics or carbides. The extremely high velocities and consequent kinetic energy of the particles in the Super D-Gun process allow most of the coatings to be deposited with residual compressive stress, rather than tensile stress as is typical of most of the other thermal spray coatings. This is particularly important relative to coating thickness limitations and the effect of the coating on the fatigue properties of the substrate.

Virtually all metallic, ceramic, and cermet materials can be deposited using detonation gun deposition. Detonation gun coatings are used extensively for wear and corrosion resistance as well as for many other types of applications. They are frequently specified for the most demanding applications, but often can be also the most economical choice because of their long life.

Process Comparison. A comparison of some of the characteristics of the major thermal spray processes is given in Table 2.

Table 2 Comparison of typical thermal spray processes

Process	Materials	Feed material	Surface preparation	Substrate temperature		Particle velocity	
				°C	°F	m/s	ft/s
Powder flame spray	Metallic, ceramic, and fusible coatings	Powder	Grit blasting or rough threading	105-160	225-325	65-130	200-400
Wire flame spray	Metallic coatings	Wire	Grit blasting or rough threading	95-135	200-275	230-295	700-900
Ceramic rod spray	Ceramic and cermet coatings	Rod	Grit blasting	95-135	200-275	260-360	800-1100
Two-wire electric-arc	Metallic coatings	Wire	Grit blasting or rough threading	50-120	125-250	240	800
Nontransferred arc plasma	Metallic, ceramic, plastics, and compounds	Powder	Grit blasting or rough threading	95-120	200-250	240-560	800-1850
High-velocity oxyfuel	Metallic, cermet, some ceramic	Powder	Grit blasting	95-150	225-300	100-550	325-1800
Detonation gun	Metallic, cermet, and ceramic	Powder	Grit blasting or as-machined	95-150	225-300	730-790	2400-2600
Super D-Gun	Metallic, cermet, and ceramic	Powder	Grit blasting or as-machined	95-150	225-300	850-1000	2800-3300

Transferred arc plasma	Metallic fusible coatings	Powder	Light grit blasting or chemical cleaning	Fuses base metal	Fuses base metal	490	1600

Ancillary Equipment. All thermal spray processes depend on the accurate control of gas flows, electric power, and powder, wire, or rod feedrates. A variety of equipment is available to do this, but it is essential for the best quality control of the coatings produced that all of this equipment be accurately calibrated, not only when it is initially installed, but also on a periodic basis thereafter. In addition, all of the plumbing for gases and water cooling, both internal to the torch or gun and external, must be checked to ensure that it is leak-tight.

Computer control of the more advanced thermal spray processes is being developed. On-line monitoring with closed-loop feedback control of electrical power, gas flows, cooling water flow and temperature, and powder feed rates are all possible. Although a variety of real-time coating thickness measurement techniques have been evaluated, most have been unsuccessful. The best technique currently seems to be that of accurate, reproducible deposition rate.

While some thermal spray devices are handheld, the only way to ensure uniform deposits is to automate the coating process to accurately control the rate of traverse of the gun or torch relative to the part being coated. This not only provides a uniform deposition of coating mass per unit area per unit of time, but also provides an accurate overlap between passes and uniform thermal input to the part. (Obviously this control is only meaningful if it is coupled with a uniform spray rate, which in turn requires uniform material flow and power to the torch or gun.) One of the simplest and most commonly used methods of automation for cylindrical parts is to rotate the part in a lathe-type machine and traverse the torch on what would correspond to the tool post. Small parts can be mounted on a circular plate and rotated on the lathe as an annular plate. Large, flat parts can be coated using a traversing two-axis machine. More complex shapes can be coated using robotics.

Surface Preparation

To ensure adequate bonding of thermal spray coatings, it is critical that a substrate be properly prepared. Surfaces must be clean, and usually substrates must be roughened after cleaning by grit blasting or some other means. Of course, the surface must remain uncontaminated by lubricants from handling equipment or body oils from hands and arms after it is prepared. It is recommended that the prepared surface be coated as soon as possible after preparation to prevent the possibility of contamination or surface oxidation.

Cleaning and Degreasing. Rust or other corrosion products; oils, grease, or other lubricants; paint; or other surface contaminants must be removed before coating deposition is begun. They can be removed by scraping, wire brushing, machining, grit blasting, or chemical action. Care should be taken not to embed scale and the like in the surface when trying to remove it, particularly when using grit blasting. Solvent degreasing has been the most common method for removal of lubricants and body oils, most conveniently with vapor degreasers. Large parts, and parts with attached hardware that may be damaged by vapor degreasing, should be degreased manually using the least hazardous material available. All solvents should be used only in well-ventilated areas, by properly protected personnel who are trained in their use and who follow local regulations for the use, care, and handling of solvents. More recently there has been a trend toward the use of aqueous detergents and alkaline cleaners, sometimes with ultrasonic agitation, to avoid the hazards and environmental concerns of organic solvents. Additional information is available in the Section "Surface Cleaning" in this Volume.

Surface Roughening. Three methods of surface roughening for thermal spray are widely used: rough threading, grit blasting, and a combination of rough threading followed by grit blasting. Rough threading is generally used for cylindrical surfaces and with thick flame sprayed coatings. The part to be prepared is mounted in a lathe and a single thread cut is taken. Tools for this purpose have a 60° to 70° point with a slight negative back rake. Screw feeds are approximately 0.80 to 1.25 mm (0.032 to 0.050 in.) or 0.78 to 1.26 threads/mm (20 to 32 threads/in.). The depth of the cut should vary with the screw feed and the required coating thickness. This technique is obviously limited to substrate sections thick enough to support the machining without significantly reducing its strength. It is most frequently used with flame sprayed coatings and is not recommended for thin coatings. Higher bond strengths are obtained when threading is followed by grit blasting. When the use of cutting fluid is necessary for threading, the part must be degreased before grit blasting or coating.

Grit blasting equipment used for thermal spray should not be used for other purposes, because dirt, paint, and lubricants contaminating the grit can be redeposited on the grit blasted surfaces. The grit should be continuously reclassified to remove fines. The air supply to the grit blast equipment must be clean and dry (including oil and particle filtration).

Aluminum oxide and chilled iron are the most widely used abrasive grits for thermal spray surface preparation. However, sand, crushed steel, and silicon carbide are also used in some situations. Sand is commonly used on large exterior structures such as bridges, towers, and piping where recovery of the grit is impractical. Crushed steel grit, obtained commercially in hardnesses to 65 HRC, is used in preparing some steels. Silicon carbide is used for some special applications (e.g., for very hard substrates or to minimize contamination), but it is relatively expensive, breaks down quickly, and tends to embed in softer substrates.

Consideration should be given to the substrate material in the selection of grit type. Traces of residual grit may adversely affect some coatings. Chemical compatibility in the finished coating system must be considered. Alumina, sand, and especially silicon carbide may embed in softer metals such as aluminum, copper, and their alloys. For these metals, lower air pressures are recommended to minimize embedding. Chilled iron or crushed steel should be used in preparing surfaces to be flame sprayed and fused. Alumina, silica, or silicon carbide may inhibit bonding of some of these coatings.

Practical grit size ranges are -10/+30 mesh, -14/+40 mesh, and -30/+80 mesh. Surface roughness is primarily the result of grit particle size, so the selection of the grit size is determined, in part, by the roughness required for adequate bonding and may be limited by coating thickness. Table 3 gives general recommendations for grit size selection. Surface roughness can also be varied slightly by air pressure. This factor should be considered on an individual basis for each combination of grit size, type, and substrate material. Grit blasting air pressure varies from 210 to 620 kPa (30 to 90 psi), with standoff or working distances of 50 to 150 mm (2 to 6 in.). Grit blast nozzle openings are generally 6 to 10 mm (0.25 to 0.375 in.) in diameter. The grit blasting angle to the substrate should be about 90°. Excessive grit blasting should be avoided to minimize grit inclusion in the surface.

Table 3 Recommended grit sizes for preparation of surfaces to be thermal spray coated

Roughness	Grit size, mesh	Sieve openings		Applications
		mm	in.	
Coarse	-10/+30	2.007/0.610	0.079/0.024	For coatings exceeding 0.25 mm (0.010 in.) and best adherence
Medium	-14/+40	1.422/0.432	0.056/0.017	For fair adherence and smoother finishes of coatings less than 0.25 mm (0.010 in.) thick
Fine	-30/+80	0.610/0.175	0.024/0.007	For smoothest finishes on coatings less than 0.25 mm (0.010 in.) thick to be used

The substrate should be cleaned following grit blasting to remove residual dust. Clean, dry air may be used. Again, it is very important that the surface remain uncontaminated by lubricants from handling equipment or body oils from hands and arms. It is recommended that the prepared surface be coated as soon as possible after preparation to prevent surface oxidation or contamination.

Finishing Treatment

Sealing. Thermal spray coatings usually have a structure with inherent porosity that ranges from less than 2 to more than 15 vol%, depending on the process by which the coating is deposited and the material sprayed. At least some of this porosity is interconnected. In many applications, coatings are exposed to corrosive fluids (liquids or gases) or hydraulic fluids that can infiltrate the pores, resulting in fluid leakage or corrosion throughout the coating or of the base material. These conditions can contribute to the premature failure of the coating. Many such applications, therefore, require the coating to be sealed before finishing. Sealing a coating may also help to reduce particle pullout from the surface during finishing for coatings with low cohesive strength.

To ensure as complete a sealing of the coating as possible, it is necessary to apply the sealant material as soon after coating as possible and prior to surface finishing. Sealant materials such as waxes, epoxies, phenolics, and inorganics are readily available and easily applied. The wax sealants are useful in preventing infiltration of liquids at low service temperatures. Resin-based sealants may be effective at temperatures up to about 260 °C (500 °F). Some silicone-based sealants have been reported to provide effective protection in salt spray tests conducted in accordance with military standards up to 480 °C (900 °F). Epoxy and phenolic sealants are usually more effective on coatings with higher porosity within their limits of stability (up to about 300 °C, or 570 °F).

One of the most effective methods of sealing coating porosity is vacuum impregnation. This method will usually fill all interconnected pores open to the exterior surface. To vacuum impregnate, the part is immersed in the sealant and placed in a vacuum chamber, and a soft vacuum is drawn. When the vacuum is released, air pressure forces the sealant into the pores. Most applications do not require this procedure, however. Low-viscosity anaerobic sealers may also be particularly penetrating. The depth of penetration of some sealants may exceed 1.8 mm (0.070 in.). Regardless of the method or type of sealant used, pores or interconnected channels that are not connected to the exterior surface cannot be sealed and machining or wear in service may open these with consequent loss of corrosion protection.

Coating Finishing. Although thermal spray coatings are used with their surfaces in the as-deposited condition for some applications, these surfaces are too rough for most service conditions. Therefore they are usually finished by methods such as grinding, lapping, polishing, machining, abrasive brushing, or vibratory finishing. Although the techniques are common to those used for finishing solid metallics and ceramics, great care must be taken not to damage the coatings, causing excessive surface porosity due to pullout of coating particles or cracking due to thermal stresses. The ultimate surface finish that can be achieved with a thermal spray coating is a function not only of its composition, but also of the deposition parameters used to produce it, because they are largely responsible for the amount and size of the true porosity in the coating and the cohesive strength or particle-to-particle bonding within the coating. The best finish that can be achieved may vary, therefore, from a matte surface with a roughness of about 1 μm (40 μin.) R_a and pits exceeding 0.05 mm (0.002 in.) in diameter for a flame-sprayed coating to a virtually pit-free mirror finish with a roughness of less than 0.025 μm (1 μin.) R_a for some very-high-velocity coatings.

If a coating is to be sealed, the sealing should be done before any finishing operation. It is extremely difficult to remove finishing fluids and debris from an unsealed surface, and these will interfere with the sealing. Sealing may also help to prevent the embedment of finishing debris in a surface, which would cause abrasive wear in service.

Some of the softer metallic coatings can be machined with single-point high-speed tool steels. Better surface finishes can be achieved with carbide or coated carbide tools. Table 4 includes typical parameters for machining some classes of metallic coatings. Usually, lower infeeds are used than with wrought materials. Figure 10 shows the configuration of typical carbide and steel tools. Burnishing is occasionally used with soft materials such as tin, zinc, and babbitt to produce a smooth, dense bearing surface.

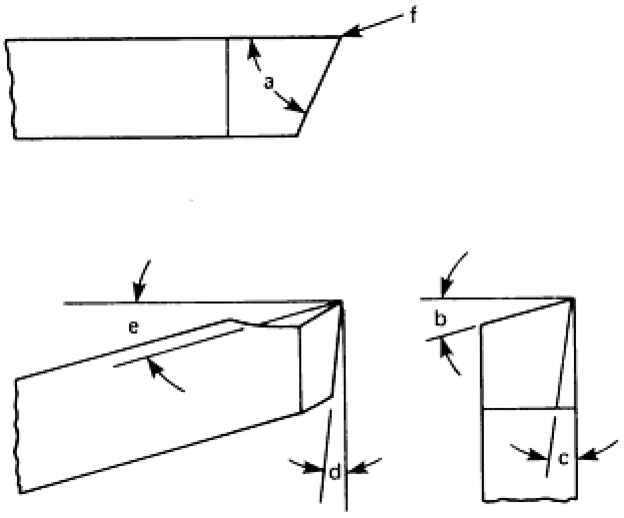
Table 4 Typical ranges of speeds and feeds used in machining thermal sprayed metal coatings

Coating metal	High-speed steel tool				Carbide tool[a]			
	Speed		Feed		Speed		Feed	
	m/s	sfm	mm/rev	in./rev	m/s	sfm	mm/rev	in./rev
Steels								
Low-carbon, medium-carbon, low-alloy	0.25-0.50	50-100	0.075-0.125	0.003-0.005	0.25-0.50	50-100	0.075-0.125	0.003-0.005
High-carbon, stainless	. . .	. . .	. . .	. . .	0.15-0.200	30-40	0.075-0.100	0.003-0.004

Nonferrous metals								
Brass, bronze, nickel, copper, Monel	0.50-0.75	100-150	0.075-0.125	0.003-0.005	1.25-1.80	250-350	0.050-0.150	0.002-0.006
Lead, tin, zinc, aluminum, babbitt	0.75-1.00	150-200	0.075-0.175	0.003-0.007	1.25-1.80[b]	250-350[b]	0.050-0.100	0.002-0.004[b]

(a) Composition: 6% Co, 94% WC.

(b) Aluminum only



Dimension	Carbide	High-speed metal
a	65-90°	80°
b	0°	0 to 15°
c	7°	10°
d	7° max	7° max
e	0-8° max	15° max
f	0.79375 mm	0762-1.016 mm

	(0.03125 in.)	(0.030-0.040 in.)

Fig. 10 Recommended shapes for carbide and high-speed steel cutting tools used in machining sprayed metal coatings

Cermet and ceramic coatings require grinding, and many metallic coatings can be more effectively ground than single-point machined. Some coatings can be ground with oxide or silicon carbide wheels, but cubic boron nitride or diamond wheels may be necessary for some of the hardest coatings, and they are frequently more cost-effective and produce better finishes for many other coatings. Specific grinding wheel selection is important and varies with the coating composition and type. It is probably best to consult with wheel manufacturers for specific coatings. Some guidelines for diamond grinding:

1. Check diamond wheel specifications. (a) Use only 100 concentration. (b) Use only resinoid bond.
2. Make sure your equipment is in good mechanical condition. (a) Machine spindle must run true. (b) Backup plate must be square to the spindle. (c) Gibs and ways must be tight and true.
3. Balance and true the diamond wheel on its own mount--0.005 mm (0.0002 in.) maximum runout.
4. Check peripheral wheel speed--25 to 33 m/s (5000 to 6500 sfm).
5. Use a flood coolant--water plus 1 to 2% water-soluble oil of neutral pH. (a) Direct coolant toward point of contact of the wheel and the workpiece. (b) Filter the coolant.
6. Before grinding each part, clean wheel with minimum use of a silicon carbide stick.
7. Maintain proper infeeds and crossfeeds. (a) Do not exceed 0.01 mm (0.0005 in.) infeed per pass. (b) Do not exceed 2.03 mm (0.080 in.) crossfeed per pass on revolution.
8. Never spark out--stop grinding after last pass.
9. Maintain a free-cutting wheel by frequent cleaning with a silicon carbide stick.
10. Clean parts after grinding. (a) Rinse in clean water, then dry. (b) Apply a neutral-pH rust inhibitor to prevent atmospheric corrosion.
11. Visually compare the part at 50× with a control sample of known quality.

Regardless of the type of grinding wheel used, the wheel should be dressed frequently enough, and operating parameters should be chosen, to ensure clean cutting of the coating. Sparkout passes (passes with low contact pressure run until virtually no contact is being made) should never be used. The smeared material created by such a procedure can be easily dislodged in service and cause abrasive wear and other problems.

If grinding does not produce a sufficiently smooth surface, it may be necessary to lap the coating after grinding. Again, it is advisable to consult the manufacturers of lapping materials for specific recommendations. Some guidelines:

1. Use a hard lap.
2. Use a serrated lap.
3. Use recommended diamond abrasives--Bureau of Standards No. 1, 3, 6, or 9.
4. Embed the diamond firmly into the lap.
5. Use a thin lubricant such as mineral spirits.
6. Maintain lapping pressures of 0.14 to 0.17 MPa (20 to 25 psi) when possible.
7. Maintain low lapping speeds of 0.5 to 1.5 m/s (100 to 300 sfm).
8. Recharge the lap only when lapping time increases 50% or more.
9. Clean parts after grinding and between changes to different-grade diamond laps--use ultrasonic cleaning if possible.
10. Visually compare the part at 50× with a control sample of known quality.

In addition to the traditional finishing techniques discussed above, a variety of other methods have been developed, particularly for nondimensional finishing. These include various abrasive brushes, belt grinding, "super" finishing,

peening, and vibratory techniques. The use of nondimensional finishing is usually possible only when the dimensional specifications for the part are very loose, or when the part can be precisely and accurately preground and the deposition thickness and other characteristics such as waviness can be tightly controlled.

Coating Repair. The repair of thermal spray coatings by coating over service-worn or in-process damaged coatings is not generally recommended, even if the predeposited coating is reference ground, cleaned, and grit blasted. Adequate bond strength between the coating layers is seldom achieved, and there are no reliable nondestructive test techniques currently available to verify an adequately bonded interface. Therefore, the preferred procedure is to strip the existing coating and apply a completely new coating. Note that when applying a multilayered coating, it is best to apply each new layer over the as-deposited surface of the previous layer, not to grind and grit blast between layers.

Quality Assurance

There are few, if any, nondestructive evaluations that can be performed on a final coating, so the assurance of the quality of thermal spray coatings is more dependent on process control than on inspection of the final coating. This implies, of course, that the equipment used must be accurately and precisely produced and assembled, that all gages, flow meters, and the like must be calibrated, that the powders or other feed-stocks must be tightly controlled, and that standard procedures and operating parameters must be developed and followed for each coating. To ensure that the process is in control, it is common practice to coat a small sample using a standard set of parameters (standoff, traverse rate, angle of deposition, etc.) for metallographic examination of the coating before coating a part. The cross section of the coating sample is compared with standards to ensure that its microstructure, and usually its microhardness, are within acceptable ranges.

It should be kept in mind that the microstructure, hardness, and other properties of the coating on a small metallographic sample may not be the same as those of the coating on a part because of differences in standoff, angle of impingement, masking effects, cooling, and so on. Thus the evaluation of the coating on the metallographic sample only ensures that the process is in control. However, this, in turn, should ensure that the coating on the part will perform as it has in the past on the same part in the same environment, if the other deposition parameters, such as setup, traverse speed, and cooling, are unchanged.

Other features of a coating that must be controlled include finished surface characteristics and part dimensions. Standard techniques are adequate for these purposes. There is growing recognition that the average roughness of a surface may not be an adequate characterization of its fitness for service, and that other parameters, such as bearing area, peak-to-valley, skewness, and kurtosis, may need to be specified. Areas of coating coverage, including areas of optional overspray, must be specified and controlled in addition to dimensions such as diameters or thicknesses.

Metallography is usually done on cross sections of small samples coated under standard setup conditions of standoff, angle of deposition, traverse rate, and so on. These samples, if appropriately sized, may be mounted for examination directly, or, if too large, sectioned using abrasive cutoff saws. Some recommendations for cutting are found in Table 5. Standard mounting and polishing techniques may be used, but special precautions should be taken to ensure minimal damage to the coatings and as accurate and reproducible a representation of the structure as possible. It is fairly easy to induce cracking and pullout of the coating using overly aggressive cutting, grinding, and polishing techniques. It is also very important to minimize edge rounding of the coating, because the coating being examined is usually only about 0.25 mm (0.010 in.) thick. The major manufacturers of metallographic consumables and equipment have taken an interest in the metallography of thermal spray coatings in recent years and can provide useful recommendations for mounting and polishing. A substantial amount of training and skill is necessary to be able to grind and polish thermal spray coatings properly and reproducibly by hand. It is therefore recommended that automated polishing equipment be used following procedures established for each coating. A few guidelines are listed in Tables 6, 7, and 8.

Table 5 Guidelines for abrasive cutting of thermal spray coatings

Parameter	Notes
Wheel selection	

Abrasive	
Al_2O_3	To cut ferrous substrates
SiC	To cut nonferrous and ceramic
Diamond	Fine, precise cuts on small samples
Bond	
Rubber	General use, long life
Resin	Dry cutting
Combination	Wet cutting of hard materials
Grit size	
Coarse	Rough cuts, fast
Fine	Precise cuts, slow
Fixturing	
Direction of cut	Coating in compression
Clamps	Both sides of cut
Blocking	Wooden to protect coating
Coolant	Flood if possible
Cutting speed and pressure	Adjusted to prevent heating of part

Table 6 Typical metallographic preparation procedure for metallic and cermet thermal spray coatings using silicon carbide grinding paper

Number of specimens, 1-6; specimen size, 32 mm (1 $\frac{1}{4}$ in.); cutting equipment, universal cutoff saw with an Al_2O_3 thin wheel; mounting equipment, vacuum impregnation unit; mounting resin, fast-curing epoxy cold mount; holder, 32 mm (1 $\frac{1}{4}$ in.) plate; automated grinding-polishing machine

Process step	Disk or cloth	Abrasive	Grit or grain size	Abrasive dosing	Speed, rpm	Load per specimen, N	Lubricant/ dosing	Time, s
Grinding								
Planar grinding	Paper	SiC	220	. . .	150	25	Water	Until plane
Fine grinding								
Step 1	Paper	SiC	320	. . .	150	25	Water	30-45
Step 2	Paper	SiC	500	. . .	150	25	Water	30-45
Step 3	Paper	SiC	1200	. . .	150	25	Water	30-45
Polishing								
Diamond polishing	Hard polishing cloth	Spray diamond	3 µm	4	150	25	Low-viscosity alcohol-base lubricant/5	5-10 min
Final polishing	Soft, chemical-resistant cloth	Alumina polishing suspension	0.04 µm	10	150	10	. . .	30-60

Source: Struers

Table 7 Typical metallographic preparation procedure for metallic and cermet thermal spray coatings using an advanced diamond grinding format

Number of specimens, 1-6; specimen size, 32 mm ($1\frac{1}{4}$ in.); cutting equipment, universal cutoff saw with an Al_2O_3 thin wheel; mounting equipment, vacuum impregnation unit; mounting resin, fast-curing epoxy cold mount; holder, 32 mm ($1\frac{1}{4}$ in.) plate

Process step	Disk or cloth	Abrasive	Grit or grain size	Abrasive dosing	Speed, rpm	Load per specimen, N	Lubricant/ dosing	Time, min
Grinding								
Planar grinding	Paper	SiC	220	. . .	150	25	Water	Until plane

Fine grinding	Very hard polishing cloth	Spray diamond	9 µm	4	150	25	Alcohol-base lubricant/6	5
Polishing								
Diamond polishing	Hard polishing cloth	Spray diamond	3 µm	4	150	25	Low-viscosity alcohol-base lubricant/5	5-10
Final polishing	Soft, chemical-resistant cloth	Alumina polishing suspension	0.04 µm	10	150	10	. . .	$\frac{1}{2}$-1

Source: Struers

Table 8 Typical metallographic preparation procedure for tungsten carbide-cobalt thermal spray coatings

Specimens sectioned using a precision cutting saw with a diamond wafering blade and mounted using a pressure-cooled mounting press and edge-retention molding compound; specimen size 32 mm (1 $\frac{1}{4}$ in.); no etchant used after polishing

Process step	**Grinding/ polishing surface**	**Abrasive**	**Abrasive grain size, µm**	**Time min**	**Force per sample, lb**	**Speed, rpm**	**Relative rotation**	**Dispensing sequence**
Planar grinding	Very hard grinding platen	Diamond suspension	45	2 or until plane	5	240	Against	1 s spray on; 30 s spray off
Fine grinding								
Step 1	Medium-hard grinding platen	Diamond suspension	9	5	5	120	Same	1 s spray on; 30 s spray off
Step 2	Hard cloth	Diamond suspension	3	1.5	5	120	Same	1 s spray on; 30s spray off
Final polishing	Hard cloth	High-purity alumina-base mild attack polishing suspension	. . .	1.5	10	120	Against	. . .

Source: Buehler Ltd.

The microstructural features frequently examined include compositional phases, porosity, and oxide inclusions. These may be determined quantitatively by comparison with photographic standards or by standard metallographic techniques including point counting, line segment measurement, or optical electronic analysis techniques. Most of these analyses use light microscopes; however, scanning electron microscopes can be used if necessary.

Porosity is one of the more frequently specified parameters, but it is probably one of the most difficult to accurately determine metallographically. A distinction should always be made between absolute porosity and metallographically

apparent porosity. Some porosity may be too small to be visible using light microscopy, or the amount of porosity on the surface may be more or less than the absolute bulk porosity because of pullout of coating or because polishing debris fills some real porosity. Thus, metallographic porosity standards or specifications can only have meaning if very reproducible grinding and polishing procedures are used.

The same considerations apply to other metallographic characterizations, although they may be somewhat less sensitive to preparation. The identification of the various phases present in a coating can be enhanced using standard etching techniques or optical enhancement, such as differential interference or polarized lighting. The use of advanced scanning electron microscopy techniques may minimize the need for these techniques.

Hardness Testing. Both surface and cross-sectional hardness measurements can be used for the quality control of coatings. If surface hardness measurements (e.g., Rockwell hardness measurements) are used, the thickness of the coating and the hardness of the substrate must be high enough to ensure that an accurate measurement is achieved. Microhardness measurements on cross sections are used more often than surface hardness measurements for the quality control of thermal spray coatings.

The guidelines of the ASTM recommended practices should be followed, regardless of the type of test used. The coating must be thick enough to support the indentation for the load chosen, and particular attention should be paid to the positioning of the indentations. Statistically valid procedures should be followed. These include calibration of the hardness tester, confirmation of the operator's skill using frequent measurement of standard test blocks, the proper placement of indentations, and an adequate number of indentations. All of these should be monitored using control charts and other statistical quality control tools. A greater number of measurements may be needed than with wrought materials because of the greater inhomogeneities in the microstructures of most thermal spray coatings.

Bond Strength Testing. A variety of tests have been developed to measure both the tensile and shear strength of thermal spray coatings. The most commonly used test is defined by ASTM C 633, "Standard Test Method for Adhesion or Cohesive Strength of Flame-Sprayed Coatings," which measures the strength in tension perpendicular to the surface. In this test, a 25.4 mm (1 in.) diameter cylinder is coated on one end and then bonded to a mating cylinder, usually with epoxy. The couple is then pulled apart using a tensile testing machine. ASTM C 633 calls for a coating thickness of 0.45 mm (0.018 in.) to prevent penetration of the coating by the bonding agent. This may be necessary for some flame-sprayed coatings, but it is much thicker than necessary for the denser plasma, HVOF, or detonation gun coatings. A thickness of 0.25 mm (0.010 in.) is frequently used for the denser coatings, because it is closer to the thicknesses used in service and provides a more realistic measure of strength in light of the residual stresses that may be present in the coatings. The ASTM procedure should be referred to for dimensional and alignment requirements as well as specific preparation, coating, bonding, and testing procedures.

For the ASTM C 633 test to have practical meaning in a given application, the coated cylinder must be of the same or a very similar material and of the same hardness as the part, must be prepared in the same manner (e.g., grit blasted with the same grit at the same pressure and angle), and must be coated with the same deposition parameters (i.e., coated at the same angle, standoff, and traverse rate) as the part. This test is limited by the strength of the epoxy or other bonding agent used, currently a maximum of approximately 69 MPa (10 ksi). Most detonation gun coatings, many HVOF coatings, and a few plasma coatings exceed this, so the test is simply a proof test and not a measure of the actual bond or cohesive strength of the coating.

While a few lap shear and bend tests have been used to qualify coatings for specific applications, none is universally recognized. All of the known tests of this type have significant theoretical limitations, making interpretations of the results difficult. Because few applications place a coating in tension perpendicular to the surface, the value of the ASTM C 633 test is limited as well.

Health, Safety, and Environmental Concerns

There are some health, safety, and environmental concerns associated with thermal spray coating processes, as with most industrial processes. In general they are similar to those associated with welding processes. Obviously, all plant or laboratory, local, state, and federal government directives should be followed. None of the thermal spray processes should be attempted without proper training of all of the personnel involved and careful consideration of any hazards associated with the particular materials being used to prepare for or produce the coating. Proper care and maintenance of the equipment, including all gas and electric lines, will greatly reduce any hazards. In addition, design and procedure reviews

for safety by qualified engineers are advisable. These should include the ancillary processes of surface preparation, part handling, and finishing as well as the coating process itself.

Dust and Fumes. All thermal spray processes produce dust and fumes, so operators must be protected and the dust and fumes collected. When possible, the coating process should be conducted in a cubicle equipped with ventilation and dust collection equipment and with the operators outside. Each thermal spray process has its own airflow requirement to provide adequate ventilation, and the equipment manufacturer should be able to provide guidelines. Nonetheless, dust monitors should be periodically used to ensure that the ventilation system is working properly. If the operators must be in the cubicle or the coating must be done in the open, the operators should wear respirators. It is no longer considered adequate to rely only on air flow away from the operator to provide adequate protection. The type of respirator used depends on the material being deposited. The effluent from the dust collection system should be periodically monitored to ensure compliance with all regulations.

Noise generated by thermal spray processes ranges from about 80 dB for some of the flame spray processes to over 120 dB for some of the HVOF processes, over 140 dB for some plasma spray processes, and to over 150 dB for the detonation gun processes. Individual ear protection is adequate for the former, but the latter must be operated in sound-reducing cubicles. Sound levels at the operator's position should be measured and compliance with all regulations ensured. In addition, all personnel in the vicinity of the spray operation should have their hearing checked periodically.

Light Radiation. The spectrum of light emitted by the thermal spray devices ranges from the far infrared to extreme ultraviolet. Adequate eye and skin protection must be used. Shade 5 lenses may be sufficient for some flame spray processes, but shade 12 is required for plasma spray and electric (wire) arc. Fire-retardant, closely woven fabrics should be worn to protect the skin from burns. Burns can be caused by heated particles bouncing from the substrate, hot gases, or light. Ultraviolet radiation will burn exposed skin and penetrate loosely woven fabrics, causing burns similar to a severe sunburn in minutes.

Coating Structures and Properties

Coating Microstructures. Thermal spray coatings consist of many layers of thin, overlapping, essentially lamellar particles, frequently called splats. Cross sections of several typical coatings are shown in Fig. 2, 11, 12, 13, and 14. Generally, the higher-particle-velocity coating processes produce the densest and better bonded coatings, both cohesively (splat-to-splat) and adhesively (coating-to-substrate). Metallographically estimated porosities for detonation gun coatings and some HVOF coatings are less than 2%, whereas most plasma sprayed coating porosities are in the range of 5 to 15%. The porosities of flame sprayed coatings may exceed 15%.

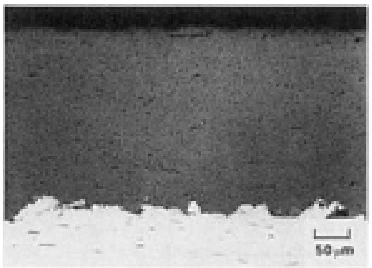


Fig. 11 Microstructure of plasma-sprayed chromium oxide. As-polished

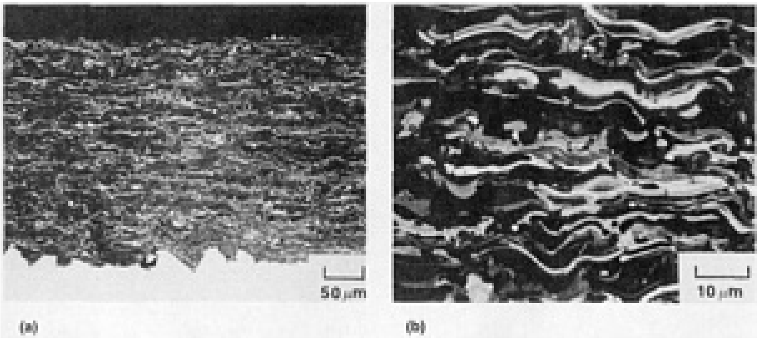


Fig. 12 Microstructure of detonation gun deposited alumina and titania. As-polished

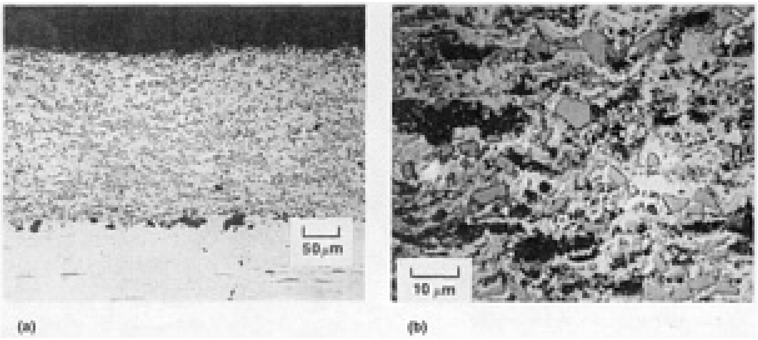


Fig. 13 Microstructure of a detonation gun deposited tungsten carbide/cobalt cermet coating. (a) As-polished. (b) Etched

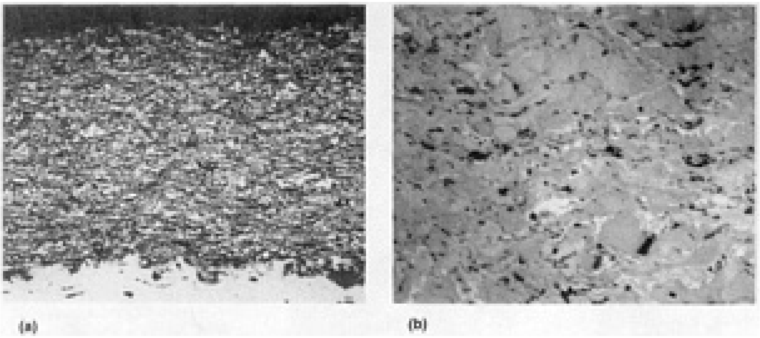


Fig. 14 Microstructure of a mechanically mixed chromium carbide/nickel chromium cermet coating. (a) As-polished.(b) Etched

The extent of oxidation that occurs during the deposition process is a function of the material being deposited, the method of deposition, and the specific deposition process. Oxidation may occur because of the oxidizing potential of the fuel-gas mixture in flame spraying, HVOF, or detonation gun deposition or because of air inspirated into the gas stream in plasma spraying or any of the other methods. Recall that the latter cause can be ameliorated by using inert-gas shrouds or low-pressure chambers with plasma spraying. Using carbon-rich gas mixtures with oxyfuel processes can cause carburization rather than oxidation with some metallic coatings. Metallic coatings are probably most susceptible to oxidation, but carbide coatings may suffer a substantial loss of carbon that is not particularly obvious in metallographic examination. Oxidation during deposition can lead to higher porosity and generally weaker coatings, and it is usually considered to be undesirable.

Most of the thermal spray processes lead to very rapid quenching of the particles on impact. Quench rates have been estimated to be 10^4 to 10^6 °C/s for ceramics and 10^6 to 10^8 °C/s for metallics. As a result, the materials deposited may be in thermodynamically metastable states, and the grains within the splats may be submicron-size or even amorphous. The metastable phases present may not have the expected characteristics, particularly corrosion characteristics, of the material, and this factor should be kept in mind in the selection of coating compositions.

The mechanical properties of thermal spray coatings are not well documented with the exception of their hardness and bond strength. These are discussed in the section "Quality Assurance" in this article. The sensitivity of the properties of the coatings to specific deposition parameters makes universal cataloging of properties by simple chemical composition and general process (e.g., WC-12Co by plasma spray) virtually meaningless. The situation is even more complex because the properties of coatings on test specimens may differ somewhat from those on parts because of differences in geometry and thermal conditions. Nonetheless, coatings made by competent suppliers using adequate quality control will be quite reproducible, and therefore the measurement of various mechanical properties of these standardized coatings may be very useful in the selection of coatings for specific applications. Properties that may be of value include the modulus of rupture, modulus of elasticity, and strain-to-fracture in addition to hardness. Examples of some of these are given in Table 9.

Table 9 Mechanical properties of representative plasma, detonation, and high-velocity combustion coatings

Parameter	**Type of coating Tungsten-carbide-cobalt**				**Alumina**	
Nominal composition, wt%	W-7Co-4C	W-9Co-5C	W-11Co-4C	W-14Co-4C	Al_2O_3	Al_2O_3
Thermal spray process	Detonation gun	High-velocity combustion	Plasma	Detonation gun	Detonation gun	Plasma
Rupture modulus, 10^3 psi[a]	72	. . .	30	120	22	17
Elastic modulus, 10^6 psi[a]	23	. . .	11	25	14	7.9
Hardness, kg/mm^2, HV_{300}	1300	1125	850	1075	>1000	>700
Bond strength, 10^3 psi[c]	>10,000[b]	>10,000[b]	>6500	>10,000	>10,000[b]	>6500

Source: Publication 1G191, National Association of Corrosion Engineers

(a) Compression of freestanding rings of coatings.

(b) Epoxy failure.

(c) ASTM C 633-89, "Standard Test Method for Adhesion or Cohesive Strength of Flame-Sprayed Coatings," ASTM, 1989.

Any measurement or use of mechanical properties must take into account the anisotropic nature of the coating microstructure and hence its properties (i.e., the coating properties are different parallel to the surface than perpendicular to the surface because of the lamellar nature of the microstructure). Most mechanical properties are measured parallel to the surface, in part because it is easier to produce test specimens in this plane because the coatings are typically thin. Unfortunately, the major load in service is usually perpendicular to the surface. This does not, however, make measurements in the plane of the coating useless. It is frequently important to know, for example, how much strain can be

imposed on a coating due to extension or deflection of the part without cracking the coating. Cracks in a coating may not only affect its performance, but also initiate cracks and fatigue failures in the part.

Uses of Thermal Spray Coatings

Wear Resistance. One of the most important uses of thermal spray coatings is for wear resistance. They are used to resist virtually all forms of wear, including abrasive, erosive, and adhesive, in virtually every type of industry. The materials used range from soft metals to hard metal alloys to carbide-based cermets to oxides. Generally, the wear resistance of the coatings increases with their density and cohesive strength, so the higher-velocity coatings such as HVOF and particularly detonation gun coatings provide the greatest wear resistance for a given composition.

A variety of laboratory tests have been developed to rank thermal spray coatings and compare them with other materials. Examples of abrasive and erosive wear data are shown in Tables 10 and 11. It should be kept in mind that laboratory tests can seldom duplicate service conditions. Therefore these tests should only be used to help select candidate coatings for evaluation in service. Only rarely, with good baseline data, can any precise prediction of wear life in service be made from laboratory data.

Table 10 Abrasive wear data for selected thermal spray coatings

Material	Type	Wear rate, mm^3/1000 rev
Carballoy 883	Sintered	1.2
WC-Co	Detonation gun	0.8
WC-Co	Plasma spray	16.0
WC-Co	Super D-Gun	0.7
WC-Co	High-velocity oxyfuel	0.9

ASTM G 65 dry sand/rubber wheel test, 50/70 mesh Ottawa silica, 200 rpm, 30 lb load, 3000-revolution test duration

Table 11 Erosive wear data for selected thermal spray coatings

Material	Type	Wear rate,µm/g
Carballoy 883	Sintered	0.04
WC-Co	Detonation gun	1.3
WC-Co	Plasma spray	4.6
AISI 1018 steel	Wrought	21

Silica-based erosion test; particle size, 15 µm; particle velocity, 139 m/s; particle flow, 5.5 g/min, ASTM Recommended Practice G 75

Friction Control. Thermal spray coatings are used in some applications to provide specific frictional characteristics to a surface, covering the full spectrum from low friction to high. Obviously, the surface topography is critical in these applications, and unique finishing techniques have been developed to provide the desired coefficient of friction without causing excessive wear or damage of the mating surface. The textile industry provides, as an example, applications covering the complete range of friction characteristics and surface topography to handle very abrasive synthetic fiber. Oxide coatings such as alumina are usually used with surfaces that vary from very smooth to nodular to quite rough, depending on the coefficient of friction required.

Corrosion Resistance. Flame sprayed aluminum and zinc coatings are frequently used for corrosion resistance on bridges, ships, and other structures. In this application, reliance is placed primarily on their anodic protection of the substrate. Other thermal spray coatings are used for their corrosion resistance, often coupled with their wear resistance, but the inherent porosity of the coatings must be taken into account and the coatings sealed, either by using an epoxy or other infiltrant or by sintering, as in the case of the M-Cr-Al-Y coatings. These aspects are discussed in the section "Processes" in this article.

Dimensional Restoration. Thermal spray coatings are often used to restore the dimensions of a worn part. On occasion, a coating with low residual stress and/or low cost is used to build up the worn area and then a thin, more wear-resistant coating is applied over it. In any use of thermal spray coatings for buildup, it should be kept in mind that the properties of the coating are probably far different than those of the substrate, and that the coating will not add any structural strength to the part. In fact, if care is not taken, the coating may degrade the fatigue strength of the part.

Thermal Applications. Plasma spray coatings, and to a more limited extent other thermal spray coatings, are used as thermal barriers. In particular, partially stabilized zirconia coatings are used on gas-turbine combustors, shrouds, and vanes and on internal combustion cylinders and valves to improve efficiency and reduce metal temperatures or cooling requirements. In other applications they may be used to dissipate heat as either surface conductors or thermal emitters. Because of their unique lamellar microstructure and porosity, the thermal conductivity of thermal spray coatings is usually anisotropic and significantly less than that of their wrought or sintered counterparts.

Electrical Applications. As with thermal properties, the electrical conductivity of thermal spray materials is anisotropic and is reduced compared to their wrought or sintered counterparts due to their lamellar microstructure and porosity. Metallic or conductive cermet coatings are, however, used as electrical conductors where wear resistance must be combined with electrical conductivity. Conversely, thermal spray oxide coatings are used as electrical insulators. In this application, it is usually important to seal the coating to prevent moisture, even from the air, from penetrating the coating and reducing its insulating capability. Thermal spray coatings have also been used to produce high-temperature thermocouples and strain gages. Electromagnetic or radio-frequency shielding can also be provided by flame or electric-arc sprayed layers of zinc, tin, or other metals.

Other Applications. A variety of other applications have been developed for thermal spray coatings, including coatings used as nuclear moderators, catalytic surfaces, and parting films for hot isostatic presses. Thermal spray materials can also be used to produce freestanding components such as rocket nozzles, crucibles, and molds.

Chemical Vapor Deposition of Nonsemiconductor Materials

Hugh O. Pierson, Consultant

Introduction

CHEMICAL VAPOR DEPOSITION (CVD) is a versatile process that can be used to deposit layers of nearly any metal, as well as nonmetallic elements, such as carbon and silicon (Ref 1). Compounds such as carbides, nitrides, oxides, intermetallics, and many others also can be deposited. This technology has become very important in these applications:

- Semiconductor and other electronic component manufacturing processes
- Coatings on tools, bearings, and other wear-resistant parts
- Optical, opto-electronic, and corrosion-resisting products
- Monolithic parts, ultrafine powders, and high-strength fibers

This article emphasizes the CVD of hard, tribological, and high-temperature coatings, as well as free-standing structures.

Reference

1. H.O. Pierson, *Handbook of Chemical Vapor Deposition,* Noyes Publications, 1992

Principles of Chemical Vapor Deposition

The CVD process can be defined as the deposition of a solid on a heated surface via a chemical reaction from the vapor or gas phase. It belongs to the class of vapor-transport processes that are atomistic in nature, that is, the deposition species are atoms or molecules, or a combination thereof. Other vapor-transport processes include the physical vapor deposition (PVD) techniques, such as vacuum, evaporation, sputtering, ion plating, ion-beam assist, arc, and ion implantation, which are described in other articles in this Section of the Volume, as well as in Ref 2. Unlike CVD processes, the PVD processes do not rely on a chemical reaction in the gas phase to form the product that will be deposited.

Although CVD competes directly with PVD, an important recent trend is the merging of these two techniques. For instance, CVD now makes extensive use of plasma (a physical phenomenon), whereas PVD is often carried out in a chemical environment (reactive evaporation and reactive sputtering). Likewise, CVD and PVD operations are often processed in the same integrated equipment in a sequential fashion without breaking the vacuum (thus minimizing contamination), and the distinction between the two basic processes becomes blurred (Ref 3).

CVD Reactions. The numerous chemical reactions used in CVD include thermal decomposition (pyrolysis), reduction, hydrolysis, disproportionation, oxidation, carburization, and nitridation. These reactions can take place either singly or in combination. Descriptions of certain reactions are provided in the section "Typical CVD Materials and Reactions" in this article.

A CVD reaction is controlled by these factors:

- Thermodynamic, mass transport, and kinetic considerations
- Chemistry of the reaction
- Processing parameters of temperature, pressure, and chemical activity

In most cases, a theoretical analysis of these factors is a recommended preliminary step. Such an analysis can predict the reaction mechanism (i.e., the path of the reaction as it forms the deposit), the resulting composition of the deposit (i.e., its stoichiometry), and the structure of the deposit (i.e., the geometric arrangement of its atoms). This analysis may then provide guidelines for choosing the appropriate CVD parameters, thereby avoiding a strictly empirical approach to the desired product. Computer programs are available to facilitate these studies (Ref 4, 5).

However, when a reaction is kinetically controlled, and when only one single condensed phase can form, the theoretical thermodynamic modeling of a CVD reaction has very limited applicability. It is becoming more evident that a useful modeling approach requires an examination of the chemical equilibrium aspects of the reaction, as well as the fluid dynamic aspects of the reactor system, to improve process efficiency. Many computational fluid-dynamic codes are now being used to design reactors that maximize the possible yields from a given reaction. These codes account for the reaction rate theory, thermodynamic equilibrium aspects, and the constraints imposed by the design of the deposition chamber. This means that one can design a complete CVD reactor on a computer workstation, change parameters to model fluid flow, velocity, and temperature profiles, and optimize deposition rates, *instead of* building the equipment and then using trial-and-error methods to optimize the process.

References cited in this section

2. K.K. Shuegraf, Ed., *Handbook of Thin Film Deposition Processes and Techniques,* Noyes Publications, 1988

3. M.E. Bader et al., Integrated Processing Equipment, *Solid State Technology,* May 1990, p 149-154

4. Outokumpu AT Computer Program, Outokumpu Research OY PO 60 SF 28101, Pori, Finland, 1992

5. T.M. Besmann, "SOLGASMIX-PV: A Computer Program to Calculate Equilibrium Relationships in Complex Chemical Systems," TM-5775, Oak Ridge National Laboratory, 1977

CVD Processes and Equipment

Like all chemical reactions, CVD reactions require activation energy to proceed. This energy can be provided, in practice, by several methods. Thermal activation is the original process, and it is still the major method for the chemical vapor deposition of metals and ceramics.

In thermal CVD, the reaction is activated by high temperature, generally above 900 °C (1650 °F) (Ref 6). A typical thermal CVD apparatus consists of three interrelated components: the reactant-gas supply system; the deposition chamber, or reactor; and the exhaust system (Fig. 1). A fourth component that is often used is a closed-loop process-control monitor, which is now available in a PC-based design.

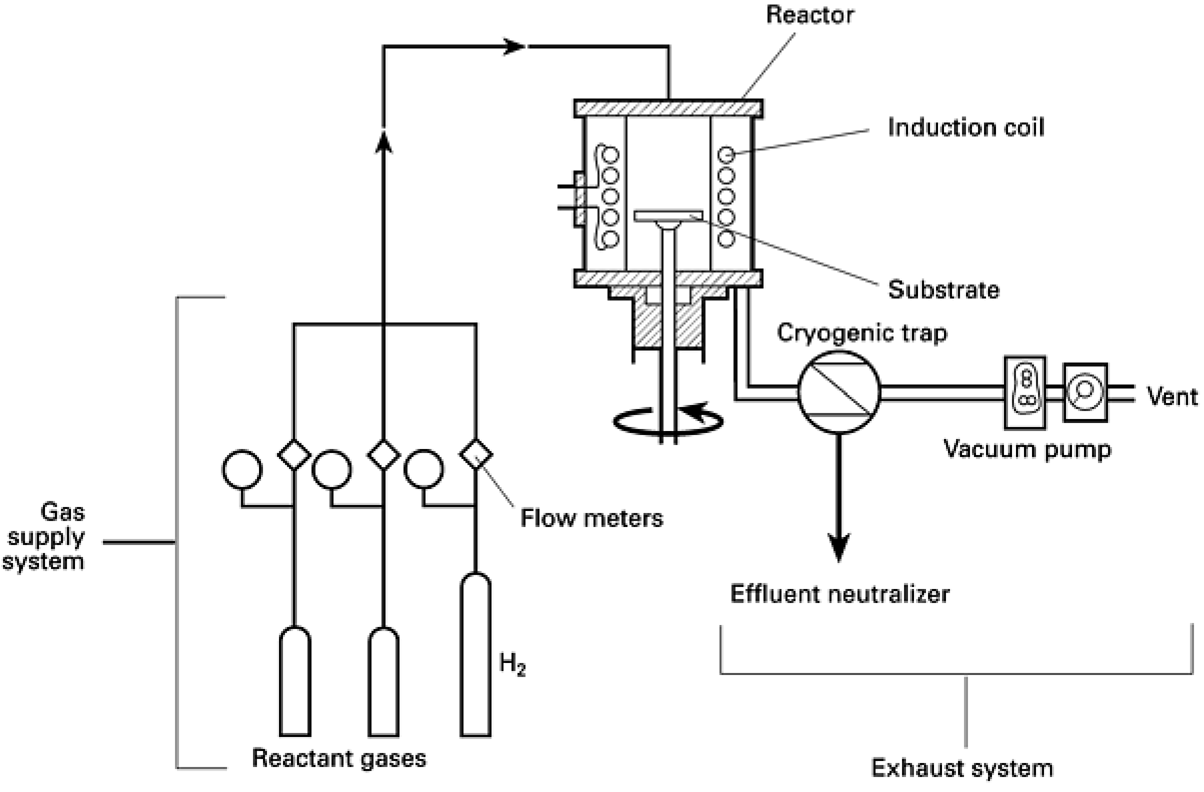


Fig. 1 Thermal CVD reactor

Plasma CVD is a method that operates at lower temperatures than thermal CVD. The reaction is activated by a plasma at temperatures between 300 and 700 °C (570 to 1290 °F). The process was developed because the high deposition temperature of thermal CVD precludes the use of many substrates, such as low-melting-point metals; materials that undergo solid-state phase transformation over the range of deposition temperatures; polymers; and others. In addition, large mismatches in the thermal expansion of a substrate and a coating will generate stresses that can lead to cracking and delamination or spalling during cooling (Ref 7, 8). In the plasma CVD process, the stress that is due to thermal-expansion mismatch is reduced, and temperature-sensitive substrates can be more readily coated. Table 1 compares the deposition temperatures for thermal and plasma CVD for several commercially important coatings.

Table 1 Typical deposition temperatures for thermal and plasma chemical vapor deposition

Material	Deposition temperature

	Thermal CVD		Plasma CVD	
	°C	**°F**	**°C**	**°F**
Silicon nitride	900	1650	300	570
Silicon dioxide	800-1100	1470-2010	300	570
Titanium carbide	900-1100	1650-2010	500	930
Titanium nitride	900-1100	1650-2010	500	930
Tungsten carbide	1000	1830	325-525	615-975

Plasma CVD was initially developed in the 1960s for use in the semiconductor industry, but applications have been expanding ever since and are now common in the nonsemiconductor applications discussed in this article. Most plasma CVD systems use radio frequency (RF) with operating frequencies of 450 KHz or 113.56 MHz. A typical RF reactor with parallel electrodes is shown in Fig. 2. Microwave glow discharge is also used at a standard frequency of 2.45 GHz.

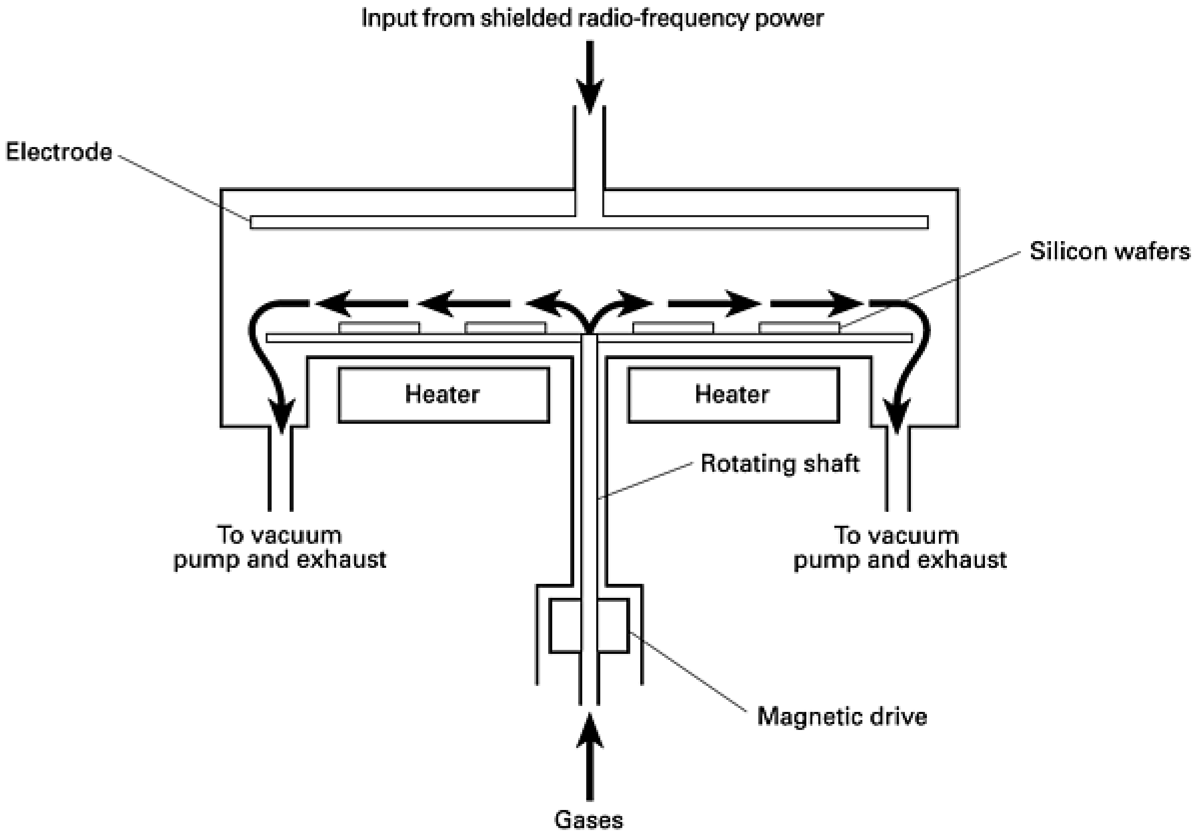


Fig. 2 Radio-frequency plasma CVD reactor configured for deposition on silicon wafers

A recent and promising development in the production of plasma is based on electron cyclotron resonance (ECR) and the proper combination of an electric field and a magnetic field (Ref 9). Cyclotron resonance is achieved when the frequency

of the alternating electric field matches the natural frequency of the electrons orbiting the lines of force of the magnetic field. An ECR plasma reactor is shown schematically in Fig. 3. ECR and other plasma techniques are used extensively in semiconductor production but so far have remained mostly experimental in other areas of application (Ref 10).

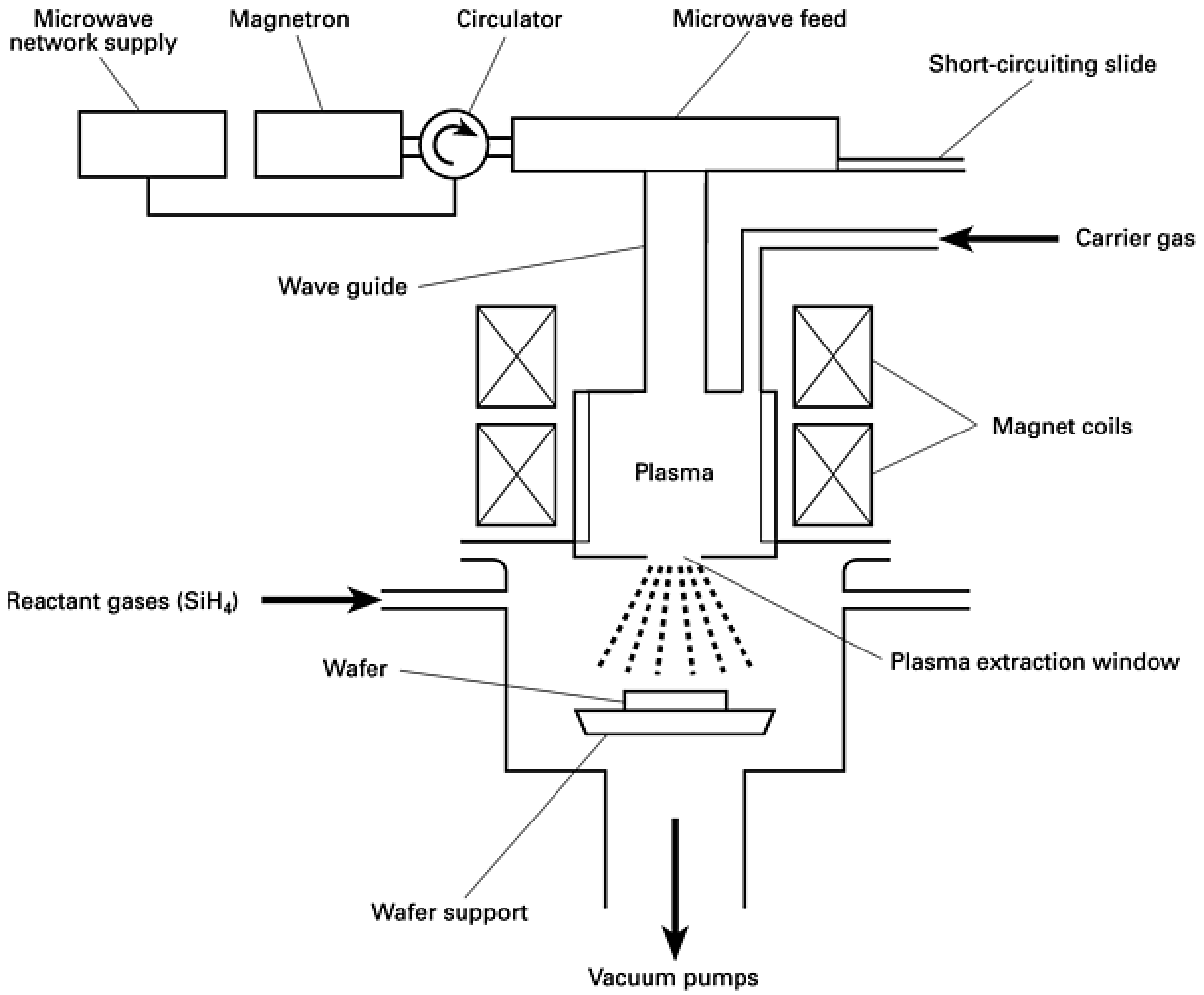


Fig. 3 Microwave/electron cyclotron resonance (ECR) plasma CVD reactor

Laser CVD. Two other activation methods based on a laser have recently been developed (Ref 8, 11). As of the mid-1990s, the thermal-laser and photo-laser CVD methods are still essentially in the experimental stage, but have great potential, at least in specialized areas. The materials that can be deposited include oxides, nitrides, tungsten, aluminum, and others.

Thermal-laser CVD (Ref 12), or laser pyrolysis, occurs when the laser thermal energy contacts and, thereby, heats an absorbing substrate. The wavelength of the laser can be such that little or no energy is absorbed by gas molecules. Because the substrate is locally heated, deposition is restricted to the heated area. Figure 4 illustrates the deposition of a thin stripe by moving a laser beam linearly across the substrate.

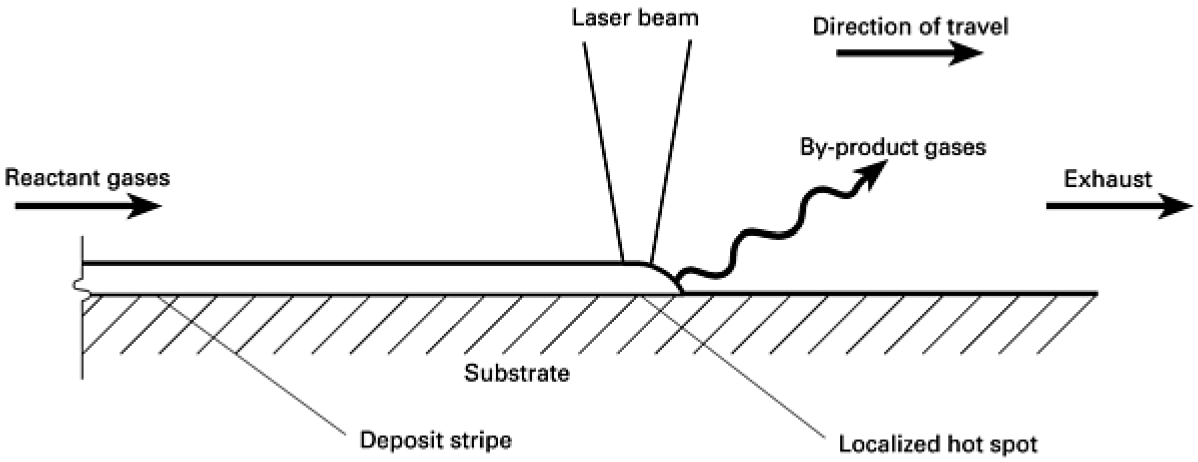


Fig. 4 Thermal-laser CVD growth mechanism

In photo-laser CVD, the chemical reaction is induced by the action of light, specifically ultraviolet (UV) radiation, which has sufficient photon energy to break the chemical bonds in the reactant molecules. In many cases, these molecules have a broad electronic absorption band and are readily excited by UV radiation. Although UV lamps have been used, more energy can be obtained from UV lasers, such as the excimer (e.g., excited dimer) lasers with photon energies ranging from 3.4 eV (XeFlaser) to 6.4 eV (ArFlaser). A typical photo-laser CVD system is shown in Fig. 5.

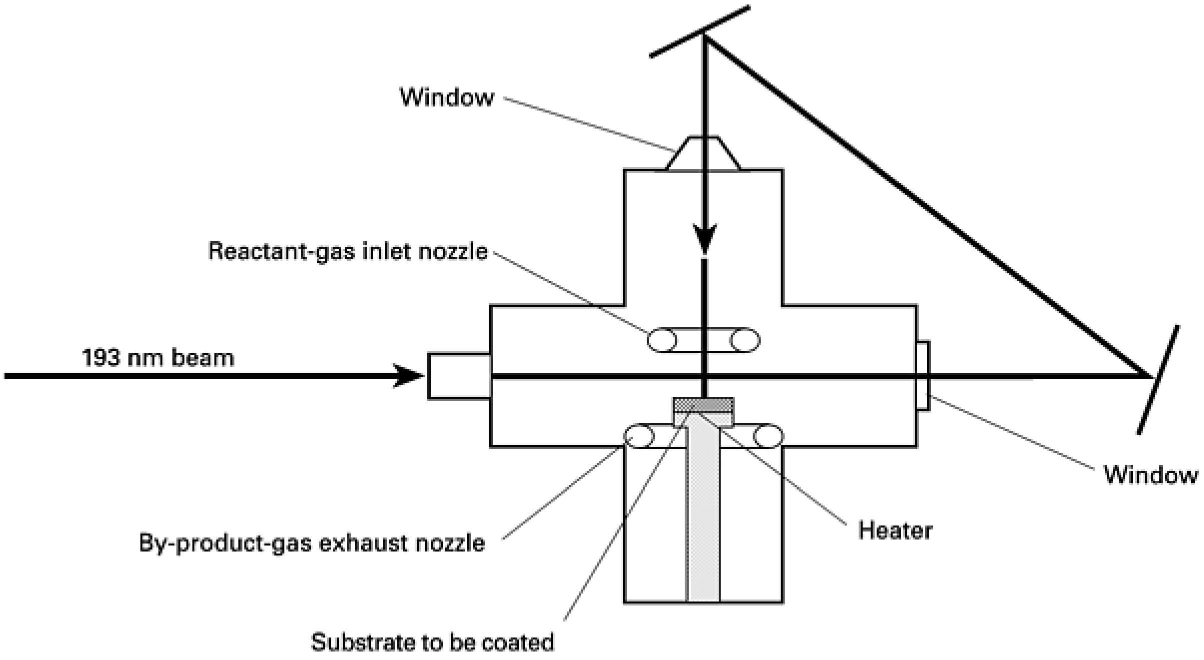


Fig. 5 Photo-laser CVD apparatus

Photo-laser CVD differs from thermal-laser CVD in that it does not require heat, because the reaction is photon-activated, and the deposition essentially occurs at room temperature. Moreover, there is no constraint on the type of substrate that can be used. It can be opaque, absorbent, transparent, or even temperature-sensitive.

A limitation of this method that has, to date, restricted its application is a slow deposition rate. If higher-power excimer lasers can be made more economical, then the process could compete with thermal CVD and thermal-laser CVD, particularly in critical applications where low temperature is essential.

Closed-Reactor CVD or Pack Cementation. The CVD systems described above use open reactors, in which reactants are introduced continuously and flow through the reactor (Ref 1). Another important system utilizes a closed reactor. The chemical vapor deposition in such a system is also known as pack cementation (Ref 13).

The entire process is carried out isothermally, because the driving mechanism for the reaction is not a difference in temperature, as in thermal CVD, but rather a difference in chemical activity between a metal in the free state and a metal in solution with another metal. A common reaction involves coating iron objects (such as turbine blades) with chromium, using chromium powder and ammonium iodide as reactants and aluminum oxide as an inert filler. Parts and chemicals are loaded in a molybdenum container that is then sealed, as shown schematically in Fig. 6. Pack cementation is a common industrial process with large-scale applications in chromizing, aluminizing, and siliconizing.

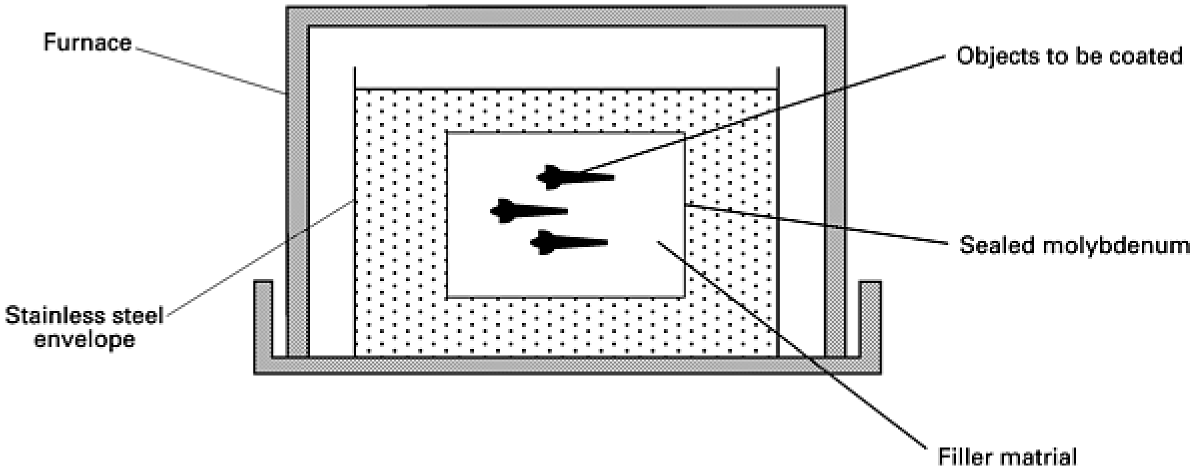


Fig. 6 Pack-cementation chromizing/siliconizing apparatus. Pack material composed of 3 wt% Cr, 11 wt% Si, 0.25 wt% NH_4I, and balance, Al_2O_3

Chemical vapor infiltration (CVI) refers to the particular CVD process in which gaseous reactants infiltrate a porous structure, such as an inorganic open foam or a fiber array. Deposition occurs on the foam or fiber, and the structure is gradually densified to form a composite (Ref 14).

In a typical CVI system (Fig. 7), both the gas inlet and substrate are water cooled, and only the top of the substrate is heated. Under pressure, the gaseous precursors enter the cool side of the substrate and flow through it to reach the hot zone, where the deposition reaction occurs.

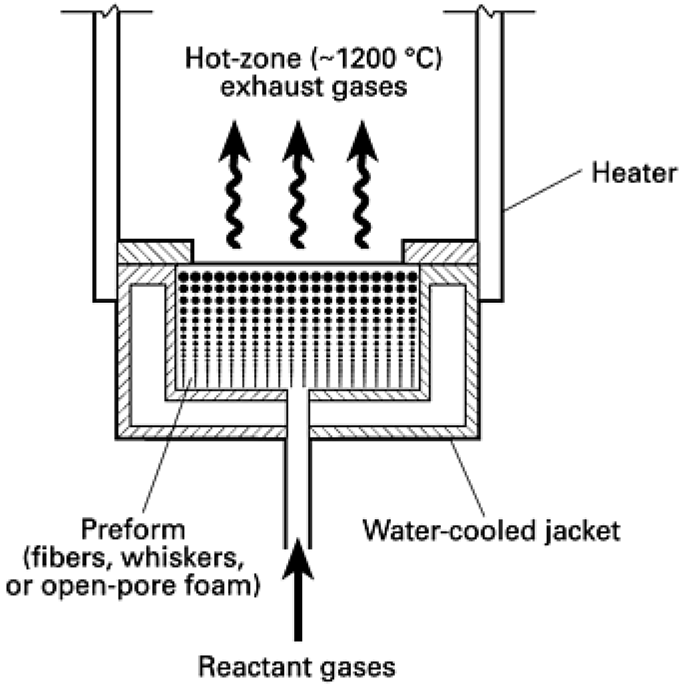


Fig. 7 Chemical vapor infiltration apparatus. Source: Ref 15

This process is used to produce high-strength silicon carbide and carbon-carbon composites, as well as other reinforced metal or ceramic composites. As contrasted with sintering, CVI does not require high pressure, and the processing temperatures are lower. As a result, mechanical and chemical damage to the substrate is minimized.

The major limitation of this method is the necessity for the interdiffusion of reactants and byproducts through relatively long and narrow channels. Chemical vapor infiltration is a slow process that can take several weeks. Full densification is nearly impossible to obtain because of the formation of closed porosity.

Metal-organic CVD (MOCVD) is a specialized process that utilizes organometallic compounds as precursors, usually in combination with hydrides or other reactants. Most MOCVD reactions occur at temperatures between 600 and 1000 °C (1110 and 1830 °F). When the most precise controls and high-purity gases are used, extremely thin deposits (<10 nm, or 0.4 μin.) with abrupt interfaces (<1 nm, or 0.04 μin.) can be produced. Because MOCVD equipment and chemicals are expensive and production costs are high, this method is considered most often when high performance is essential or when substrates are temperature sensitive.

The MOCVD method is being used extensively in microwave and optoelectronic applications, as discussed in detail in the article "Chemical Vapor Deposition of Semiconductor Materials" in this Section of the Volume. In addition, it is being introduced in wear and corrosion applications. An example of a nonsemiconductor application of MOCVD is the deposition of iridium via the decomposition of iridium acetylacetonate for oxidation protection (up to 2200 °C, or 3990 °F) of the maneuvering thruster nozzle of a spacecraft satellite (Ref 16). Additional information on the use of MOCVD in nonsemiconductor applications is provided in Ref 8.

References cited in this section

1. H.O. Pierson, *Handbook of Chemical Vapor Deposition,* Noyes Publications, 1992
6. T.M. Besmann et al., Chemical Vapor Deposition Techniques, *MRS Bulletin,* Nov 1988, p 45-50
7. P.K. Bachman, G. Gartner, and H. Lydtin, Plasma Assisted CVD Processes, *MRS Bulletin,* Dec 1988, p 51-59
8. D. Bhat, Techniques of Chemical Vapor Deposition, *Surface Modification Technologies--An Engineer's*

Guide, T. Sudarshan, Ed., Marcel Dekker, 1989

9. Y.Z. Hu, M. Li, J. Sunko, J. Andrews, and E. Irene, Characterization of Microwave ECR Plasma for Low Temperature Chemical Vapor Deposition, *Proc. 11th Int. Conf. on CVD,* K. Spears and G. Cullen, Ed., Electrochemical Society, 1990, p 166-172
10. R.F. Bunshah, Ed., *Handbook of Deposition Technologies for Films and Coatings,* 2nd ed., Noyes Publications, 1994
11. D. Bauerle, Laser Induced Chemical Vapor Deposition, *Laser Processing and Diagnostics,* D. Bauerle, Ed., Springer-Verlag, 1984
12. R. Solanki et al., Laser-Induced Chemical Vapor Deposition, *Solid State Technology,* Vol 28, June 1985, p 220-226
13. J.M. Blocher, Jr., Chemical Vapor Deposition, *Handbook of Deposition Technologies for Films and Coatings,* R.F. Bunshah, Ed., Noyes Publications, 1982
14. W.J. Lackey, Review, Status and Future of the CVI Process for Fabrication of Fiber-Reinforced Ceramic Composites, *Ceram. Eng. Sci. Proc.,* Vol 10 (No. 7-8), 1989, p 577-584
15. N. Tai and T. Chou, Modeling of an Improved Chemical Vapor Infiltration Process for Ceramic Composites Fabrication, *J. Am. Ceram. Soc.,* Vol 73 (No. 6), 1990, p 1489-1498
16. J.T. Harding, R.H. Tuffias, and R.B. Kaplan, "Oxidation Resistance of CVD Coatings," Technical Report 86-099, Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, CA, 1987

Typical CVD Materials and Reactions

A wide variety of materials can be produced by CVD but, as mentioned earlier, only the most important of those related to hard, tribological, and high-temperature coatings and to free-standing structures are reviewed here. The CVD of other materials is described in Ref 1 and 17.

The metals most often deposited by the CVD technique include molybdenum, nickel, rhenium, and tungsten.

Molybdenum (Ref 17, 18). The hydrogen reduction of the chloride is most commonly used to deposit molybdenum:

$$MoCl_6 + 3H_2 \rightarrow Mo + 6HCl$$

The reaction temperature ranges from 400 to 1350 °C (750 to 2460 °F). The best deposits are obtained at the high end of this range and at low pressure (<2.7 kPa, or 20 torr).

Another well-established reaction is the decomposition of the carbonyl:

$$Mo(CO)_6 \rightarrow Mo + 6CO$$

The reaction temperature ranges from 300 to 700 °C (570 to 1290 °F), and pressure ranges from approximately 0.13 to 101 kPa (1 to 760 torr) in a hydrogen atmosphere.

Nickel (Ref 19, 20). The decomposition of nickel carbonyl is the most frequently used reaction to deposit nickel:

$$Ni(CO)_4 \rightarrow Ni + 4CO$$

The reaction temperature ranges from 180 to 200 °C (355 to 390 °F), and the pressure can be as high as 101 kPa (760 torr). More ductile nickel is obtained at low deposition rates.

Rhenium (Ref 21, 22) is generally deposited by the hydrogen reduction of the fluoride:

$$ReF_6 + 3H_2 \rightarrow Re + 6HF$$

The reaction temperature ranges from 500 to 900 °C (930 to 1650 °F). The best deposits are obtained at 700 °C (1290 °F) and at low pressure (<2.7 kPa, or 20 torr).

Another common reaction is the pyrolysis of the chloride:

$$2ReCl_5 \rightarrow 2Re + 5Cl_2$$

The reaction temperature ranges from 1000 to 1250 °C (1830 to 2280 °F). The best deposits are obtained at low pressure (<2.7 kPa, or 20 torr). This reaction usually gives a more ductile and purer material than the reaction given in Eq 4, although a higher temperature is necessary.

Tungsten (Ref 23, 24, 25) is usually obtained by the hydrogen reduction of the halide:

$$WF_6 + 3H_2 \rightarrow W + 6HF$$

The reaction temperature ranges from 300 to 700 °C (570 to 1290 °F), and pressure ranges from 1.3 to 101 kPa (10 to 760 torr). Deposition at a lower temperature (500 °C, or 930 °F) gives a finer grain structure with high strength (83 MPa, or 12 ksi) than deposition at a high temperature (700 °C, or 1290 °F).

Another deposition reaction for tungsten is the hydrogen reduction of the chloride:

$$WCl_6 + 3H_2 \rightarrow W + 6HCl$$

The reaction temperature ranges from 900 to 1300 °C (1650 to 2370 °F), and the pressure ranges from 2.0 to 2.7 kPa (15 to 20 torr). This reaction, which yields high-purity deposits, is used to coat x-ray targets and to produce structural parts.

Graphite (Ref 26). The CVD of graphite, which is relatively simple, is obtained by the thermal decomposition of a hydrocarbon. The most common precursor is methane, which is generally pyrolyzed at 1100 °C (2010 °F) and at a pressure ranging from approximately 0.25 to 101 kPa (2 to 760 torr):

$$CH_4 \rightarrow C + 2H_2$$

Another common precursor is acetylene (C_2H_2), which decomposes at temperatures between 300 and 750 °C (570 and 1380 °F) and at pressures up to 101 kPa (760 torr) in the presence of a nickel catalyst. A third precursor is propylene (C_3H_6), which decomposes at temperatures between 1000 and 1400 °C (1830 and 2550 °F) and at low pressure (13 kPa, or 100 torr).

Diamond (Ref 26, 27, 28). The CVD of diamond requires the presence of atomic hydrogen, which selectively removes graphite and activates and stabilizes the diamond structure. To dissociate hydrogen requires a high-energy source. In addition to the need for atomic hydrogen, other factors, such as energy input and the presence of oxygen, have been shown to be important, as well.

The deposition mechanism is complex and not fully understood at this time. The basic reaction involves the decomposition of a hydrocarbon, such as methane:

$$CH_4 \rightarrow C(\text{diamond}) + 2H_2$$

The reaction can be activated by microwave plasma, thermal means (hot filament), or plasma arc.

Diamond-like carbon (DLC) represents a new form of carbon coating that is neither diamond nor graphite. A common deposition method is a high-frequency RF gas discharge (13.56 MHz) generated in a mixture of hydrogen and a hydrocarbon, such as methane (CH_4), *n*-butane (C_4H_{10}), or acetylene (C_2H_2).

The technology of CVD diamond and DLC has progressed considerably, and applications are reaching the production stage in electronics, optics, and tribology. Cutting tools coated with CVD diamond have performed remarkably well and should enter the market soon.

The deposition of ceramics usually involves titanium diboride, boron carbide, silicon carbide, titanium carbide, boron nitride, silicon nitride, titanium nitride, or alumina, each of which is described below.

Titanium diboride (Ref 29) is deposited by the hydrogen reduction of the halides. A typical reaction is:

$$TiCl_4 + 2BCl_3 + 5H_2 \rightarrow TiB_2 + 10HCl$$

The reaction temperature ranges from 800 to 1100 °C (1470 to 2010 °F), and the pressure ranges from approximately 0.25 to 101 kPa (2 to 760 torr) in a hydrogen atmosphere. Titanium diboride also can be deposited with diborane as the boron and hydrogen source in the same pressure range, but at a reaction temperature ranging from 600 to 1000 °C (1110 to 1830 °F):

$$TiCl_4 + B_2H_6 \rightarrow TiB_2 + 4HCl + H_2$$

Boron carbide (Ref 30) is commonly deposited by this reaction:

$$4BCl_3 + CH_4 + 4H_2 \rightarrow B_4C + 12HCl$$

The reaction temperature ranges from 1200 to 1400 °C (2190 to 2550 °F), and pressure ranges from 1.3 to 2.7 kPa (10 to 20 torr).

Boron carbide also is deposited from diborane in a plasma:

$$2B_2H_6 + CH_4 \rightarrow B_4C + 8H_2$$

The reaction temperature is typically 400 °C (750 °F).

Silicon carbide (Ref 31, 32). Silicon carbide coatings and free-standing shapes are both important applications of the CVD process. A common CVD reaction is the decomposition of methyl trichlorosilane (MTS):

$$CH_3SiCl_3 \rightarrow SiC + 3HCl$$

The reaction temperature ranges from 900 to 1400 °C (1650 to 2550 °F), and pressure ranges from 1.3 to 6.7 kPa (10 to 50 torr) in a hydrogen atmosphere. The deposition rate and the crystallite size increase with the increasing partial pressure of MTS. Other precursor combinations are $SiCl_4/CH_4$, $SiCl_4/CCl_4$, SiH_2Cl_2/C_3H_8, and $SiHCl_3/C_3H_8$, usually in a hydrogen atmosphere.

Titanium carbide (Ref 33) is of major industrial importance in the coating of wear-resistant tools by the CVD process. The most common deposition system is the reaction of the metal chloride with a hydrocarbon:

$$TiCl_4 + CH_4 \rightarrow TiC + 4HCl$$

The reaction temperature ranges from 850 to 1050 °C (1560 to 1920 °F), and pressure varies from less than 0.13 to 101 kPa (1 to 760 torr) in a hydrogen atmosphere. Other carbon sources are toluene ($CH_3C_6H_5$) and propane (C_3H_8).

Boron nitride (Ref 34) is produced in a hydrogen atmosphere by the reaction of boron trichloride and ammonia:

$$BCl_3 + NH_3 \rightarrow BN + 3HCl$$

At a deposition temperature of 1300 °C (2370 °F), a low-density (1.5 g/cm^3) boron nitride is obtained. Density increases with increasing temperature and reaches 2.0 g/cm^3 at 1600 °C (2910 °F). Vapor-phase precipitation can be a problem in the high-temperature range. A more convenient reaction uses boron trifluoride:

$$BF_3 + NH_3 \rightarrow BN + 3HF$$

The reaction temperature ranges from 1100 to 1200 °C (2010 to 2190 °F), and the pressure is 101 kPa (760 torr).

Low-temperature deposition is possible with diborane:

$$B_2H_6 + 2NH_3 \rightarrow 2BN + 6H_2$$

The reaction temperature ranges from 300 to 400 °C (570 to 750 °F), and the pressure is less than 0.13 kPa (1 torr).

Silicon nitride (Ref 35) is deposited by the reaction of silicon tetrachloride with ammonia:

$$3SiCl_4 + 4NH_3 \rightarrow Si_3N_4 + 12HCl$$

The reaction temperature is 850 °C (1560 °F), and the pressure can go up to 101 kPa (760 torr). Silicon nitride also is deposited by the reaction of dichlorosilane and ammonia with a high nitrogen dilution:

$$3SiH_2Cl_2 + 4NH_3 \rightarrow Si_3N_4 + 6HCl + 6H_2$$

The reaction temperature ranges from 755 to 810 °C (1390 to 1490 °F). When a high-frequency (13.56 MHz) plasma is used, the deposition temperature is lowered (400 to 600 °C, or 750 to 1110 °F).

Titanium Nitride (Ref 36). A common reaction for the CVD of TiN uses N_2 $TiCl_4$ at temperatures above 900 °C (1650 °F) and at pressures up to 101 kPa (760 torr). Another reaction uses ammonia as a nitrogen source, as follows:

$$TiCl_4 + NH_3 + \frac{1}{2}H_2 \rightarrow TiN + 4HCl$$

Alumina (Ref 37, 38). A common reaction for the deposition of alumina is the hydrolysis of the aluminum trichloride:

$$2AlCl_3 + 3H_2 + 3CO_2 \rightarrow Al_2O_3 + 3CO + 6HCl$$

This reaction takes place in excess hydrogen, at an optimum temperature of 1050 °C (1920 °F) and at low pressure (approximately 0.13 kPa, or 1 torr).

References cited in this section

1. H.O. Pierson, *Handbook of Chemical Vapor Deposition,* Noyes Publications, 1992
17. N.J. Ianno and J.A. Plaster, Plasma Enhanced CVD of Molybdenum, *Thin Solid Films,* Vol 147 (No. 2), 2 March 1987, p 193-202
18. J.A. Sheward and W.J. Young, The Deposition of Molybdenum and Tungsten Coatings on Gun Steel Substrates by a Plasma Assisted CVD Technique, *Vacuum,* Vol 36 (No. 1-3), Jan-March 1986, p 37-41
19. T.R. Jervis and L.R. Newkirk, Metal Film Deposition by Laser Breakdown CVD, *J. Mater. Res.,* Vol 1 (No.

3), May/June 1986, p 420-424

20. M. Skibo and F. Greulich, Characterization of CVD Ni-(0.05-0.20wt%)B Alloys, *Thin Solid Films,* Vol 113, 1984, p 225-234
21. J.G. Donaldson, A Preliminary Study of the Vapor Deposition of Rhenium and Rhenium-Tungsten, *Journal of the Less Common Metals,* Vol 14, 1968, p 93-101
22. D. Bauerle, Laser Induced Chemical Vapor Deposition, *Laser Processing and Diagnostics,* D. Bauerle, Ed., Springer-Verlag, 1984
23. M.L. Green, Y. Ali, T. Boone, B. Davidson, L. Feldman, and S. Nakahara, The Formation and Structure of CVD W Films Produced by the Si Reduction of WF_6, *J. Electrochem. Soc.,* Vol 134 (No. 9), Sept 1987, p 2285-2292
24. C.C. Tang, Plasma Enhanced CVD of Beta-Tungsten, a Metastable Phase, *App. Phys. Lett.,* Vol 45 (No. 6), 15 Sept 1984, p 633-635
25. R. Kaplan and R. Tuffias, Large Seamless Tungsten Crucibles Made by CVD*, Int. J. Refract. Hard Metals,* Vol 3 (No. 3), 15 Sept 1984
26. H.O. Pierson, *Handbook of Carbon, Graphite, Diamond and Fullerenes,* Noyes Publications, 1994
27. K. Spear, Diamond: Ceramic Coating of the Future, *J. Am. Ceram. Soc.,* Vol 7 (No. 2), 1989, p 171-191
28. W.A. Yarborough, Diamond Growth with Locally Supplied Methane and Acetylene, *J. Mater. Res.,* Vol 7 (No. 2), 1992, p 379-383
29. H.O. Pierson, A Survey of the Chemical Vapor Deposition of Refractory Transition Metal Borides, *Chemical Vapor Deposited Coatings,* American Ceramic Society, 1981, p 27-45
30. A. Mellendore, Chemical Vapor Deposition of Boron-based Refractory Solids, *AIP Conf. Proc.,* 4-140, American Institute of Physics, 1986
31. F. Langlais and C. Prebende, On the Chemical Process of CVD of SiC-based Ceramics from the Si-C-H-Cl System, *Proc. 11th Int. Conf. on CVD,* K. Spear and G. Cullen, Ed., Electrochemical Society, 1990, p 686-695
32. D. Stinton, T. Besmann, and R. Lowden, Advanced Ceramics by Chemical Vapor Deposition Techniques, *Ceram. Bull.,* Vol 67 (No. 2), 1988, p 350-355
33. M. Dariel, R. Aparicio, T. Anderson, and M. Sacks, CVD of TiC_x on Refractory Materials, *Proc. 11th Int. Conf. on CVD,* K. Spear and G. Cullen, Ed., Electrochemical Society, 1990, p 659-669
34. L. Kempfer, The Many Faces of Boron Nitride, *Mater. Eng.,* Nov 1990, p 41-44
35. J. Marks, D. Witty, A. Short, W. Laford, and B. Nguyen, Properties of High Quality Nitride Films by Plasma Enhanced Chemical Vapor Deposition, *Proc. 11th Int. Conf. on CVD,* K. Spear and G. Cullen, Ed., Electrochemical Society, 1990, p 368-373
36. D.G. Bhat, A Thermodynamic and Kinetic Study of CVD TiN Coating on Cemented Carbide, *Proc. 11th Int. Conf. on CVD,* K. Spear and G. Cullen, Ed., Electrochemical Society, 1990, p 648-655
37. S. Choi, C. Kim, J. Kim, and J. Chun, Nucleation and Growth of Al_2O_3 on Si in the CVD Process, *Proc. 9th Int. Conf. on CVD,* M. Robinson et al., Ed., Electrochemical Society, 1984, p 233-241
38. G. Pauer, H. Altena, and B. Lux, Al_2O_3 CVD with Organic Al-Donors, *Int. J. Refract. Hard Metals,* Vol 5 (No. 3), Sept 1986, p 165-170

Applications

Wear-, erosion-, and corrosion-resistance applications extensively utilize CVD coatings, as do applications that require low friction characteristics. Table 2 lists the properties of typical CVD coating materials for these applications. Some materials, such as titanium diboride, titanium carbide, and silicon carbide, provide extremely low wear rates. Table 3 lists specific production applications for the wear-, erosion-, and corrosion protection provided by CVD coatings.

Table 2 Selected wear and corrosion properties of CVD coating materials

Material	Hardness		Thermal conductivity, W/m · K	Coefficient of thermal expansion at 25 °C (77 °F), 10^{-6}/K	Remarks
	GPa	10^6 psi			
Titanium carbide	31.4	4.5	17	7.6	High wear and abrasion resistance, low friction
Titanium nitride	20.6	3.0	33	9.5	High lubricity; stable and inert
Titanium carbonitride	24.5-29.4	3.5-4.3	20-30	8	Stable lubricant
Chromium carbide	22.1	3.2	11	10	Resists oxidation to 900 °C (1650 °F)
Silicon carbide	27.4	4.0	125	3.9	High conductivity, shock resistant
Titanium diboride	33.0	4.7	25	6.6	High hardness, high wear resistance
Alumina	18.8	2.7	34	8.3	Oxidation resistant, very stable
Diamond-like carbon	29-49	4.2-7.1	200	. . .	Very hard, high thermal conductivity
Diamond	98	14.2	180	2.9	Extreme hardness and high thermal conductivity

Table 3 Wear-, erosion-, and corrosion-resistance applications of CVD

Metal forming (noncutting)
Tube and wire-drawing dies (TiN) Stamping, chamfering, and coining tools (TiC) Drawing punches and dies (TiN) Deep-drawing dies (TiC) Sequential drawing dies (Cr_7C_3) Coating on dressing sticks for grinding wheels (B_4C)
Ceramic and plastic processing
Molding tools and dies for glass-filled plastics [Ti(CN)] Extrusion dies for ceramic molding (TiC) Kneading components for plastic mixing (TiC)
Chemical and general processing industries
Pump and valve parts for corrosive liquids (SiC) and abrasive liquids (TiB_2) Valve liners (SiC) Positive-orifice chokes (SiC, TiB_2) Packing sleeves, feed screws (TiC) Thermowells (SiC, Al_2O_3)

Abrasive-slurry transport (WC) Sandblasting nozzles (TiC, B_4C, TiB_2) Textile-processing rolls and shafts (Al_2O_3, TiC, WC) Paper-processing rolls and shafts (TiC) Valves for coal-liquefaction components (TiB_2) Cathode coating for aluminum production (TiB_2) Oxidation-resistant coatings for carbon-carbon composites (SiC)
Machine elements
Gear components (TiN) Coating on stainless-steel spray-gun nozzles (TiC) Components for abrasive processing (TiC) Coating on ball bearings (TiC) Turbine blades (SiC, TiC)
Nuclear
Coating for neutron flux control in nuclear reactors (B_4C) Coating for shielding against neutron radiation (B_4C) Coatings for fusion reactor applications (SiC) Nuclear waste container coatings (SiC)
Instruments
Radiation sensor (SiC) Thermionic cathodes (W-Th) Target coatings for x-ray cathodes (W-Re)

Note: TiN, titanium nitride; TiC, titanium carbide; B_4C, boron carbide; Ti(CN), titanium carbonitride; SiC, silicon carbide; TiB_2, titanium diboride; Al_2O_3, alumina; WC, tungsten carbide

The cutting-tool industry relies heavily on coatings. The technology associated with CVD has made some of its most important gains in this area. Major applications are represented by titanium carbide coatings on the majority of cemented (cobalt-bonded) tungsten carbide tools and both titanium nitride and carbonitride coatings on high-speed tool steel and cemented carbide tools.

The materials identified in Table 2 can be used as multilayer structures that utilize the strongest characteristics of each layer of material. Nearly all coatings are multilayer systems that combine titanium nitride for lubricity and galling resistance; alumina for chemical inertness and thermal insulation; and titanium carbide, as well as titanium carbonitride, for abrasion resistance. Selecting the optimum combination of materials depends on the type of machining operation, the material to be machined, and other factors. Criteria for such a selection are summarized in Table 4.

Table 4 Criteria for selecting coating materials for cutting tools

Property	**Best materials**[(a)]
Oxidation and corrosion resistance; high-temperature stability	Al_2O_3, TiN, TiC
Crater-wear resistance	Al_2O_3, TiN, TiC

Hardness and edge retention	TiC, TiN, Al_2O_3
Abrasion resistance and flank wear	Al_2O_3, TiC, TiN
Low coefficient of friction and high lubricity	TiN, Al_2O_3, TiC
Fine grain size	TiN, TiC, Al_2O_3

Source: Ref 39

(a) Al_2O_3, alumina; TiN, titanium nitride; TiC, titanium carbide. For each property, best material is identified first.

Titanium nitride, the most common coating material, is generally combined with a very thin undercoating of titanium carbide or titanium carbonitride to promote adhesion. Alumina coatings are preferred in high-speed machining applications in which oxidation resistance and high-temperature stability are the critical factors. Like titanium nitride, alumina is deposited on an intermediate titanium carbide layer.

A large variety of free-standing structures of refractory metals and ceramics are produced by the CVD process (Table 5).

Table 5 Free-standing structures produced by CVD

High-strength structural parts of nickel alloyed with small amount of boron
Shapes such as tubes, rods, and plates
Furnace muffles (tungsten)
Hollow spheres with thin walls (tungsten)
Boats and crucibles for liquid-phase and molecular-beam epitaxy (pyrolytic graphite), and crucibles for silicon single-crystal processing (silicon nitride)
Electrodes for plasma etching (pyrolytic graphite)
Trays for silicon-wafer handling (pyrolytic graphite)
Heating elements for high-temperature furnaces (pyrolytic graphite)
Aircraft disk brakes (carbon-carbon)
Re-entry heat shields, rocket nozzles, and other aerospace components (carbon-carbon)
High-temperature turbine blades and components for internal combustion engines (silicon nitride)
Heart valves and dental implants (pyrolytic carbon)

Note: Pyrolytic carbon is a generic term commonly used for CVD carbon, but usually applied to the low-temperature form (900 to 1400 °C, or 1650 to 2550 °F) with limited preferred orientation. Pyrolytic graphite is the higher-temperature product (1900 to 2300 °C, or 3450 to 4170 °F) with a high degree of preferred orientation in the "C" direction.

Ultrafine Powders by CVD. Powder is precipitated from the gas phase if the temperature and supersaturation of a CVD reaction are sufficiently high. The powder has few impurities, small diameter, and great uniformity, which are important factors in the production of high-quality hot-pressed or sintered ceramic bodies with good mechanical and electrical properties. In addition, the sintering temperatures required for CVD powders are lower than those for conventional powders.

The following powders are made experimentally or on a production basis:

- Beta SiC powder from methyl-trichlorosilane in the presence of hydrogen in an argon plasma or from tetramethylsilane in a flow-through reactor between 850 and 1500 °C (1560 and 2730 °F) (Ref 40)
- An amorphous silicon nitride powder produced by laser CVD from halogenated silanes and ammonia with an inert sensitizer such as SF_6 (Ref 41)

- Aluminum nitride produced from aluminum alkyl, and magnesium oxide produced from magnesium vapor and O_2 at 800 °C (1470 °F) and tungsten carbide (Ref 42)
- Iron, nickel, cobalt, molybdenum, and tungsten powders produced by the pyrolysis of the metal carbonyls or halides

CVD ceramic powders, such as SiC and Si_3N_4, are used either experimentally or in production in applications such as reciprocating engines, gas turbines, turbochargers, bearings, machinery, and process equipment.

Metallic and ceramic powders as small as 5 μm (200 μin.) in diameter can be coated with nickel or iron by CVD by the fluidized bed technique. A typical application is the coating of tungsten particles to promote sintering in powder metallurgy. Sintering time, sintering temperature, and grain growth are reduced, contamination is lessened, and properties are improved (Ref 43).

Boron and silicon carbide fibers are produced industrially by CVD (Ref 44, 45, 46). A monofilament starter core is required that is capable of being heated resistively, such as a tungsten or graphite fiber.

Boron fibers are produced by the hydrogen reduction of boron chloride at 1300 °C (2370 °F). The "boron" fiber actually consists of a boron envelope surrounding a tungsten boride core, which typically occupies 5% of the fiber cross section. The fiber has high strength, high modulus, and low density, but it also has a tendency to further grain growth at high temperatures, is highly reactive with many metals, and is costly.

CVD silicon carbide fibers are a recent development that show promise, and if the production cost can be reduced they may take over some of the applications of CVD boron fibers or other refractory fibers. They are generally produced by the reaction of silane and a hydrocarbon in a tubular glass reactor (Fig. 1). The substrate is a carbon monofilament that is precoated with a 1 μm (40 μin.) layer of pyrolytic graphite to ensure a smooth deposition surface and a constant resistivity.

SiC fibers have properties similar to those of CVD boron fibers, except that SiC is more refractory and less reactive than boron. The fibers retain much of their mechanical properties when exposed to high temperatures in air, up to 800 °C (1470 °F) for as long as 1 h. Most applications of CVD silicon carbide fibers are still under development, including:

- Reinforcement for ceramic and polymer composites
- Reinforcement for metal-matrix composites with such metals as titanium, titanium aluminide, aluminum, magnesium, and copper. Applications for these fibers are found mostly in advanced aerospace programs and include fan blades, drive shafts, and other components.

References cited in this section

39. D.G. Bhat and P.F. Woerner, Coatings for Cutting Tools, *J. Metals,* Feb 1986, p 68
40. H.D. Wu and D.W. Ready, Silicon Carbide Powders by Gaseous Pyrolysis of Tetramethylsilane, *Silicon Carbide 87,* Vol 2, *Ceramic Transactions,* 1987, p 35-46
41. R. Bauer, R. Smulders, E. Geus, J. van der Put, and J. Schoomman, Laser Vapor Phase Synthesis of Submicron Silicon and Silicon Nitride Powders from Halogenated Silanes, *Ceram. Eng. Sci. Proc.,* Vol 9 (No. 7-8), 1988, p 949-956
42. A. Kato, Study of Powder Preparation in Japan, *Ceramic Bulletin,* Vol 66 (No. 4), 1987, p 647-650
43. S. Mulligan and R.J. Dowding, "Sinterability of Tungsten Powder CVD Coated with Nickel and Iron," Technical Report 90-56, U.S. Army Mater. Tech. Lab., Watertown, MA, 1990
44. L.M. Sheppard, Progress in Composites Processing, *Ceramic Bulletin,* Vol 69 (No. 4), 1990, p 666-673
45. J.E. Gatica and V. Hlavacek, Laboratory for Ceramic and Reaction Engineering: A Cross-Disciplinary Approach, *Ceramic Bulletin,* Vol 69 (No. 8), 1990, p 1311-1318

46. "AVCO Silicon Carbide Fiber," Textron, Lowell, MA, 1990

Advantages and Disadvantages of CVD

The CVD process has a number of important advantages that often make it the preferred method when producing hard, tribological, and high-temperature coatings and free-standing structures:

- Refractory materials can be deposited at temperatures far below their melting point or sintering temperatures.
- Near-theoretical density is readily achieved.
- Preferred grain orientation and grain size can be controlled.
- Processing at atmospheric pressure is possible.
- Good bonding to a substrate is generally obtained.

Furthermore, the process is not restricted to line-of-sight deposition, as it is for most PVD processes. Deep recesses, high-aspect-ratio holes, and other difficult three-dimensional configurations can usually be coated with relative ease.

In addition, the deposition rate is high and thick coatings can be readily obtained (in some cases, centimeters thick). The process also is generally competitive and, sometimes, even more economical than other coating processes.

Finally, the equipment is relatively simple, does not require ultrahigh vacuum, and generally can be adapted to many process variations. Its flexibility allows many composition changes during deposition, and the codeposition of compounds is readily achieved.

However, the CVD process is not the universal coating panacea. Because it is most versatile at a temperature of 600 °C (1110 °F) or higher, its applications are limited to substrates that are thermally stable at such a temperature. (The development of the plasma and metal-organic CVD processes partially offsets this problem.)

A second problem is that some chemical precursors are hazardous or extremely toxic, which necessitates a closed system.

A third problem is that many reactions either leave solid byproducts or generate solid byproducts with neutralizing solutions. These byproducts can be toxic and corrosive, which necessites the careful consideration of disposal procedures and incurs additional costs. The Environmental Protection Agency (EPA) has been very active, even stringent, in this regard, as have the state regulators of the EPA and Occupational Safety and Health Administration.

A fourth problem is that energy requirements can be high, especially when high deposition temperatures are required.

Finally, the efficiency of the process is sometimes low, resulting in high costs.

Chemical Vapor Deposition of Semiconductor Materials

Manijeh Razeghi, Northwestern University

Introduction

CHEMICAL VAPOR DEPOSITION (CVD) is the deposition of thin, solid films from gas-phase precursors. Growth usually occurs through heterogeneous reactions catalyzed by a heated surface, although homogeneous reactions also can occur in the gas phase. Gas-phase, or parasitic, reactions should be avoided, because they deplete the precursor process and may produce deleterious solid particles, or "dust."

Epitaxial deposition is a process that produces single-crystal films with the same crystallographic orientation as the underlying substrate. Epitaxial growth from a CVD process is sometimes referred to as vapor-phase epitaxy (VPE). Other epitaxial processes that have been developed since 1960 include molecular-beam epitaxy (MBE) and liquid-phase epitaxy.

The vapor-phase methods that are discussed in this article have several advantages, when compared with liquid-phase epitaxy. One is the flexibility of depositing films with distinctly different compositions than the substrates. Even disparate chemistries can be used to deposit epitaxial films, as long as the lattice constant is matched sufficiently to the substrate. An example is the growth of gallium arsenide on silicon. A second advantage is the availability of high-purity gaseous precursors. The refinement of liquid sources is much more difficult, and it limits the quality of the resultant films. Vapor-phase techniques permit the growth of multilayered structures with excellent compositional and dimensional control, as well as abrupt interfaces. A third advantage is that selected gas-phase processes can be scaled to large areas and batch processing for commercial production.

The ability to grow thin, epitaxial films and multilayers on a variety of substrates has led to the development of new devices and technologies. Silicon epitaxial films are used routinely in the manufacture of high-performance bipolar and complementary metal-oxide semiconductor (CMOS) integrated circuits. The deposition of compound semiconductors with direct bandgaps has led to the production of millimeter and microwave devices, as well as optoelectronic devices, such as lasers, light-emitting diodes, and high-efficiency photovoltaic cells. The ability to grow thin, multilayered structures with very fine dimensional and compositional control has made possible quantum-well devices and strained-layer superlattices. The development of devices with novel capabilities and higher performance levels will certainly continue as the control and understanding of the growth process matures.

This article describes vapor-phase growth techniques that are applied to the epitaxial deposition of semiconductor films. The growth of Group III-V compounds via the metal-organic CVD (MOCVD) method is emphasized, because that method has become the most widely used and commercially important process for depositing these materials. The advantages of MOCVD, when compared with techniques such as MBE and VPE, are defined. The thermodynamic and kinetic processes responsible for epitaxial growth also are presented.

Technique Principles

Vapor-Phase Epitaxy. Tietjen and Amick (Ref 1) demonstrated the growth of gallium arsenide phosphide (GaAsP) by VPE in 1966. The growth of materials based on indium phosphide (InP) can be achieved in a horizontal reactor with two temperature zones, such as a fused-silica tube surrounded by multiple furnace windings. High-purity hydrogen (H_2) is a common carrier gas, and arsine (AsH_3) and phosphine (PH_3) are used as the arsenic and phosphorus sources, respectively. Pure indium metal is used as the Group III elemental source. Gaseous species are generated in the first zone (source zone), which is held at a higher temperature than the second zone (deposition zone). For the growth of InP, gaseous species are generated at 750 to 800 °C (1380 to 1470 °F), according to the reactions:

$$2\ In + 2\ HCl \rightarrow 2\ InCl + H_2 \quad \textbf{(Eq 1)}$$

$$4PH_3 \rightarrow P_4 + 6H_2 \quad \textbf{(Eq 2)}$$

Deposition occurs in the temperature range of 650 to 750 °C (1200 to 1380 °F) in the second zone, according to the reaction:

$$P_4 + 4\ InCl + 2\ H_2 \rightarrow 4\ InP + 4\ HCl \quad \textbf{(Eq 3)}$$

To achieve the growth of multilayered structures, the substrate must be moved between reactors that use different chemistries. It is therefore difficult, if not impossible, to achieve layer thicknesses on the order of 5 nm (50 Å), as required for quantum-well or superlattice structures. Fine compositional manipulation favors the techniques of MBE or MOCVD, where the transport of source materials, rather than substrates, is controlled.

The MOCVD process uses at least one metal-organic chemical as a deposition precursor. The growth of Group III-V compounds from metal-organic and hydride sources was first reported by Manasevit in 1960 (Ref 2). In that experiment, InP was deposited from trimethylindium (TMIn) and PH_3 in a closed-tube system. Later, it was established that many common compound semiconductors could be deposited from metal-organic materials (Ref 3, 4, 5, 6). Manasevit coined the MOCVD acronym, which is used in this article. Other authors refer to organometallic CVD (OMCVD). When applied to the growth of epitaxial films, this technique is sometimes called metal-organic vapor-phase epitaxy or organometallic VPE. As used for the epitaxial growth of compound semiconductors, MOCVD has advanced rapidly since the mid-1980s. It has become established as a unique and important epitaxial crystal growth technique, yielding high-quality, low-

dimension structures for fundamental semiconductor physics research and production of useful electronic and photonic semiconductor devices.

A typical MOCVD reactor is shown in Fig. 1. Gaseous precursors are introduced to the reaction chamber from the gas manifold. To achieve the growth of Group III-V compound semiconductors, Group III alkyls and Group V hydrides can be introduced to the reaction chamber. The substrate, located on a hot susceptor, has a catalytic effect on the decomposition of the gaseous products. Growth occurs primarily on this hot surface. The MOCVD technique is attractive because of its relative simplicity, when compared with other growth methods. Excellent control over film composition can be achieved by precisely metering the amounts of gaseous species introduced to the chamber. Thus, MOCVD can be used to produce heterostructures, multiquantum wells, and superlattices with very abrupt transitions in composition, as well as alloys with tailored doping profiles.

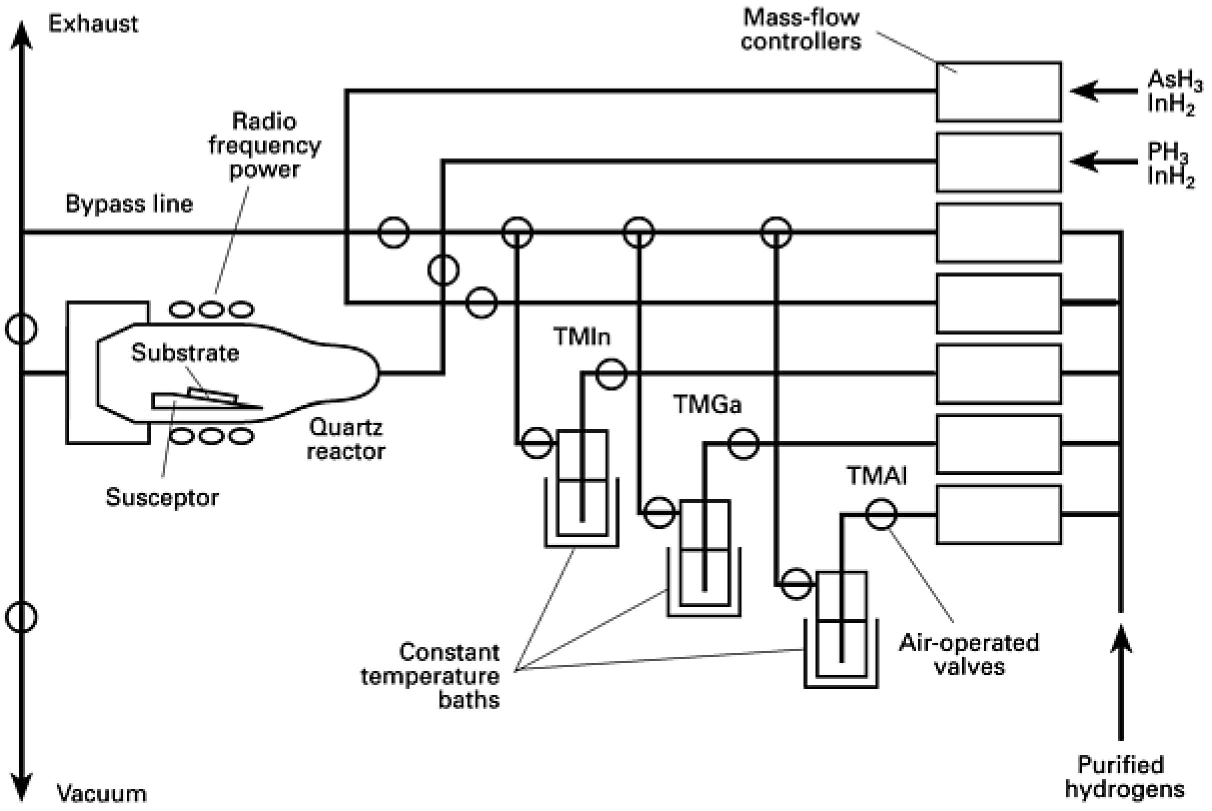


Fig. 1 Typical reactor design for metal-organic chemical vapor deposition. Source: Ref 7

Uniform layers with low background doping densities and sharp interfaces have been grown using MOCVD. Some reactor configurations in use are scalable to large areas, and are therefore attractive for commercial applications. This technique also has been used to produce multilayer structures with layers as thin as a few atomic layers (Ref 8, 9). These abrupt changes in composition produce quantum size effects (Ref 10, 11), and permit the study of two-dimensional electron gases (Ref 12, 13, 14, 15), two-dimensional hole gases (Ref 16, 17), and other charge-transport effects observed in a variety of Group III-V compound semiconductors, heterojunctions, and multilayers (Ref 18, 19). It is also possible to tailor the doping level or alloy composition of ternary and quaternary compounds. Varying the film composition results in a change in the bandgap (Ref 20). This ability to engineer the bandgap has created entirely new classes of electronic and photonic devices (Ref 21). Another recent advance is the ability to grow strained-layer superlattices, in which the crystal lattices of the two materials are purposely mismatched to produce a built-in strain in each layer (Ref 22, 23, 24, 25, 26).

A major disadvantage of MOCVD is the need for large quantities of toxic gases, such as AsH_3 and PH_3. However, less hazardous precursors, such as tertiarybutylphosphine (TBP) (Ref 27, 28) and tertiarybutylarsine (TBAs) (Ref 29, 30), are being developed to address this problem.

The MBE technique has been used to prepare epitaxial films of Group IV (Ref 31, 32), III-V (Ref 33, 34), and II-VI (Ref 35, 36) semiconductors, as well as metals (Ref 37, 38). In this technique, elemental sources are evaporated at

controlled rates by heating and then condensed onto a crystalline substrate surface held at a suitable temperature. This is an ultrahigh vacuum (UHV) technique, in which the beams of evaporated molecules or atoms are focused on the substrate. UHV conditions are necessary to ensure sufficient film purity. The use of UHV has two advantages. First, atoms and molecules reach the growth surface in a very clean condition. Second, the growth process can be monitored by in-situ diagnostic techniques as the crystal grows one atomic layer at a time (Ref 39). The diagnostic techniques that are used include reflection high-energy electron diffraction (RHEED), Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), secondary-ion mass spectroscopy (SIMS), and ellipsometry.

The MBE technique is recognized as an excellent crystal growth technology for the production of complex and varied structures, especially for GaAs-based multilayer structures. It provides extremely precise control of layer thickness and doping profile. However, this technique is expensive because it requires UHV apparatus.

Another major problem is the incorporation of specific dopants. The typical approach is to add dopants by effusion of the elemental impurity, which leads to difficulty when the dopant vapor pressure is either too high (Ref 40) or too low (Ref 41) to be handled conveniently in an ultrahigh vacuum system. Because the MBE process is a near-equilibrium one, dopant incorporation can be hindered by low incorporation probabilities (Ref 42) or surface segregation effects (Ref 43). Phosphorus is one such dopant that suffers from a low incorporation probability. Instead of becoming incorporated into the growing film, it tends to "bounce around" the system, and eventually collects in the vacuum pumps. In addition, the growth of alloys containing both arsenic and phosphorus is particularly difficult because of surface segregation effects.

Hybrid MBE and CVD Techniques. Versatile growth techniques have been developed by combining the beneficial aspects of MBE and CVD. These hybrid techniques employ the gas-handling system of MOCVD and the growth chamber of MBE.

To overcome the limitations of growing phosphide compounds, elemental Group V sources are replaced by those that can decompose AsH_3 and PH_3. This technique is called gas-source molecular-beam epitaxy (Ref 44). In addition, Group III elemental sources can be replaced by simple metal-organic compounds to create the metal-organic molecular-beam epitaxy growth technique (Ref 45, 46). This technique is also known as chemical-beam epitaxy or metal-organic chemical-beam deposition (MOCBD).

The MOCBD technique has numerous advantages, when compared with MOCVD, including:

- Use of a fraction of the amount of PH_3 and AsH_3 for the growth of GaAs- and InP-based materials and the elimination of chemical waste-disposal systems, such as the scrubbers normally used in MOCVD
- Elimination of parasitic reactions in the gas phase because of UHV conditions
- Possible use of in-situ surface diagnostic techniques
- Improvement in homogeneity, composition uniformity, and reproducibility of InP-based materials over large-area substrates
- In-situ etching and removal of oxide during the growth of InP on silicon substrates
- Reduction of contamination from previous chemistries (the memory effect) during *p*-type doping
- Reduction of boundary-layer thickness on hot substrate surfaces
- Compatibility with other high-vacuum, thin-film processing techniques, such as plasma etching, metal evaporation, ion-beam etching, and ion implantation

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References cited in this section

1. J.J. Tietjen and J.A. Amick, *J. Electrochem. Soc.,* Vol 113, 1966, p 724
2. R. Didchenko, J.E. Alix, and R.H. Toeniskoetter, *J. Inorg. Nucl. Chem.,* Vol 14, 1960, p 35
3. H.M. Manasevit, *Appl. Phys. Lett.,* Vol 12, 1968, p 156
4. H.M. Manasevit and W.I. Simpson, *J. Electrochem. Soc.,* Vol 116, 1969, p 1725
5. H.M. Manasevit, *J. Electrochem. Soc.,* Vol 118, 1971, p 647
6. H.M. Manasevit, F.M. Erdmann, and W.I. Simpson, *J. Electrochem. Soc.,* Vol 118, 1971, p 1864
7. R.D. Dupuis, *Science,* Vol 226, 1984, p 623

8. R.D. Dupuis, P.D. Dapkus, C.M. Garner, C.Y. Su, and W.E. Spicer, *Appl. Phys. Lett.,* Vol 34, 1979, p 335
9. P.M. Frijlink and J. Malvenda, *Jpn. J. Appl. Phys.,* Vol 21, 1982, p L574
10. M. Razeghi, *Rev. Tech. Thomson-C.S.F.,* Vol 15, 1983, p 1
11. R.D. Dupuis, P.D. Dapkus, N. Holonyak, and R.M. Kolbas, *Appl. Phys. Lett.,* Vol 35, 1979, p 487
12. M. Razeghi, *Lightwave Technology for Communication,* W.T. Tsang, Ed., Academic Press, 1985
13. F. Delahaye, D. Dominguez, F. Alexandre, J.P. Andre, J.P. Hirtz, and M. Razeghi, *Metrologia,* Vol 22, 1986, p 103
14. Y. Guldner, J.P. Vieren, M. Voos, F. Delahaye, D. Dominguez, J.P. Hirtz, and M. Razeghi, *Phys. Rev. B,* Vol 23 (No. 6), 1986, p 3990
15. M. Razeghi, P. Maurel, F. Omnes, S. Ben Amor, L. Dmowski, and J.C. Portal, *Appl. Phys. Lett.,* Vol 48, 1986, p 1267
16. M. Razeghi, P. Maurel, A. Tardella, L. Dmowski, D. Gauthier, and J.C. Portal, *Appl. Phys. Lett.,* Vol 60, 1986, p 2453
17. D.C. Rogers, R.J. Nicholas, J.C. Portal, and M. Razeghi, *Semicon. Sci. Technol.,* Vol 1, 1986, p 350
18. M. Razeghi, J.P. Duchemin, J.C. Portal, L. Dmowski, G. Remeni, R.J. Nicholas, and A. Briggs, *Appl. Phys. Lett.,* Vol 48, 1986, p 712
19. R.J. Nicholas, L.C. Brunel, S. Huant, K. Karrai, J.C. Portal, M.A. Brummell, M. Razeghi, K.Y. Chang, and A.Y. Cho, *Phys. Rev. Lett.,* Vol 55, 1985, p 8883
20. M. Razeghi, P. Maurel, F. Omnes, and J.P. Pochell, *Appl. Phys. Lett.,* Vol 49, 1986, p 1110
21. M. Razeghi, A. Hosseini, J.P. Vilcot, and D. Decoster, *Proc. 1987, GaAs and Related Compounds Conf.,* Creta, 1987
22. J.W. Matthews and A.E. Blakeless, *J. Cryst. Growth,* Vol 27, 1974, p 119
23. J.W. Matthews and A.E. Blakeless, *J. Cryst. Growth,* Vol 29, 1975, p 273
24. J.W. Matthews and A.E. Blakeless, *J. Cryst. Growth,* Vol 32, 1976, p 265
25. G.C. Osbourn, *Mater. Res. Soc. Symp. Proc. 37,* 1985, p 220-237
26. A.P. Roth, M. Sacilotti, R.A. Masut, P.J. D'Arch, B. Watt, G.T. Sproule, and D.F. Mitchell, *Appl. Phys. Lett.,* Vol 48, 1986, p 1452
27. C.H. Chen, C.A. Larse, G.B. Stringfellow, D.W. Brown, and A.J. Robertson, *Appl. Phys. Lett.,* Vol 48, 1986, p 1531
28. S.R. Kurtz, J.M. Olson, and A. Kibbler, *J. Electron. Mater.,* Vol 18, 1989, p 15
29. C.H. Chen, C.A. Larsen, and G.B. Stringfellow, *Appl. Phys. Lett.,* Vol 50, 1987, p 218
30. A. Brauers, M. Weyers, and P. Balk, *Chemtronics,* Vol 4, 1989, p 8
31. Y. Ota, *J. Appl. Phys.,* Vol 51, 1980, p 1102
32. S. Shimizu and S. Komiya, *J. Vac. Sci. Technol.,* Vol 17, 1980, p 489
33. C.T. Foxon, B.A. Joyce, and M.T. Norris, *J. Cryst. Growth,* Vol 49, 1980, p 132
34. K. Ploog, *Crystals: Growth, Properties, and Applications,* Vol 3, *III-V Semiconductors,* H.C. Freyhardt, Ed., Springer, 1980, p 78
35. A.Y. Cho and J.R. Arthur, *Prog. Solid State Chem.,* Vol 10, 1975, p 157
36. D.L. Smith and V.Y. Pickhardt, *J. Appl. Phys.,* Vol 46, 1975, p 2366
37. C. Argile and G.E. Phead, *Surf. Sci.,* Vol 78, 1978, p 115
38. C. Argile and G.E. Phead, *Surf. Sci.,* Vol 78, 1978, p 125
39. E.H.C. Parker, *The Technology and Physics of Molecular Beam Epitaxy,* Plenum Press, 1985
40. C.E.C. Wood, *Appl. Phys. Lett.,* Vol 33, 1978, p 770
41. M. Ilegems and R. Dingle, *Proc. Symp. GaAs and Related Compounds 1974,* Institute of Physics and Physical Society, London, 1975
42. J.R. Arthur, *Surf. Sci.,* Vol 38, 1973, p 394
43. F. Alexandre, C. Raisin, M.I. Abdalla, A. Brenac, and J.M. Masson, *J. Appl. Phys.,* Vol 51, 1980, p 4296

44. M.B. Panish, *J. Electrochem. Soc.,* Vol 127, 1980, p 2729
45. N. Vodjdani, "These de Doctorate 3e Cycle University Paris XI," Ph.D. dissertation, 1982
46. W.T. Tsang, *Appl. Phys. Lett.,* Vol 45, 1984, p 11

Fundamentals of CVD

The fundamental processes that occur during crystal growth are commonly categorized into thermodynamic and kinetic components. Thermodynamics determine the driving force behind the overall growth process, whereas kinetics define the rates at which the various processes occur. Figure 2 depicts the fundamental processes involved in MOCVD. A study of the dependence of a macroscopic quantity, such as growth rate, on external parameters, such as substrate temperature and input precursor (source) flow rates, provides insight into the overall growth mechanism.

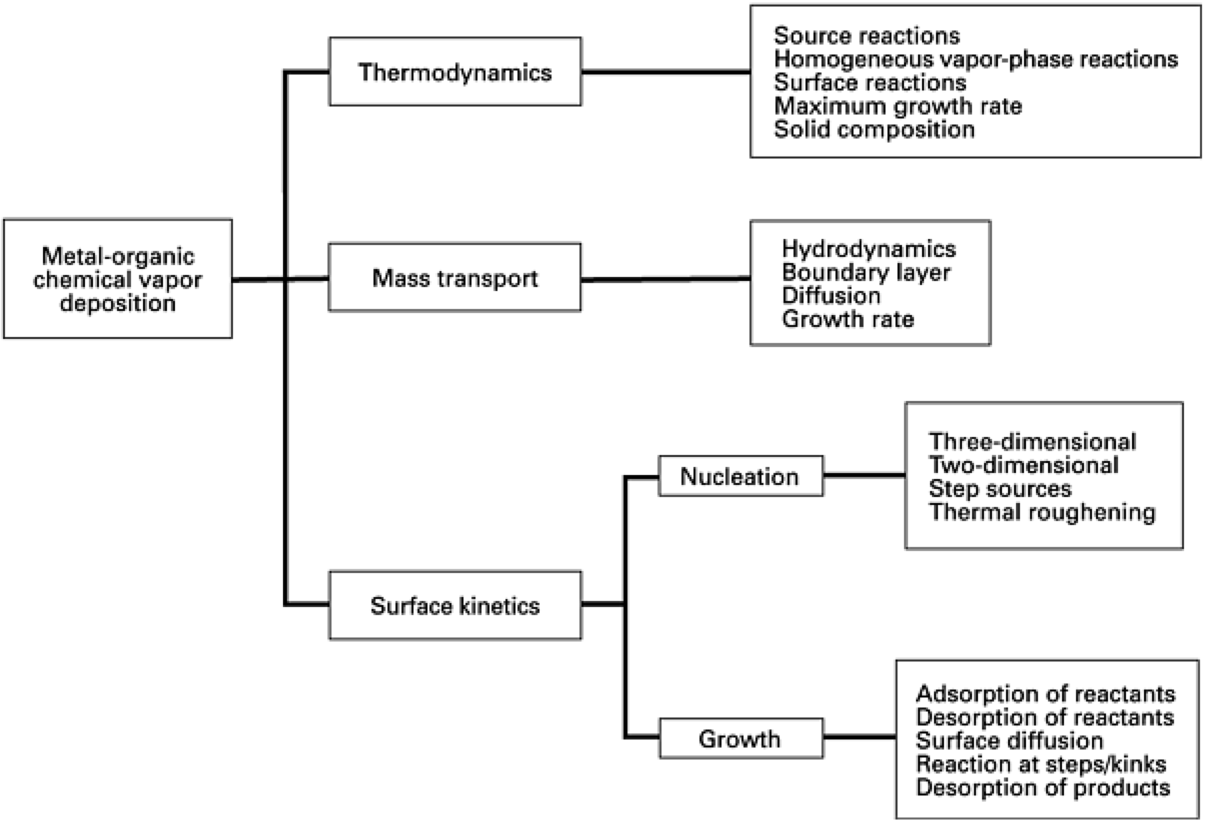

Fig. 2 Fundamental processes involved in metal-organic chemical vapor deposition. Source: Ref 47

Thermodynamics

The goal of thermodynamics is to define the composition of various phases in an equilibrium system at a constant temperature and pressure. Although many aspects of MOCVD growth are nonequilibrium, thermodynamics limits the possible outcomes. Thermodynamics can be used to describe the driving force for epitaxy and to specify the maximum growth rate. In addition, thermodynamic calculations often give an accurate account of the composition of multicomponent solids grown by MOCVD.

Equilibrium is the state that minimizes the Gibbs free energy, G, of the system:

$$G = H - TS \quad \textbf{(Eq 4)}$$

where H is the enthalpy, S is the entropy, and T is the temperature of the system. Entropy is a measure of the degree of randomness in a system, and enthalpy is a measure of the heat content, which can be defined as:

$$H = E + PV \qquad \textbf{(Eq 5)}$$

where E is the internal energy and V is the volume. The quantities G, H, S, E, and V are all extensive quantities, that is, they depend on the size of the system. They are therefore expressed on a per mole basis. For a system containing two phases, α and β, equilibrium is attained when a redistribution between phases causes no further decrease in free energy. This can be expressed mathematically as:

$$\left(\frac{\partial G'}{\partial n_i}\right)^{a}_{T,P,n_j} - \left(\frac{\partial G'}{\partial n_i}\right)^{b}_{T,P,n_j} = 0 \qquad \textbf{(Eq 6)}$$

where G' is the total free energy of the system (as opposed to the free energy per mole). The change in G' with respect to n_i is considered as all other variables (temperature, pressure, and molar amount of other components) are held constant. The partial derivative of G' with respect to n_i is such an important thermodynamic concept that it is given its own name, the chemical potential (μ_i). Thus, equilibrium is reached when:

$$m_i^a = m_i^b \qquad \textbf{(Eq 7)}$$

for each component, i, in the system.

When a system is not at equilibrium, the thermodynamic driving force to restore equilibrium is:

$$\Delta\mu = m_i^a - m_i^b \qquad \textbf{(Eq 8)}$$

This also is the driving force for epitaxial growth. In MOCVD, a nonequilibrium situation is intentionally created, in which the chemical potential of the solid phase differs from that of the vapor. The system restores equilibrium by producing the desired solid phase. The maximum quantity of solid produced is that which is needed to establish equilibrium. It is thus limited by the thermodynamics and size of the system.

The growth rate observed in MOCVD is almost always less than that calculated from thermodynamic principles. Kinetic factors, that is, either surface reaction rates or the diffusion of gas species through the vapor phase, are what limits the growth rate because they hinder the establishment of equilibrium. Driving forces for epitaxial growth are created in the vapor phase and the diffusion boundary layer, and at the interface between the solid and vapor, as depicted in Fig. 3(a). This diagram shows the driving forces necessary to sustain the flux for mass-transport processes ($\Delta\mu_D$) and surface reactions ($\Delta\mu_s$).

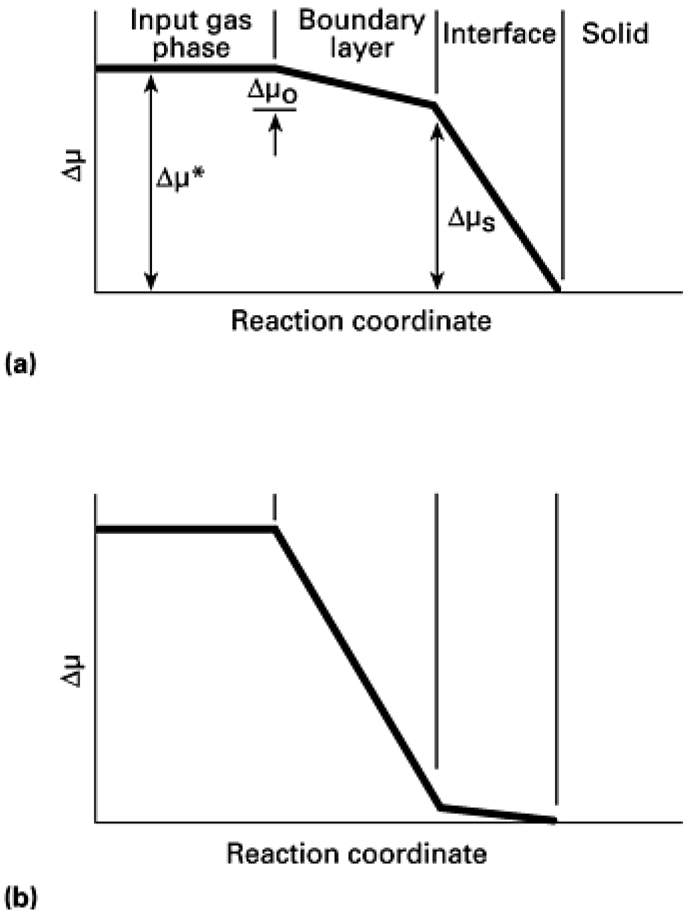

Fig. 3 Chemical potential in metal-organic chemical vapor deposition processes. (a) General case. (b) Mass-transport limited growth. Source: Ref 48

In any given MOCVD process, the shape of the Fig. 3(a) diagram depends on whether growth is limited by mass transport or by surface reactions. Even when there is a large supersaturation in the input vapor phase (a high degree of nonequilibrium), near-equilibrium conditions can exist near the growing surface. This occurs when the surface reactions are much faster than mass transport through the vapor. This situation, termed mass-transport limited growth, is depicted in Fig. 3(b).

Besides describing the driving force for epitaxy, thermodynamic calculations often give an accurate indication of the composition of multicomponent solids grown by MOCVD. Phase diagrams, calculated from the free energy of mixing, specify the number and composition of the phases in equilibrium at a constant temperature, pressure, and overall composition. An important quantity needed for the calculation of solid-solid, solid-liquid, and solid-vapor-phase equilibria is the heat of mixing in the solid, ΔH^M. This quantity, coupled with the assumption that constituents distribute randomly on their respective sublattices, allows calculation of the free energy of mixing of the solid alloy.

The simplest model that describes the free energy of mixing of semiconductor liquid and solid solutions is the regular-solution model. A regular solution, as defined by Hildebrand (Ref 49), is nonideal, but comprises a random arrangement of constituents. Two additional assumptions are that interactions occur only between nearest neighbors, and that atoms reside on a lattice, where each atom is surrounded by Z neighbors. For a solution consisting only of A and C atoms, the nearest neighbor bond energies that must be considered are H_{AC}, H_{AA}, and H_{CC}. The entropy of mixing is simply the ideal configurational entropy of mixing:

$$\Delta S^M = -R[x\ln x + (1 - x)\ln(1 - x)] \quad \textbf{(Eq 9)}$$

The enthalpy of mixing is obtained by summing the nearest neighbor bond energies:

$$\Delta H^{M} = x(1 - x)\Omega \qquad \textbf{(Eq 10)}$$

where the interaction parameter, Ω, is:

$$\Omega = ZN^{\circ}\left[H_{AC} - \frac{1}{2}(H_{AA} + H_{cc}\right] \qquad \textbf{(Eq 11)}$$

where N^0 is Avogadro's number.

Phase-diagram calculations are based on the free energy of mixing:

$$\Delta G^{M} = \Delta H^{M} - T\Delta S^{M} \qquad \textbf{(Eq 12)}$$

where the values for ΔH^M and ΔS^M are provided by Eq 9 and 10.

The regular-solution model does not provide much physical insight into the bonding and mixing of semiconductor solutions. As an empirical model, however, it can be used to interpolate and extrapolate phase-diagram information from limited experimental data. The regular-solution model has been used to calculate the phase diagrams in binary, ternary, and quaternary semiconductor systems.

Phase diagrams of many multicomponent systems are available in the literature (Ref 50, 51, 52). Thermodynamic analyses of solid composition against vapor composition have been published for the systems $GaAs_{1-x}P_x$, $InAs_{1-x}P_x$, $In_{1-x}Ga_xAs$ (Ref 53), and for the quaternary $Ga_{1-x}In_xAs_{1-y}P_y$ (Ref 54). Generally, good agreement between calculations and experimental results is obtained.

Kinetics and Gas-Phase Transport

Thermodynamics determine the state of a closed system at equilibrium and indicate what to expect from the reactants on a surface (substrate) at a given temperature. However, the MOCVD process is not, by definition, an equilibrium process. Thermodynamics can only define certain limits for the growth process. It is not possible to use thermodynamics to predict the time required to attain equilibrium, what steps to take to achieve the lowest energy state, or the rates at which various processes occur during the transition from precursors to solid. These problems can only be approached in terms of kinetics (Ref 48).

Deposition Reactions. Several types of reactions occur in the CVD growth process. Reactions that occur entirely in the gas phase are called homogeneous, whereas those that occur at a solid surface are called heterogeneous. Homogeneous and heterogeneous reactions are usually either unimolecular or bimolecular. The unimolecular process involves a single energetically activated species, and the bimolecular process requires the collision of two species to produce an activated complex. The probability of higher-order reactions is extremely low.

A simplified depiction of the growth processes for Group III-V compounds that occur near and at the substrate surface is shown in Fig. 4. This figure exemplifies the growth of GaAs by trimethylgallium (TMGa) and AsH_3. Several steps are involved in the growth of GaAs. First, both AsH_3 and TMGa, which are carried by hydrogen gas, diffuse through the boundary layer to reach the substrate. Second, gas-phase reactants are adsorbed on the surface through a series of surface reactions. Third, these species are incorporated into the solid GaAs film. Finally, the reaction products are removed. This four-step description is an oversimplification, because many individual reactions actually occur in the gas phase and at the substrate surface to achieve thin-film growth. Table 1 lists those gas-phase and surface reactions that likely operate in the growth of GaAs from TMGa and AsH_3.

Table 1 Gas-phase and surface reactions operative in the growth of gallium arsenide from trimethylgallium and arsine

Gas-phase reactions

(G1)	$Ga(CH_3)_3 \rightarrow Ga(CH_3)_2 + CH_3*$
(G2)	$Ga(CH_3)_2 \rightarrow GaCH_3 + CH_3*$
(G3)	$CH_3* + AsH_3 \rightarrow AsH_2 + CH_4$
(G4)	$CH_3* + H_2 \rightarrow CH_4 + H*$
(G5)	$H* + H* + M \rightarrow H_2 + M$
(G6)	$CH_3 + H* + M \rightarrow CH_2 + M$
(G7)	$CH_3* + CH_3* \rightarrow C_2H_6$
(G8)	$GaCH_3 + CH_3* \rightarrow GaCH_2 + CH_4$
(G9)	$GaCH_2 + H* \rightarrow GaCH_3$
(G10)	$Ga(CH_3)_3 + CH_3 \rightarrow Ga(CH_3)_2CH_2 + CH_4$
(G11)	$Ga(CH_3)_2CH_2 + H* \rightarrow AsH_2 + Ga(CH_3)_3$
(G12)	$Ga(CH_3)_2CH_2 \rightarrow Ga(CH_3)_2 + CH_3*$
(G13)	$Ga(CH_3)CH_2 \rightarrow Ga(CH_2) + CH_3*$
(G14)	$Ga(CH_3)_3 + H* \rightarrow Ga(CH_3)_2 + CH_4$
(G15)	$Ga(CH3)_2 + H* \rightarrow Ga(CH_3) + CH_4$
(G16)	$Ga(CH_3)_2 + CH_3* \rightarrow Ga(CH_3) + CH_4$
(G17)	$Ga(CH_3)CH_2 + H* \rightarrow Ga(CH_3)_2$
Surface reactions	
(S1)	$H* + S_G \rightarrow H_G*$
(S2)	$H* + S_A \rightarrow H_A*$

(S3)	$CH_3 + S_G \leftrightarrow (CH_3)_G*$
(S4)	$CH_3 + S_A \leftrightarrow (CH_3)_A*$
(S5)	$GaCH_3 + S_G \leftrightarrow CH_3*$
(S6)	$Ga(CH_3)_2 + S_G \rightarrow GaCH_3* + CH_3*$
(S7)	$Ga(CH_3)_3 + S_G \rightarrow GaCH_3* + 2CH_3*$
(S8)	$GaCH_2 + S_G + S_A \rightarrow GaC + H_2$
(S9)	$Ga(CH_3)CH_2 + S_G + S_A \rightarrow GaC + CH_3* + H_2$
(S10)	$Ga(CH_3)_2CH_2 + S_G + S_A \rightarrow GaC + 2CH_3* + H_2$
(S11)	$AsH + S_A \leftrightarrow AsH*$
(S12)	$AsH_2 + S_A \rightarrow AsH* + H*$
(S13)	$AsH_3 + S_A \rightarrow AsH* + H_2$
(S14)	$CH_3* + H_G* \rightarrow CH_4 + S_G$
(S15)	$CH_3* + H_A* \rightarrow CH_4 + S_A$
(S16)	$H* + (CH)_G* \rightarrow CH_4 + S_G$
(S17)	$H* + (CH)_A* \rightarrow CH_4 + S_A$
(S18)	$H_G* + (CH)_A* \rightarrow CH_4 + S_A + S_G$
(S19)	$H_A* + (CH)_G* \rightarrow CH_4 + S_A + S_G$
(S20)	$H_A* + H_G* \rightarrow H_2 + S_A + S_G$
(S21)	$(CH_3)_A* + (CH_3)_A* \rightarrow C_2H_6 + S_A + S_G$
(S22)	$GaCH_3* + AsH* \rightarrow GaAs + CH_4 + S_A + S_G$

(S23)	$AsH^* + AsH^* \rightarrow As_2 + H_2 + 2S_A$
(S24)	$CH_3^* + AsH_G^* \rightarrow As^* + CH_4$
(S25)	$As^* + As^* \rightarrow As_2 + CH_4$
(S26)	$GaCH_3^* + As^* \rightarrow GaAs + CH_3^* + S_G + S_A$

Note: * refers to surface adsorption, S_A to arsenic site, and S_G to gallium site.

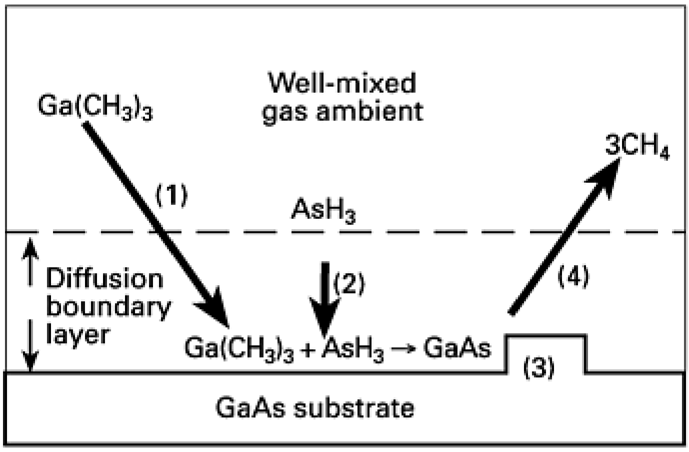

Fig. 4 Processes involved in the growth of gallium arsenide from trimethylgallium and arsine

A physicochemical model of the MOCVD process that combines models of fluid flow and heat transfer for a typical horizontal MOCVD has been presented by Jensen (Ref 55). This model predicts GaAs growth rates and carbon incorporation trends as a function of temperature, pressure, and Group V/III ratio.

In the general case of film growth from precursors, the chemical reaction pathways are not clearly understood. The surface reaction mechanism for growth is complicated by the large number of possible reactions. In Table 1, the general reaction pathway involves chemical reaction processes such as multistep pyrolytic decomposition of metal-organics and reactions with hydrogen radicals in the gas phase (G1 to G17) (Ref 56, 57, 58, 59), heterogeneous decomposition (S11 to S13), and surface adsorption and desorption (S1 to S13). The growth of the GaAs solid phase occurs via reactions between gallium- and arsenic-containing surface precursors (S22 and S26). Volatile reaction byproducts are removed from the surface by adsorption, interaction with colliding gas-phase radicals (S14 to S17, S24) and bimolecular surface recombination reactions (S18 to S21, S23, S25). Carbon incorporation occurs because of reactions S8 to S10.

Gas Flow Patterns. The gas velocities and temperature gradients in the vicinity of the hot susceptor play a significant role in the deposition process. The problems of reactor cell design and their solutions are best discussed in terms of the hydrodynamics of the reactant gas flowing into the cell. Important parameters include pressure, viscosity, volume, and temperature variation.

Laminar and Turbulent Flow. Consider a case of steady fluid flow through a uniform pipe. The flow may start uniformly, but can soon become nonuniform. After traversing a distance, *z*, which is the velocity entry length, the flow velocity $v(r)$ attains a parabolic profile, as shown in Fig. 5(a):

$$v(r) = -\frac{1}{4h}\frac{dp}{dz}(a^2 - r^2),\ for(0 \le r \le a) \quad \textbf{(Eq 13)}$$

where d*p*/dz is the pressure gradient, *a* is the cross-section radius, *r* is the radial axis, and ηis the dynamic viscosity. The flow in Fig. 5(a) is steady, nonuniform, and laminar. In laminar flow, the velocity is always the same at a fixed position. Each element of the reactive species travels smoothly along a simple, well-defined path, and each element starting at the same place follows the same path.

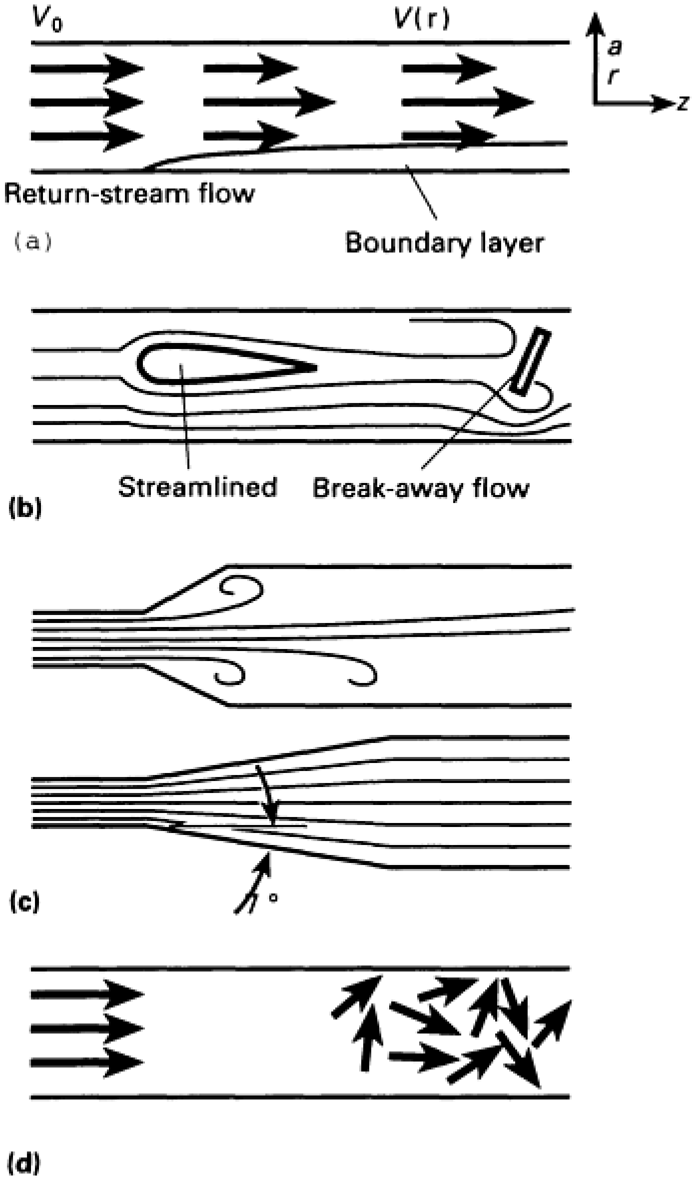

Fig. 5 Different gas flow patterns possible in chemical vapor deposition reactors. (a) Boundary layer of a gas flowing in a pipe and velocity distribution. (b) Stream lines showing adhered flow and break-away flow. (c) Flow patterns effected by expansion angle of tubes. (d) Effect of Reynolds number on flow properties. Source: Ref 48

The laminar pattern can easily be disturbed by either putting a barrier in the flow path (Fig. 5b) or changing the tube diameter (Fig. 5c). Stream lines are used to show the direction of gas molecules. In Fig. 5(b), the stream lines illustrate gas molecules that both break away from, and adhere to, the wall. In the first barrier in Fig. 5(b), a stream line adheres along the whole of its surface. The second barrier produces a break-away flow. The stream line that touches the edge of the barrier does not touch the plate anywhere else. The flow breaks away from the surface at this point. The wave behind the break-away flow may rotate slowly and form a stable eddy wave. When a susceptor is placed inside the reactor chamber at a large angle with respect to the flow direction, a break-away and return-stream flow is produced. This type of flow should be avoided because it can produce a "memory effect," that is, the composition of the growing layer is contaminated by residual gases used to grow previous layers.

Figure 5(c) illustrates gas flowing in a pipe that has a sudden change in cross-sectional area. When the cross-sectional area either increases or decreases, the gas will experience either a decrease or an increase in pressure, respectively. This kind of sudden momentum change can produce vortices. More importantly, vortices can be created by high flow velocities. As the mean velocity becomes larger, the velocity gradients also increase. The friction between adjacent layers of flow can become so high that local velocity components normal to the flow direction are no longer smoothed out. Instead, they progressively develop into turbulent or chaotic flow. When a pipe expands, the rate of decrease in pressure determines whether or not flow is smooth or turbulent. The rule of thumb for maintaining laminar flow is to avoid linear expansion angles, θ greater than 7° (Ref 55, 60).

When the flow becomes turbulent, it develops a highly random character with rapid, irregular fluctuations of velocity in both space and time. In this case, an element of gas flow will follow a highly irregular, distorted path (Fig. 5d). Different elements starting at the same place will follow different paths, because the pattern of irregularities changes all the time (Ref 61). The irregular motions do not affect all the molecules at the same instant, so that when the velocity is averaged out, it can still be thought of as a steady flow with a steady average velocity. The criteria that establish whether a gas will flow in a turbulent or laminar regime are characterized by the Reynolds number, R_e, which is defined as:

$$R_e = \frac{r v d}{h} \quad \textbf{(Eq 14)}$$

where ρ is the density in kg/m^3, ν is the average flow rate in m/s, and d is the diameter of the tube in m. When R_e is small (< 100), the flow regime is laminar.

Consider the case of parallel flow over a flat plate. The velocity distribution in the fluid phase is shown in Fig. 6. The flow is uniform, with velocity V_0, before the plate is inserted into the system. After the plate is introduced, a contiguous, low-velocity boundary layer develops. The width of the resulting boundary a layer for the condition $z > \delta_0$ is given by:

$$\delta_0 \approx 4.56\,(Dz/V_0)^{1/2} \quad \textbf{(Eq 15)}$$

where z is the distance measured from the leading edge of the susceptor, D is the diffusion coefficient, and V_0 is the entry velocity (Ref 62). The boundary layer width is proportional to the square root of z and inversely proportional to the square root of V_0.

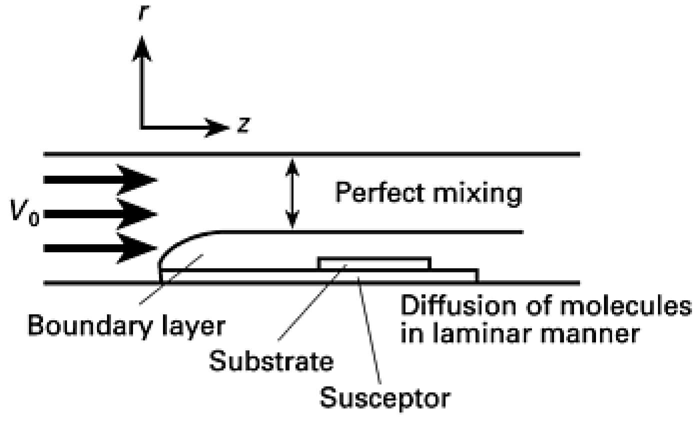

Fig. 6 Gas flow in a horizontal reactor

Effect of Substrate Heating. The introduction of heat adds another dimension of complexity to the gas flow, because convection is important in controlling gas flow along length of pipe. In a horizontal reactor chamber, the temperature difference from the chamber wall to the heated susceptor is enough to influence the flow of gas. When the thermal diffusivity is large and the temperature difference is small, the exchange of momentum is so fast, on a microscopic scale, that no real macroscopic gas-density gradients can develop. Hence, no buoyancy is observed, and the gas is said to be metastable. For higher temperature gradients and smaller heat diffusivities, the heavy, cold gas moves downward and the

light, hot gas near the susceptor moves upward. The buoyancy forces are so large that free convection occurs. The onset of free convection is characterized by the Rayleigh number, *Ra*:

$$\mathrm{R}a = \frac{a\, g C_p\, r^2 h^3 \Delta T}{h\, k} \qquad \textbf{(Eq 16)}$$

where α is the coefficient of thermal expansion in 1/K, *g* is the gravitational constant in m/s^2, C_p is the specific heat in J/kg · K, ρ is the gas density in kg/m^3, *h* is the free height above the susceptor in m, ΔT is the difference in temperature between the susceptor and the reactor wall, η is the dynamic viscosity in kg/ms, and *k* is the thermal conductivity in J/m · s · K). When *Ra* is less than or equal to 1700, the gas is stable. When *Ra* is greater than 1700, free convection occurs.

The flux, J_i, of a chemical species, μ_i, toward the susceptor surface now depends on the local temperature, the local temperature gradient, and the creation or annihilation of molecules during the reaction (Ref 63). Flux can be expressed as:

$$J_i = \frac{D_i}{RT}\left(\frac{P_1}{P_1 + (n-1)P_i}\frac{\partial P_i}{\partial z} + a\,\frac{\partial T}{\partial z} \right) \qquad \textbf{(Eq 17)}$$

where $D_i(T) = D_0(T/T_0)^2$ is the binary diffusion coefficient of species *i* as a function of *T, R* is a gas constant equal to 8.31 J/mol · K, P_t is the total pressure, P_i is the partial pressure of component *i*, *n* is the ratio of the number of molecules after and before the reaction, *z* is the direction normal to the susceptor surface, and α_i is the thermal diffusion factor for species *i*.

Modeling Gas Flow Patterns to Optimize Reactor Design. Two approaches are used to study gas flow patterns and the effect of reactor geometry on those patterns. The first approach is based on experimental observations, whereas the second is based on numerical calculation.

Flow patterns can be visualized by using smoke particles (Ref 64, 65, 66). Generally, titanium dioxide smoke is used. These experiments provide information about the existence of a boundary layer adjacent to the susceptor, the presence of temperature gradients perpendicular to the flow, and additional evidence of a convection-induced gas motion. Flow visualization experiments also provide a qualitative insight into the momentum transfer in the gas phase. The problem with a smoke test is that it does not give a clear boundary layer thickness, because smoke is heavier than the process gases.

Giling used holographic interference techniques to visualize temperature gradients (Ref 63). In this method, a light beam that passes through the reactor is compared with a reference beam that does not pass through the reactor. Small differences in the light paths become visible as interference patterns. If the flow is turbulent, then all fringe lines will move around, giving an incoherent image. When the flow is convective, the isotherms will be curved such that an upward or downward flow can be recognized. When the flow is laminar and stable against convection, fringes parallel to the hot surface will be formed. Giling analyzed flow images for hydrogen, nitrogen, argon, and helium carrier gases.

Berkman et al. (Ref 67) developed a detailed model of the flow dynamics, mass, and thermal gradients in a horizontal cold-walled reactor heated from below. The engineering formulas derived from hydrodynamic flow theories are easy to apply and correlate well with experimental observations.

There are two distinct zones above the susceptor in a reactor. The gas near the susceptor flows in a nearly laminar manner. Above that, the gas flow is turbulent, with oscillations of 3 to 5 Hz. The turbulence is caused by both thermal entry effects and buoyancy forces originating at the leading edge of the hot susceptor. The Berkman model treats the upper turbulent zone as a cold finger of well-mixed gas that acts as a reservoir of reactants. The lower zone acts like a laminar boundary layer, with a velocity profile that has average characteristics of both laminar and turbulent flow, through which the reactant is transported by diffusion. For a flat susceptor, the growth rate decreases exponentially along the susceptor as:

$$\exp(-Az) \qquad \textbf{(Eq 18)}$$

where

$$A = {2D_T}/{VTb_o^2} \quad \textbf{(Eq 19)}$$

and where V_T is the temperature-corrected gas velocity, D_T is the reactant diffusion coefficient at temperature T, and b_0 is the initial channel height above the susceptor. The exponential variation can be nullified by tilting the susceptor at an angle, θ_c (3 to 5°), such that:

$$\sin(q_c) = \frac{2D0}{b_0V_0}\left(\frac{T_a}{T_0}\right)^{0.88} \quad \textbf{(Eq 20)}$$

where D_0 is the diffusion coefficient of the precursor molecule measured at room temperature (T_0), T_a is the average temperature of the gas above the susceptor, and V_0 is the initial horizontal gas velocity at T_0 in front of the susceptor. Low-pressure MOCVD (~10 kPa, or 0.1 atm) increases V_0, allowing $\sin(\theta_c)$ to approach zero.

The rigorous simulation of mass transport in epitaxial systems involves solving the mass continuity equation and the Navier-Stokes equation of momentum conservation, according to the appropriate boundary conditions set by the geometry of the reactor, the heating method, and gas inlet and outlet flow (Ref 68). With the rapid advances in computation speed and memory over the last decade, numerical models have expanded from simple boundary-layer descriptions, to two-dimensional models, to three-dimensional descriptions of horizontal reactors (Ref 55).

The numerical modeling effort has focused on different reactor cells, such as return cells (Ref 69, 70), horizontal reactors (Ref 71, 72), and recirculation cells in the vertical reactor configuration (Ref 73, 74). The influence of inlet flow rate, pressure, and geometry on the flow pattern has been studied to understand the origin and nature of mixed-convection flows. Two-dimensional simulations of flow patterns have been generated for both horizontal and vertical reactor configurations (Ref 73, 74, 75).

The modeling of three-dimensional flow patterns for the growth of GaAs using TMGa and AsH_3 has been reported (Ref 55). The following boundary conditions were used to simplify the solution of the partial differential equations:

- No slip at solid walls
- Constant wall temperature or insulated side walls
- No flux on nonreacting surfaces or a flux balanced by the rate at which the species is incorporated into the growing film

Surface adsorptions are also considered in boundary conditions. The partial differential equations and the associated boundary conditions were transformed into a large set of nonlinear algebraic equations (on the order of 40,000 to 90,000) that were solved on a supercomputer using Newton's method.

References cited in this section

47. G.B. Stringfellow, *Crystal Growth of Electronic Materials,* E. Kaldis, Ed., Elsevier Science, 1985, p 247
48. G.B. Stringfellow, *Organometallic Vapor-Phase Epitaxy: Theory and Practice,* Academic Press, 1989, p 8, 18
49. J.H. Hildebrand, *J. Am. Chem. Soc.,* Vol 51, 1929, p 66
50. G.B. Stringfellow, *Semiconductors and Semimetals,* Vol 22A, W.T. Tsang, Ed., Academic Press, 1985, p 209
51. G.B. Stringfellow, *Inter. Rev. Science, Inorganic Chemistry,* Series 2, Vol 10, Butterworths, London, 1975, p 111-145
52. M. Razeghi, *The MOCVD Challenge,* A. Hilger, 1989, p 14
53. J.B. Mullin and D.T.J. Hurle, *J. Luminesc.,* Vol 7, 1973, p 176

54. A. Koukitu and H. Seki, *J. Cryst. Growth,* Vol 49, 1980, p 325
55. K.F. Jensen, *J. Cryst. Growth,* Vol 107, 1991, p 1-11
56. G.A. Hebner, K.P. Kileen, and R.M. Biefeld, *J. Cryst. Growth,* Vol 98, 1989, p 293
57. D.K. Gaskill, V. Kolubeyev, N. Bottka, R.S. Sillmon, and J.E. Butler, *J. Cryst. Growth,* Vol 93, 1988, p 127
58. C.A. Larsen, N.I. Buchan, and G.B. Stringfellow, *Appl. Phys. Lett.,* Vol 52, 1988, p 480
59. M. Yoshida, H. Watanabe, and F. Uesugi, *J. Electrochem. Soc.,* Vol 132, 1985, p 677
60. J.L. Fitzjohn and W.L. Holstein, *J. Electrochem. Soc.,* Vol 137, 1990, p 699
61. A.H. Shapiro, *Shape and Flow,* Heinemann, London, 1961
62. H. Schlicting, *Boundary Layer Theory,* 6th ed., McGraw-Hill, 1968
63. L.J. Giling, *Crystal Growth of Electronic Materials,* E. Kaldis, 1985, p 83
64. F.C. Eversteijn, *Philips Res. Rep.,* Vol 29, 1974, p 45
65. R. Takahashi, Y. Koga, and K. Sugawara, *J. Electrochem. Soc.,* Vol 119, 1972, p 1406
66. V.S. Ban, *J. Electrochem. Soc.,* Vol 125, 1978, p 317
67. S. Berkman, V.S. Ban, and N. Goldsmith, *Heterojunction Semiconductors for Electronic Devices,* G.W. Cullen and C.C. Wang, Ed., Springer, 1977, p 264
68. F. Rosenberger, *Fundamentals of Crystal Growth,* Springer-Verlag, Berlin, 1979
69. E.P. Visser, C.R. Kleijn, C.A.M. Govers, C.J. Hoogendoorn, and L.J. Giling, *J. Cryst. Growth,* Vol 95, 1989, p 929
70. D.I. Fotiadis, M. Boekholt, K.F. Jensen, and W. Richter, *J. Cryst. Growth,* Vol 100, 1990, p 577
71. J. Quazzani and F. Rosenberger, *J. Crys. Growth,* Vol 100, 1990, p 545
72. H.K. Moffat and K.F. Jensen, *J. Electrochem. Soc.,* Vol 135, 1988, p 459
73. S. Patnaik, R.A. Brown, and C.A. Wang, *J. Cryst. Growth,* Vol 96, 1989, p 153
74. D.I. Fotiadis, S. Kieda, and K.F. Jensen, *J. Cryst. Growth,* Vol 102, 1990, p 441
75. K.F. Jensen, *J. Cryst. Growth,* Vol 98, 1989, p 148

The MOCVD Growth Technique

This section describes not only the reactor systems and hardware, but the engineering considerations that optimize growth, the MOCVD starting materials, and the growth parameters for a variety of Group III-V, II-VI, and IV semiconductors.

Reactor Systems and Hardware

The growth of Group III-V or II-VI compound semiconductors is achieved by introducing source materials into a reaction chamber (quartz tube or stainless steel) that contains a substrate on a heated susceptor. The hot susceptor has a catalytic effect on the decomposition of the gaseous products. Therefore, growth occurs primarily on this hot surface A typical MOCVD system (Fig. 1) consists of a gas-handling system, a reactor chamber, a heating system for pyrolysis temperatures, and an exhaust system and safety apparatus.

The purpose of the gas-handling system is to deliver the source alkyls and hydrides to the reaction chamber in precise, measured amounts. Gas manifolds, valves, flow controllers, and vacuum pumps are necessary to control the flow and mixture of gas. To grow high-quality layers, the gas-handling system must be clean. Stainless steel tubes are used to transport alkyls from the source to the reactor chamber, and electronic mass-flow controllers and thermal bath systems deliver precisely controlled amounts of gas.

Starting-material purity is one of the most important issues in modern semiconductor technology. Every material used in an MOCVD process is purified to avoid any kind of contamination. Gases used in an MOCVD reactor, including hydrogen, nitrogen, and helium carrier gases, can introduce contaminants to the semiconductor films. Contaminants can also be introduced by following improper procedures for gas-cylinder changing and vacuum-system maintenance.

Tubing, fitting, and valve selection is essential for the growth of high-purity films. Because some of the metal-organic sources and gases used in MOCVD are highly corrosive, components must be constructed of corrosion-resistant

materials. Most MOCVD reactors use seamless 316 stainless steel tubing that has been electropolished inside. Selecting the proper gasket materials in fittings and valves is equally important. More information on the selection of tubes and fittings is given in Ref 76.

Hydrogen Purifier. The standard purity of the hydrogen supplied by many gas companies is 99.99 vol%. The major impurities are oxygen and water. Standard purity is inadequate for the growth of high-quality semiconductors. Research-grade hydrogen gas, with a purity on the order of 99.9995 vol%, is an expensive solution. The normal practice is to use standard-purity hydrogen gas that is run through a purifier at the point of delivery. Besides economics, this approach minimizes any water contamination introduced in the tubing between the cylinder and purifier.

In a hydrogen purifier, the impure hydrogen is passed through a palladium alloy membrane that serves as the diffusion medium. The palladium is inside a cell, which is heated to between 400 and 425 °C (750 and 800 °F). At these temperatures, only hydrogen diffuses through the membrane; all other elements are blocked. This type of purifier effectively delivers ultra-pure hydrogen gas to the system.

Thermal Bath. The vapor pressure of metal-organic sources is a sensitive function of temperature. To ensure controlled and reproducible source delivery, the source must be kept in a well-regulated thermal bath. Commercial thermal baths are able to control the temperature with an accuracy of ±0.1 °C (0.2 °F). Temperatures can be varied in the range of -30 to 100 °C (-20 to 210 °F).

Electronic mass-flow controllers are used to regulate the amount of gas flowing into the chamber. The carrier gas flows through the metal-organic bubbler to transport the source vapor into the chamber. Gaseous hydrides are delivered directly. Each must be precisely controlled to dictate the composition of the semiconductor film. Mass-flow controllers use a closed-loop control system that compares the requested flow to the actual flow and adjusts accordingly. The typical accuracy of a mass-flow controller is ±1% of full scale. A significant advantage of electronic mass-flow controllers is the ease of automation and programming for the growth of individual layers. Mass-flow controllers from various vendors operate under different physical principles. Each has different strengths and weaknesses with respect to calibration, drift, temporal response, and maintenance.

The gas-mixing manifold is an important component of the MOCVD system. The proper design of this manifold is crucial for growing superlattices and quantum-well structures, and for reducing the memory effect associated with some dopant sources (Ref 77). Because the manifold must not introduce additional contaminants into the system, it is constructed of electropolished stainless steel tubing. Welding is used in lieu of compression fittings to avoid leakage. Because the manifold also must deliver uniformly mixed gases to the reactor, it is connected both directly to the chamber and through a bypass line to the exhaust. A process flow is first established and stabilized through the bypass line before being introduced into the chamber. The gas manifold utilizes pneumatically actuated valves to permit process automation.

Susceptor Heat System. Any of three types of heating methods are used to heat the susceptor: radio-frequency (RF) induction heating, radiant heating, and resistance heating. In RF induction heating, the graphite or silicon-carbide graphite susceptor is inductively coupled to an RF coil. This type of heating, which is used in big industrial reactors, is usually very complex. In order to avoid the complexity of RF heating, radiant heating is often used. Here the graphite susceptor is heated by absorbing the radiant energy from lamps. In resistance heating, metallic susceptors (aluminum and molybdenum) are heated by the resistance to electrical current flow. The temperature of the susceptor can be measured by using embedded thermocouples or a pyrometer. The temperature of the substrate on the susceptor usually cannot be measured directly, but is less than the susceptor temperature because of poor thermal contact.

The exhaust system is the most critical part of the MOCVD configuration in terms of safety. The two main functions of this system are to remove unreacted gases and byproducts from the reaction chamber and to provide a path for reactants to bypass the reaction zone. Unreacted gases can react in the exhaust system, creating solid particles. Because these particles can collect and block the exhaust system, great care must be taken to remove them. In addition, a blocked exhaust line can lead to sudden pressure changes in the reactor, creating a back diffusion of particles, which affects the growth quality and uniformity. The vented gas can contain unreacted sources that may be toxic, pyrophoric, or flammable. Various cleaning systems are available, such as scrubbing systems, particle filters, and burn boxes.

Effluent Scrubbing Systems. The semiconductor wafer fabrication industry uses a variety of corrosive, toxic, pyrophoric, and flammable chemicals. In order to control pollution by toxic materials, different types of scrubbers are used. In the past, it was commonly believed that many chemicals could be released into the environment without hazard if they were diluted to a safe concentration level, as determined by a regulating agency and dictated by the detection limits

of instrumentation or standards developed in response to exposure risks at the release site. The function of a scrubber was simply to reduce the concentration of contaminants produced to "safe levels." However, scientists have since demonstrated the negative impact of environmental contaminants at ever-diminishing levels. As a result, there has been a shift from scrubbers that simply dilute process gases to a new type of scrubber that can capture, isolate, and transform pollutants before allowing them to reach the environment.

As an example, a typical process for the epitaxial deposition of silicon requires the reaction of dichlorosilane (SiH_2Cl_2) and AsH_3. The scrubber is designed to remove the unreacted process gases in two stages. In the first stage, water removes unreacted SiH_2Cl by converting it to a complex mixture of solid silicon oxides. At the same time, hydrochloric acid (HCl) dissolves in the water and then exits the scrubber as aqueous HCl, which is neutralized. This reaction is summarized as:

$$SiH_2Cl_2 + AsH_3 + HCl \xrightarrow{H_2O} (SiO_2)_x + HCl_{(aq)} + AsH_3 + H_2 \qquad \textbf{(Eq 21)}$$

In the second stage, an oxidizing agent (e.g., potassium permanganate solution) oxides the arsenic to a solid residue, which then can be safely recovered for recycling. This reaction is written as:

$$AsH_3 + H_2 \xrightarrow{KMnO_{4(aq)}} As_2O_5 + MnO_2 + H_2 \qquad \textbf{(Eq 22)}$$

Because the solution used to remove toxic gases is expensive and its disposal difficult, scrubbers that use solid agents have been developed. By utilizing activated carbon, the toxic compounds from the effluent stream of MOCVD processes are adsorbed. In addition, controlled oxidation turns potentially harmful gases into solid oxides that have safer and easier disposal methods. This solid scrubbing is preferable to other methods, such as liquid scrubbers, burn boxes, and incinerators, which can cause back streaming or produce byproducts that are not wanted or have excessive disposal costs.

Burn boxes represent another way to dispose of unreacted materials from the exhaust. These boxes contain a furnace heated to a high temperature (900 to 1000 °C, or 1650 to 1830 °F), which cracks and oxidizes unreacted materials into less harmful compounds. Radical reaction products also condense on the quartz tube walls and are then removed as solids.

Particulate filters are used in conjunction with burn boxes or in front of pumping systems in low-pressure MOCVD systems. They must be able to remove particulates, resist clogging, minimize the exposure of maintenance personnel to arsenic dust, and contribute minimal internal outgassing.

Toxic-Gas Detectors. In the mid-1990s, almost all Group III-V growth systems use toxic gases such as AsH_3 and PH_3. Monitoring systems that are used to detect the presence of both AsH_3 and PH_3 provide a nearly instantaneous readout of concentration and initiate both warning and alarm signals whenever the preprogrammed concentration level for a particular gas and location is exceeded.

The solid-state gas sensors contain a heated resistor that is supplied with a specific voltage. When a gas enters the sensor, a voltage change is sensed because of the change in resistance. This voltage change is proportional to the concentration of the detected gas. The voltage is precalibrated in the factory for different gases and corresponding concentrations. The warning and alarm signals are set by the users, based on the safety level of each gas. Other types of toxic-gas detectors use chemically treated tape. Although they are more sensitive, they do not respond as quickly as solid-state detectors.

Engineering Considerations to Optimize Growth

Based on the study by Giling, as well as MOCVD growth practices (Ref 52), certain parameters are recommended for the growth of high-quality Group III-V semiconductor materials with sharp interfaces. First, laminar flows that are free of convection should exist by using a horizontal reactor, working at low pressure, and decreasing the reactor diameter. Second, temperature gradient should be present across the susceptor. Third, the memory effect should be eliminated by reactor geometries that prevent the development of vortices, and present no dead volumes. These conditions are designed to avoid parasitic reactions in the gas phase and condensation at the inlet of the deposition zone. Dead volumes should be avoided because they and the vortices will act as sources of unwanted materials that cannot be removed easily.

There have been at least 60 publications since the mid-1970s on the design of reactor cells and configurations. The essential factors in the design of horizontal cells have been established more recently (Ref 78, 79, 80, 81, 82, 83, 84). The ability to grow highly uniform compound semiconductors by MOCVD is influenced by a number of parameters in the

gas-handling manifold and the growth cell. Several reactor design modifications have been reported to improve uniformity. First, the manifold must incorporate a pressure-balanced vent-run system (Ref 78). In addition, gas mixing must occur on the atomic level to ensure sufficient homogeneity across the susceptor. Compositional nonuniformity is eliminated by using a variety of gas-mixing devices (Ref 85), including vanes, meshes, mixing jets, spray tubes, silica frits and orifices, and perforated plates that are either stationary or rotating (Ref 78). The expansion region must prevent flow separation from the cell walls that leads to recirculation, upstream deposition, and nonuniform layers (Ref 70, 84, 86, 87, 88, 89, 90). The space between the substrate and reactor wall must be small enough to prevent return flow (Ref 70).

To overcome gas-phase depletion and geometrical effects, the substrate can be rotated (Ref 91, 92, 93, 94). Another approach to this engineering problem is to levitate the wafer carrier on a gas foil (Ref 92). To avoid parasitic gas reactions and to improve layer quality (Ref 95), some reactors use two separate inlets.

The understanding of the MOCVD process, including gas flow patterns and chemical-reaction pathways, is still immature. Growth parameters, such as temperature, pressure, total gas flow, and Group III/V ratio, are optimized empirically. Material is grown and characterized by ex-situ techniques. These results are correlated with the deposition conditions to predict the best processing parameters.

MOCVD Starting Materials

The alkyls of Group II and III metals and the hydrides of Group V and VI elements are generally used as precursors in MOCVD. Dilute vapors of these chemicals are transported at or near room temperature to a hot zone, where pyrolysis reactions occur. For example, GaAs is formed by heating trimethylgallium, $(CH_3)3Ga$, or triethylgallium, $(C_2H_5)3Ga$, and AsH_3 over a suitable substrate, usually a single crystal of GaAs or silicon, at temperatures near 600 °C (1110 °F). The decomposition reactions can be expressed as:

$$(C_2H_5)_3Ga + AsH_3 \rightarrow GaAs + 3C_2H_6 \quad \textbf{(Eq 23)}$$

$$(CH_3)_3Ga + AsH_3 \rightarrow GaAs + 3CH_4 \quad \textbf{(Eq 24)}$$

The reaction for Group III-V compounds can be generalized as:

$$R_3M + EH_3 \rightarrow ME + 3RH \quad \textbf{(Eq 25)}$$

where *M* is the Group III metal (such as gallium, indium, or aluminum), *E* is the Group V element (such as arsenic, phosphorus, or antimony), and *R* is the alkyl radical (either CH_3 or C_2H_5).

Acceptable starting materials for MOCVD must be stable at room temperature and must not spontaneously decompose or polymerize. They also must vaporize in hydrogen, nitrogen, or helium gases without decomposing, be capable of purification, and have the lowest possible toxicity. Suitable starting materials and their physical properties are listed in Table 2. Each item in this table is either an alloy constituent or a dopant. Group III-V source materials will be discussed in detail, because they are primarily used in optoelectronic and high-frequency device applications.

Table 2 Physical properties of selected metal-organic materials used in metal-organic chemical vapor deposition

Compound	Formula	Abbreviation	Melting point		Boiling point		Log_{10} vapor pressure, Pa (torr); Temperature, *T*, in kelvin	Pressure, Pa (torr); Temperature, *T*, in kelvin
			°C	°F	°C	°F		
Group II sources								
Diethylberyllium	$(C_2H_5)_2Be$	DEBe	12	54	194	381	1012 (7.59); *T*,	. . .

							2200	
Dimethylberyllium	$(CH_3)_2Be$	DMBe	. . .	. . .	. . .	. . .	. . .	. . .
Bis(cyclopentadienyl)magnesium	$(C_5H_5)_2Mg$	Cp_2Mg	176	349	. . .	. . .	3351 (25.14); *T*, 4198[a]	1.33 (0.01); *T*, 273
Group IIB sources								
Dimethylzinc	$(CH_3)_2Zn$	DMZn	-42	-44	46	115	1040 (7.802); *T*, 1560	16,529 (124); *T*, 273[b]
Diethylzinc	$(C_2H_5)_2Zn$	DEZn	-28	-18	118	244	1104 (8.280); *T*, 2190	480 (3.6); *T*, 273[c]
Dimethylcadmium	$(CH_3)_2Cd$	DMCd	-4.5	24	105.5	222	1035 (7.764); *T*, 1850	1293 (9.7); *T*, 273[d]
Group III sources								
Trimethylaluminum	$(CH_3)_3Al$	TMAl	15.4	59.7	126	259	1096 (8.224); *T*, 2134	293 (2.2); *T*, 273[e]
Triethylaluminum	$(C_2H_5)_3Al$	TEAl	-58	-72	194	381	1438 (10.784); *T*, 3625	67 (0.5); *T*, 328
Trimethylgallium	$(CH_3)_3Ga$	TMGa	-15.4	4.28	55.7	132	1075 (8.07); *T*, 1703	8598 (64.5); *T*, 273[f]
Triethylgallium	$(C_2H_5)_3Ga$	TEGa	-82.3	-116	143	289	1096 (8.224); *T*, 2222	453 (3.4); *T*, 293[g]
Trimethylindium	$(CH_3)_3In$	TMIn	88.4	191	133.8	272.8	1402 (10.520); *T*, 3014	40 (0.3); *T*, 273[h]
Triethylindium	$(C_2H_5)_3In$	TEIn	-32	-26	184	363	160 (1.2); . . .	160 (1.2); *T*, 313
Dimethylaluminum hydride	$(CH_3)_2AlH$	DMAlH	. . .	. . .	154	309	1189 (8.92); *T*, 2575	267 (2); *T*, 298
Triisobutylgallium	$(C_4H_9)_3Ga$	TIBGa	. . .	. . .	. . .	. . .	636 (4.769); *T*, 1718	67 (0.5); *T*, 310
Group III adducts								

Trimethylindium-trimethyl nitrogen	. . .	TMIn-TMN	94-96	201-205	. . .	. . .	. . .	0.4 (0.003); *T*, 273[i]
Trimethylindium-trimethylphosphorus	. . .	TMIn-TMP	43-45	109-113	. . .	. . .	. . .	5.3 (0.04); *T*, 273[j]
Trimethylindium-triethylphosphorus	. . .	TMIn-TEP	33-36	91-97	. . .	. . .	. . .	0.05 (0.0004); *T*, 273[k]
Trimethylindium-trimethylarsenic	. . .	TMIn-TMAs	28-29	82-84	. . .	. . .	. . .	36 (0.27); *T*, 273[l]
Group IV sources								
Tetramethylgermanium	$(CH_3)_4Ge$	TMGe	-88	-126	43.6	110.5	18.529 (139); . . .	. . .
Tetramethyltin	$(CH_3)_4Sn$	TMSn	-53	-63	78	172	999 (7.495); *T*, 1620	. . .
Tetraethyltin	$(C_2H_5)_4Sn$	TESn	-112	-170	181	357	. . .	. . .
Group V sources								
Trimethylphosphorus	$(CH_3)_3P$	TMP	-85	-120	37.8	100	1031 (7.7329); *T*, 1512	50.787 (381); *T*, 293
Triethylphosphorus	$(C_2H_5)_3P$	TEP	-88	-126	127	260	1048 (7.86); *T*, 2000	6198 (46.5); *T*, 323
Trimethylarsenic	$(CH_3)_3As$	TMAs	-87.3	-125	50-52	122-126	1028 (7.7119); *T*, 1563	31,725 (238); *T*, 293
Triethylarsenic	$(C_2H_5)_3As$	TEAs	-91	-132	140	284	2066 (15.5); . . .	666 (5); *T*, 293[m]
Trimethylantimony	$(CH_3)_3Sb$	TMSb	-86.7	-124	80.6	177.1	1030 (7.7280); *T*, 1709	. . .
Triethylantimony	$(C_2H_5)_3Sb$	TESb	-98	-144	116	240	2266 (17); . . .	533 (4); *T*, 298
Isobutylphosphine	. . .	IBP	-20	-4	78	172	1010 (7.578); *T*, 1648	14,930 (112); *T*, 298

Tertiarybutylphosphine	. . .	TBP	4	39	54	129	1004 (7.532); *T*, 1443	23,460 (176); *T*, 273
Dimethylarsenic	$(CH_3)_2As$	DMAs	. . .	. . .	36.3	97.3	978 (7.339); *T*, 1680	5332 (40); *T*, 293
Diethylarsenic	$(C_2H_5)_2As$	DEAs	. . .	. . .	102	216	965 (7.243); *T*, 1509	10,797 (81); *T*, 283
Tertiarybutylarsenic	. . .	TBAs	-1	30	65	149	1129 (8.47); *T*, 2410	240 (1.8); *T*, 293
Phenylarsine	. . .	$PhAsH_2$	. . .	. . .	. . .	. . .	. . .	. . .
Group VI sources								
Diethylselenium	$(C_2H_5)_2Se$	DESe	. . .	. . .	108.00	226	. . .	. . .
Dimethyltellurium	$(CH_3)_2Te$	DMTe	-10	14	82.00	180	1062 (7.97); *T*, 1865	(65); *T*, 303
Diethyltellurium	$(C_2H_5)_2Te$	DETe	. . .	. . .	137-138	278-280	1065 (7.99); *T*, 2093	(12); *T*, 303

Source: Ref 48, 96

(a) ln *T*, 2.18.

(b) 40,790 Pa (306 torr); *T*, 293 K.

(c) 2000 Pa (15 torr); *T*, 293 K.

(d) 3732 Pa (28 torr); *T*, 293 K.

(e) 1200 Pa (9 torr); *T*, 293 K.

(f) 23,727 Pa (178 torr); *T*, 293 K.

(g) 2133 Pa (16 torr); *T*, 316 K.

(h) 227 Pa (1.7 torr); *T*, 293 K.

(i) 4 Pa (0.03 torr); *T*, 293 K.

(j) 29 Pa (0.22 torr); *T*, 293 K.

(k) 0.4 Pa (0.003 torr); *T*, 293 K.

(l) 160 Pa (1.2 torr); *T*, 293 K.

(m) 2066 Pa (15.5 torr); *T*, 310.

Group III Sources. Trimethyl and triethyl alkyls have been used exclusively in the early development of MOCVD. The trimethyl sources are used most often because of their high vapor pressure and good stability. The triethyl sources, such as triethylaluminum (TEAl), triethylgallium (TEGa), and triethylindium (TEIn), are only marginally stable. The latter material has been observed to decompose in storage containers. It was also discovered that TEIn reacts with the Group V hydrides, AsH_3 and PH_3, to form nonvolatile adducts upstream from the substrates (Ref 50) in atmospheric-pressure MOCVD reactors. However, in low-pressure MOCVD reactors, TEGa and TEAl were used successfully to reduce the carbon concentrations in GaAs and AlGaAs (Ref 97). These materials evidently pyrolyze without producing the highly reactive methyl radicals that are generally believed to be the main source of carbon in the epitaxial layers. Recently, triisobutylgallium (TIBGa), which has an even lower thermal stability than TEGa, has been used to grow GaAs (Ref 98).

Trimethylindium is currently the most widely used source of indium. It avoids the stability problems associated with the use of TEIn. Parasitic reactions are not observed in atmospheric-pressure MOCVD growth when TMIn is used. However, TMIn has a nonuniform evaporation rate, because it is a solid at room temperature. It also has a tendency to explode. Alternative indium sources that are liquid below room temperature, have adequate vapor pressure, and exhibit good chemical stability are still being sought.

Knauf et al. combined the advantages of TMIn (less parasitic reactions) with those of TEIn (liquid during use) by producing a new compound, ethyldimethylindium (EDMIn) (Ref 99). This material is liquid at room temperature and has a vapor pressure of 115 Pa (0.85 torr) at 17 °C (63 °F), which is similar to the value for TMIn at 135 Pa (1 torr) and an order of magnitude greater than the vapor pressure of TEIn. In early experiments, EDMIn was not as pure as TMIn. However, it is now available in high-purity form, which makes it an attractive indium source.

The growth of semiconductors containing aluminum has always been difficult because aluminum is highly reactive and readily incorporates carbon and oxygen into the solid (Ref 100). The incorporation of carbon is particularly likely when trimethylaluminum (TMAl) is used, because it pyrolyzes to form aluminum carbide. Other alkyl sources, such as triethylaluminum (TEAl) and triisobutylaluminum (TIBAl), which decompose to aluminum metal, can be used to minimize carbon incorporation. However, they have low vapor pressures at room temperature. Heating to increase the vapor pressure requires that the gas lines and the reactor tube be heated along with the source. In addition, these compounds are not sufficiently stable to be effective. Kuech et al. has reported reduced growth efficiency, when these compounds are compared with other sources (Ref 97). This indicates the occurrence of parasitic reactions, predominantly premature pyrolysis, that create wall deposits upstream from the substrate. The most unstable of these compounds is TIBAl, which can decompose in storage containers at room temperature.

In order to provide an acceptable source of aluminum, new molecules with the appropriate properties must be developed. Dimethylaluminumhydride (DMAlH) has an acceptable vapor pressure of 265 Pa (2 torr) at 25 °C (77 °F) and pyrolyzes at a temperature as low as 250 °C (480 °F) (Ref 101). Both AES and SIMS analyses of films grown from DMAlH indicate little carbon contamination. It has been shown that DMAlH can produce excellent aluminum gallium arsenide (AlGaAs) epitaxial layers. The only problem is that the layers have a high background doping level, with an approximate *n*-type carrier concentration of $2 \times 10^{18}/cm^3$ ($33 \times 10^{18}/in.^3$). The background doping level is due to silicon and sulfur impurities in the DMAlH source. Preliminary photoluminescence data indicate that the carbon concentration is substantially less than levels produced in layers grown from TMAl.

Alternative sources for the MOCVD growth of Group III-V compounds are adducts. An adduct is a compound formed between a Group III alkyl, such as MR_3, that acts as an electron-acceptor molecule (Lewis acid) and a Group V alkyl, such as ER_3, that acts as an electron-donor molecule (Lewis base), according to the following reaction:

$$MR_3 + ER_3 \rightarrow R_3MER_3 \qquad \textbf{(Eq 26)}$$

Adducts were first proposed by Harrison and Tompkins for the growth of indium antimonide (InSb) and GaAs (Ref 102).

Since 1980, acid-base adducts, for example, TMIn-triethylphosphine (TEP) (Ref 103) and TMIn-trimethylphosphine (TMP) (Ref 104), have been used as alternative metal sources to eliminate parasitic reactions in the atmospheric-pressure MOCVD growth of InP (Ref 105, 106, 107). Adducts produce fewer parasitic reactions because of their high chemical stability. Today, trimethyl and triethyl alkyls produce less parasitic reactions because of their higher purity and improved, safer handling facilities. Nevertheless, the adducts are still used in many laboratories to produce high-quality InP (Ref 107, 108), GaInAs on InP quantum-well structures (Ref 109), and InP on silicon layers (Ref 106). The films exhibit almost the same quality and background doping levels as films grown from the alkyls using the same deposition conditions. The main advantages of adducts are their low reactivity with oxygen and water vapor, and their liquid form at room temperature. The adduct TEGa-TEP is used in place of TEGa because of its higher vapor pressure, compared to the gallium alkyls (Ref 110). The indium adducts, however, have rather low vapor pressures. They are normally used at temperatures above 60 °C (140 °F), and the gas lines of the MOCVD system must be heated to prevent condensation.

The development of new precursors with tailored physiochemical properties (vapor pressure, melting point, stability) is an emerging field of research. New, intramolecularly saturated dimethyl-3-dimethylaminopropylindium $(CH_3)_2In(CH_2)3N(CH_3)_2$ and the adduct trimethylindium-diisopropylamine, $(CH_3)3In\text{-}NH(C_3H_7)_2$, have been synthesized (Ref 111). The first epitaxial results with these compounds are very promising. Indium phosphide layers with electron mobilities of 50,000 $cm^2/V \cdot s$ (7750 $in.^2/V \cdot s$) at 77 K have been produced. Aluminum- and gallium-based semiconductors also have been successfully grown using these new sources. Moreover, such sources are expected to reduce carbon incorporation when combined with organometallic Group V sources, because they can be cracked to form stable organic molecules even in the absence of atomic hydrogen. For less stable organometallics, carbon incorporation seems to be lower. Plass et al. have employed TlBGa as a starting material, but impurities in the source caused the resulting layers to show a relatively high n-type conduction (Ref 98). Another type of alternative source has been investigated in order to provide a single source for both the metal and the Group V element. Maury et al. successfully grew GaAs layers using $(ClMe_2Ga\text{-}AsEt_2)_2CH_2$ and $(C_6F_5)_3Ga\text{-}AsEt_3$ without an additional arsenic source (Ref 112, 113, 114, 115, 116). However, the importance of such compounds is limited to the growth of binary materials. For atomic-layer epitaxy by MOCVD, More and Sasaoka et al. used $Ga(C_2H_5)_2Cl$ as a starting material (Ref 117, 118). Such reactants have not previously been used in a normal MOCVD process.

Group V Sources. The hydride gases commonly used as precursors for Group V elements are extremely hazardous and toxic. Both AsH_3 and PH_3 have threshold level values of 0.05 and 0.3 ppm, respectively. A summary of the effects on human exposure to arsenic and phosphorus hydrides is given by Hess and Riccio (Ref 119). In addition, these gases must be stored in high-pressure cylinders (equilibrium vapor pressures at 20 °C, or 70 °F, are 140 and 410 kPa, or 14 and 41 bars, for arsine and phosphine, respectively). Consequently, large quantities of these toxic gases may accidentally be released in a very short time. They must be handled very carefully, especially when changing cylinders. Thus, the utilization of AsH_3 and PH_3 requires costly and delicate equipment to protect the operators and the environment from hazards, and the products from atmospheric contamination. Less toxic and hazardous alternative sources are desired for safety reasons. A number of organometallic Group V sources are less toxic than the hydrides. Another advantage of the organometallic sources is that they have moderate vapor pressures. This results in a less hazardous working environment, because computer studies show that the dispersion of these materials is approximately two orders of magnitude slower than for the release of gases from high-pressure cylinders. A good review of nonhydride Group V sources is provided by Stringfellow (Ref 120).

Finding alternatives to the highly toxic AsH_3 has been the subject of recent research. Organoarsenic materials normally have much lower vapor pressures and threshold level values, which enable safer handling (Ref 121). The commonly used reactants are trimethylarsenic (TMAs) (Ref 122, 123) and triethylarsenic (TEAs). (Ref 52, 120, 122, 123, 124, 125). It was shown that TEAs is less stable than AsH_3 under normal growth conditions, enabling lower Group V-III ratios in the MOCVD process. However, in most cases, carbon incorporation is significant ($\geq 5 \times 10^{16}/cm^3$) (Ref 80, 126). In addition, epitaxial layer morphology is inferior, probably because of the incorporation of carbon and other atomic or molecular impurities.

Other materials, such as tertiarybutylarsine (TBAs) (Ref 30, 122, 127, 128), isobutylarsine (IBAs) (Ref 29, 129), dimethylarsine (DMAsH) (Ref 130), diethylarsine (DEAsH) (Ref 105), and phenylarsine ($PhAsH_2$) (Ref 122), have been used to overcome this problem. Some of them, especially TBAs and $PhAsH_2$, have shown promising results (Ref 30, 128). Most of the organoarsenic compounds mentioned above are commercially available. In addition to excess carbon incorporation, other disadvantages include their limited purity and high cost. The use of elemental arsenic seems to be unsuitable for a reliable epitaxial process (Ref 131).

Alternative phosphorus sources are also desired to minimize toxic waste and safety hazards. Initially, experiments were carried out using TMP and triethylphosphine TEP (Ref 132). However, they must be precracked before being introduced to the growth chamber because of their high thermal stability. This rather nonreproducible technique is therefore not suitable for MOCVD. The same holds true for elemental phosphorus sources, which were investigated by Naitoh et al. (Ref 133).

Larger organophosphorus molecules, such as TBP and IBP, have exhibited better growth results (Ref 28, 134, 135, 136). Tertiarybutylphosphine, in particular, has a favorable vapor pressure and is found to pyrolyze several hundred degrees lower than PH_3 (Ref 134). This can be an advantage when growing quaternary compounds (e.g., InGaAsP), which require arsenic and phosphorus sources with comparable thermal stability. Because the toxicity of TBP is much lower than that of PH_3, it is a good candidate for future investigations (Ref 120).

Group III-V Semiconductor Growth Parameters

Group III-V semiconductors are the major materials used in optoelectronic and high-frequency electronic device applications. The ability to tailor the band structure and lattice constant in ternary and quaternary alloys by varying the composition represents one of the desirable features of these materials.

The GaAs-based materials described below include not only GaAs, but gallium indium phosphide (GaInP), gallium aluminum arsenide (GaAlAs), and gallium indium arsenide phosphide (GaInAsP).

GaAs layers can be grown either at atmospheric or low pressure in the temperature range from 500 to 550 °C (Ref 52). TEGa or TMGa and AsH_3 have been used as gallium and arsenic sources. Pure hydrogen can be used as a carrier gas. The growth rate depends linearly on the flow rate of Group III (gallium) elements and is independent of AsH_3 flow rate, substrate temperature, and substrate orientation. This suggests that epitaxial growth is controlled by the mass transport of Group III species.

The growth of GaAs layers has been carried out on <100> GaAs substrates misoriented up to 2° toward the <011> plane. The substrates were etched in a H_2SO_4:H_2O_2:H_2O (5:1:1) solution for 20 s at 40 °C (105 °F), rinsed with deionized water, and dried under pure nitrogen. Before the growth process, the substrates were initially heated to the growth temperature under hydrogen and AsH_3 for 5 min to remove any surface oxides. Table 3 lists the optimum conditions for the low-pressure MOCVD growth of GaAs.

Table 3 Optimum growth conditions of gallium arsenide (GaAs), gallium indium phosphide (GaInP), and gallium indium arsenide phosphide (GaInAsP)

	GaAs	$Ga_{0.51}In_{0.49}P$	$Ga_{0.87}In_{0.13}As_{0.73}P_{0.27}$
Growth pressure, Pa (torr)	10,130 (76)	10,130 (76)	10,130 (76)
Growth temperature, °C (°F)	510 (950)	510 (950)	510 (950)
Total hydrogen flow rate, L/min (gal/min)	3 (0.8)	3 (0.8)	3 (0.8)
Arsine, cm^3/min ($in.^3$/min)	30 (1.8)	. . .	20 (1.2)

Trimethylindium, cm^3/min ($in.^3/min$)	. . .	200 (12)	150 (9)
Triethylgallium, cm^3/min ($in.^3/min$)	120 (7)	120 (7)	170 (10)
Phosphine, cm^3/min ($in.^3/min$)	. . .	300 (18)	200 (390)
Growth rate, nm/min (μin./min)	15 (0.6)	20 (0.8)	25 (1.0)

Note: For 808 nm (31.5 μin.) materials

Epitaxial GaAs layers are of the *n*-type in a wide range of Group V/III ratios and substrate temperatures. Suitable conditions, such as growth temperature, growth rate, total flow rate, purity of starting materials, and reactor design, are responsible for the high quality of the epitaxial layers.

GaInP layers can be grown on GaAs using MOCVD, either at atmospheric pressure or low pressure, in the temperature range from 500 to 600 °C (930 to 1110 °F) (Ref 137). Different Group III alkyls can be used for gallium and indium sources, whereas hydrides or alkyls can be used for the Group V phosphorus source. Chemical reactions that occur among these sources are:

$$0.51R_3Ga + 0.49\,R'_3In + EH_3 \text{-} Ga_{0.51}In_{0.49}P + nC_nH_{2n} \qquad \textbf{(Eq 27)}$$

where *R*, *R*', and *E* can be methyl, ethyl, alkyl, or hydride.

For example, one can use:

$$0.49(C_2H_5)_3In + 0.51(C_2H_5)_3Ga + PH_3 \rightarrow InGaP + nC_2H_6\text{, or} \qquad \textbf{(Eq 28)}$$

$$0.49(CH_3)_3In + 0.51(CH_3)_3Ga + PH_3 \rightarrow InGaP + nCH_4\text{, or} \qquad \textbf{(Eq 29)}$$

$$0.49(CH_3)_3In + 0.51(C_2H_5)_3Ga + PH_3 \rightarrow InGaP + nC_2H_6\text{, or} \qquad \textbf{(Eq 30)}$$

$$0.49(C_2H_5)_3In + 0.51(CH_3)_3Ga + PH_3 \rightarrow InGaP + nC_2H_6 \qquad \textbf{(Eq 31)}$$

The GaInP layers can be grown at the lower temperatures of 500 to 550 °C (930 to 1020 °F), by using TEGa, TMIn, and PH_3 in a hydrogen carrier gas. At optimum conditions (Table 3), the growth rate (dx/dt) of GaInP depends on the flow rates of TMIn and TEGa and is independent of the PH_3 flow rate and growth temperature. The undoped GaInP layer grown as specified has a free electron carrier concentration of $5 \times 10^{14}/cm^3$ ($80 \times 10^{14}/in.^3$), with a mobility of 6000 $cm^2/V \cdot s$ (930 $in.^2/V \cdot s$) at 300 K and 40,000 $cm^2/V \cdot s$ (6200 $in.^2/V \cdot s$) at 77 K. No GaAs buffer layer was grown in this case.

GaAlAs layers can be grown on a GaAs substrate in the temperature range of 600 to 750 °C (1110 to 1380 °F) by using TMGa, TMAl, and AsH_3 as the sources of gallium, aluminum, and arsenic, respectively. Oxygen incorporation, produced by the strong reactivity of aluminum with oxygen, can deteriorate the optical and electrical properties of the GaAlAs epitaxial layer (Ref 138). To solve this problem, graphite baffles are used for internal gettering. They absorb TMAl, which then reacts with oxygen to form the extremely stable, nonvolatile Al_2O_3 (Ref 139). It was later discovered that high-quality aluminum gallium arsenide (AlGaAs) can be grown at higher temperatures (<780 °C, or 1440 °F) without using oxygen-gettering techniques (Ref 140). This is because the aluminum suboxide that absorbs on surfaces at high temperatures is more volatile. It was demonstrated that at low aluminum concentrations, the photoluminescence intensity

increases by three orders of magnitude as the substrate temperature increases from 600 to 750 °C (1110 to 1380 °F). No effect occurs at high aluminum concentrations (Ref 141).

GaInAsP layers can be grown on GaAs by using low-pressure MOCVD within the entire composition range in which the quaternary is lattice matched to GaAs. Both TMIn and TEGa are used as the sources of indium and gallium, whereas AsH_3 and PH_3 are used as the sources of arsenic and phosphorus. The optimum conditions for the growth of GaInAsP (composition having a bandgap of 808 nm, or 31.5 μin.) on GaAs are listed in Table 3. The quality of the quaternary is comparable with that of the quaternary grown on InP substrates (Ref 142).

The InP-based materials described below include not only InP, but gallium indium arsenide (GaInAs) and gallium indium arsenide phosphide (GaInAsP) grown on InP.

High-quality InP layers have been grown by using MOCVD (Ref 52). Both TEIn and PH_3 are used as indium and phosphorus sources, respectively. A mixture of hydrogen and nitrogen is used as the carrier gas. The presence of hydrogen is necessary to avoid the deposition of carbon, and the presence of nitrogen is necessary to avoid the parasitic reaction between TEIn and PH_3.

The InP layers have been grown at 10 kPa (76 torr) and at low temperatures (between 500 and 650 °C, or 930 and 1200 °F) by using TEIn, PH_3, and a mixture of hydrogen and nitrogen as the carrier gas. The growth rate (ranging from 200 to 800 cm^3/min, or 12 to 48 $in.^3$/min) is linearly dependent on the TEIn flow rate, and is independent of PH_3 flow rate, substrate temperature, and substrate orientation. This suggests that epitaxial growth is controlled by the mass transport of Group III species.

Razeghi and Duchemin (Ref 18) have studied the growth of InP layers by using 100% hydrogen and mixtures of hydrogen and nitrogen as the carrier gas. The best morphology and the highest photoluminescence intensity were obtained by using 50% hydrogen and 50% nitrogen. Using argon instead of nitrogen produced InP layers with the same surface quality. Table 4 lists the optimum conditions used in this study for the MOCVD growth of InP in the temperature range of 550 to 650 °C (1020 to 1200 °F). The InP layers grown by MOCVD are less compensating at lower growth temperatures.

Table 4 Optimum growth conditions of indium phosphide

Growth temperature		Nitrogen-triethylindium bubbler flow rate		Phosphine flow rate		Total flow rate		Growth rate	
°C	°F	cm^3/min	$in.^3$/min	cm^3/min	$in.^3$/min	L/min	gal/min	nm/min	μin./min
550	1020	450	27	260	16	6	1.6	20±1	0.8±0.04
		225	14	200	12	6	1.6	10±1	0.4±0.04
650	1200	450	27	520	32	6	1.6	22±1	0.9±0.04
		225	14	400	24	6	1.6	11±1	0.4±0.04

GaInAs layers can be grown on InP substrates at 10 kPa (76 torr) in the temperature range of 500 to 650 °C (930 to 1200 °F), using either TEIn or TMIn, TEGa, and AsH_3 (Ref 52). When TEIn is used as the indium source, then pure hydrogen is used as the carrier gas. When TMIn is used, then a mixture of hydrogen and nitrogen is used as the carrier gas. The growth rate is linearly dependent on the combined flow rates of TEGa and TEIn. It is independent of the AsH_3 flow rate within the range of 60 to 90 cm^3/min (3.5 to 5.5 $in.^3$/min). This suggests, as in the case of InP, that epitaxial growth is controlled by the mass transport of Group III species. Uniform layers of $Ga_{0.47}In_{0.53}As$ have been deposited over

large areas (10 cm^2, or 1.5 $in.^2$) of InP substrates. The quality of the epitaxial layer is sensitive to the alloy composition, as in the case of GaInAs grown by other techniques.

The surface morphology of GaInAs grown on InP depends on the pretreatment of the substrate and is independent of the lattice mismatch, even when the mismatch is 0.01 or more. $Ga_{0.47}In_{0.53}As$ grown on InP exhibits an excellent surface morphology and state-of-the-art electron mobility when grown under the optimum conditions listed in Table 5.

Table 5 Optimum growth conditions of gallium indium arsenide/indium phosphide

Growth temperature, °C (°F)	550 (1020)
Total flow rate, L/min (gal/min)	7 (1.8)
Hydrogen-triethylindium bubbler flow rate, cm^3/min ($in.^3$/min)	450 (27)
Hydrogen-triethylgallium bubbler flow rate, cm^3/min ($in.^3$/min)	180 (11)
Phosphine flow rate, cm^3/min ($in.^3$/min)	90 (5)
Growth pressure, Pa (torr)	76 (0.6)
Growth rate, nm (μin.)	27 (1.05)

Note: Stoichiometry of material is $Ga_{0.47}In_{0.53}As$.

***$Ga_xIn_{1-x}As_yP_{1-y}$* layers** can be grown on InP substrates in the range of compositions that are lattice matched. Growth occurs at 10 kPa (76 torr) and at a substrate temperature between 630 and 650 °C (1170 and 1200 °F) using TEIn, TEGa, AsH_3, and PH_3 in a mixture of hydrogen and nitrogen carrier gas (Ref 52). The growth rate is linearly dependent on the sum of the partial pressures of TEIn and TEGa, and is independent of the arsenic and phosphorus partial pressures. The epitaxial layer quality is sensitive to the pretreatment of the substrate and the alloy composition. The optimum growth conditions for the lattice-matched composition, $Ga_{0.23}In_{0.77}As_{0.51}P_{0.49}$, are listed in Table 6.

Table 6 Optimum growth conditions of gallium indium arsenide phosphide/indium phosphide

Source	**Partial pressure**		**Temperature**	
	Pa	**mbar**	**°C**	**°F**
Triethylindium	0.85	0.0085	31	88
Triethylgallium	0.3	0.003	0	32
Arsine	31	0.31	25	77
Phosphine	700	7	25	77

nitrogen, 7 L/min (1.8 gal/min). Stoichiometry of material is $Ga_{0.28}In_{0.72}As_{0.61}P_{0.39}$.

Source: Ref 52

The nitride semiconductors described below include gallium nitride (GaN) and aluminum nitride (AlN).

High-quality GaN films have been very difficult to obtain because of the large mismatch in lattice constant and coefficient of thermal expansion with available substrates. The (001) plane of sapphire is often used, although the mismatch is large. Sun et al. recently discovered that the (012) plane is better matched with GaN and produces higher-quality GaN films (Ref 143). In the cited study, GaN was grown at atmospheric pressure in the temperature range of 900 to 1000 °C (1650 to 1830 °F), using TMGa and ammonia (NH_3) as the sources of gallium and nitrogen. The carrier gas was hydrogen. The precursors were mixed just before entering the reactor, in order to reduce the parasitic reactions between the metal-organics and NH_3. The total gas flow rate of 1600 sccm comprised 3 to 10 standard cm^3/min (sccm) TMGa, 500 to 1100 sccm NH_3, and carrier gas. The bubbler was kept at -10 °C (15 °F) for TMGa.

Aluminum nitride has been grown by using atmospheric-pressure MOCVD, with TMAl and NH_3 as the aluminum and nitrogen sources, respectively. The flow rates of each precursor were: 5 sccm of TMAl, 400 sccm of NH_3, and 1200 sccm of N_2. The TMAl was maintained in a bubbler at 25 °C (77 °F). The growth temperature was 1050 °C (1920 °F). Both the (001) and (012) planes of sapphire and the (100) plane of silicon were used as substrates. Thermal annealing under hydrogen and nitrogen caused no degradation of the crystalline quality, and improved the optical quality of the films (Ref 144).

The antimony-based materials described below include indium antimonide (InSb) and indium thallium antimonide (InTlSb).

Indium antimonide can be grown by using low-pressure MOCVD, with TMIn and trimethylantimony (TMSb) as sources for indium and antimony, respectively (Ref 145). Both InSb and GaAs (100) substrates were used in the growth process. Optimum growth conditions are listed in Table 7. The full width at half maximum of an x-ray rocking curve of 174 arc · s and a Hall mobility of 76,200 $cm^2/V \cdot s$ (11,820 $in.^2/V \cdot s$) at 240 K have been observed for a layer of 4.85 μm (190 μin.) grown under the optimum conditions.

Table 7 Optimum growth conditions of indium antimonide

Growth pressure, Pa (torr)	10,130 (76)
Growth temperature, °C (°F)	465 (870)
Total hydrogen flow rate, L/min (gal/min)	1.5 (0.40)
Hydrogen flow rate through trimethylindium bubbler, cm^3/min ($in.^3$/min)	50 (3.1)
Hydrogen flow rate through trimethylantimony bubbler, cm^3/min ($in.^3$/min)	20 (1.2)
Growth rate, μm/h (μin./h)	1.2 (47)

Source: Ref 145

Indium thallium antimonide was grown for the first time by using low-pressure MOCVD, with TMIn and TMSb as sources of indium and antimony, respectively, and cyclopentadienylthallium as the source of thallium (Ref 146). The optimum growth conditions are listed in Table 8.

Table 8 Optimum growth conditions of indium thallium antimonide

Growth pressure, Pa (torr)	10,130 (76)
Growth temperature, °C (°F)	455 (851)
Total hydrogen flow rate, L/min (gal/min)	1.5 (0.4)
Hydrogen flow rate through trimethylindium bubbler, cm^3/min ($in.^3$/min)	50 (3.1)
Hydrogen flow rate through trimethylantimony bubbler, cm^3/min ($in.^3$/min)	20 (1.2) 60 (3.7)

Source: Ref 146

Other Group III-V materials that have been grown by using MOCVD are listed in Table 9.

Table 9 The principal Group III-V materials grown by metal-organic chemical vapor deposition

Film	**Substrate**	**Precursors**	**Reference**
Gallium phosphide	Gallium phosphide	TMG, PH_3	147
Gallium antimonide	Gallium antimonide	TMG, TMSb	148
Indium arsenide	Indium arsenide	TEI, AsH_3	149
Gallium aluminum phosphide	Gallium phosphide	TMG, TMAl, PH_3	147
Gallium aluminum antimony	Gallium arsenide	TMG, TMAl, TMSb	150
Gallium indium arsenide	Gallium arsenide	TMG, TEI, TMAs	151
Aluminum indium arsenide	Indium phosphide	TMAl, TMI, AsH_3	152
Indium arsenide antimonide	Indium antimonide	TMI, TMSb, AsH_3	153
Gallium aluminum arsenide antimonide	Gallium arsenide	TMG, TMAl, TMAs, TMSb	151
Indium arsenide antimonide phosphide	Indium arsenide	TEI, TESb, AsH_3, PH_3	154

Note: TMG, trimethylgallium; PH_3, phosphine; TMSb, trimethylantimony; TEI, triethylindium; AsH_3, arsine; TMAl, trimethylaluminum; TMAs, trimethylarsenic; TMI, trimethylindium; TESb, triethylantimony

Group II-VI Semiconductor Growth Parameters

The Group II-VI semiconductors have been used for electroluminescent films (zinc sulfide and zinc selenide), infrared and far-infrared photodetectors (mercury cadmium telluride), thin-film photovoltaic devices (cadmium telluride), and, most recently, blue semiconductor lasers (zinc selenide).

The wide-bandgap materials described below include zinc selenide (ZnSe), zinc sulfide (ZnS), and zinc sulfide selenide (ZnS_xSe_{1-x}).

Both ZnSe and ZnS can be grown on GaAs or GaP substrates by using diethylzinc (DEZn) or dimethylzinc (DMZn) as the source of zinc, and either hydrogen sulfide (H_2S) or hydrogen selenide (H_2Se) respectively. However, the MOCVD growth of wide-bandgap selenides and sulfides has two major problems that are not encountered in the growth of Group III-V materials. The first is a premature reaction between DMZn and DEZn and H_2Se or H_2S, and the second is the formation of native defects, such as zinc, selenium, and sulfur vacancies at high growth temperatures. The first problem leads to poor surface morphology, whereas the second problem seems to be inherent to wide-bandgap semiconductors, especially materials that contain relatively high vapor pressure elements, such as ZnSe and ZnS.

The first problem can be solved by using both Group II and Group VI dialkyl sources, such as DMZn or DEZn and dimethylselenium (DMSE) or diethylselenium (DESe) because of the high decomposition temperature of these sources. The second problem can be reduced by decreasing the growth temperature. By using laser- or plasma-assisted MOCVD growth techniques, the growth temperature can be reduced to the range of 350 to 400 °C (660 to 750 °F) (Ref 155). Alternate precursors, such as Lewis acid-base adducts of dialkylzincs with dialkyl selenides or dialkyl sulfides and either H_2Se or H_2S, also reduce the growth temperature, although the premature reaction is not completely eliminated with these source combinations (Ref 156).

ZnS_xSe_{1-x} layers are lattice matched to GaAs and GaP substrates at x = 0.06 and x = 0.83, respectively. They can be grown at 500 °C (930 °F) using the precursors diethylsulfur (DES), DEZn, and DESe. The epitaxial layer shows excellent morphology, as evidenced by a narrow x-ray rocking curve (Ref 157). The growth temperature can be lowered by using an alternative source combination of the adduct, such as DMZn-DMSe, H_2S, and H_2Se, but it then becomes more difficult to control the alloy composition and attain lattice-matched layers. The growth mechanism that impedes control of the composition in this case is not clear. Photo-assisted CVD using alkyls of zinc, sulfur, and selenium as source materials is an effective low-temperature technique for the deposition of lattice-matched ZnSSe layers.

The narrow-bandgap materials described below include cadmium telluride (CdTe), mercury telluride (HgTe), and mercury cadmium telluride (HgCdTe).

Cadmium telluride can be grown by directly combining the vapors of the two elements, which are carried by hydrogen or nitrogen. Cadmium vaporizes at 756 °C (1390 °F), and tellurium, at 990 °C (1815 °F) (Ref 158). This material also can be grown by MOCVD through this reaction:

$$(C_2H_5)_2Te + Cd\ (vapor) + H_2 \rightarrow CdTe + 2C_2H_6 \qquad \textbf{(Eq 32)}$$

which takes place in the temperature range of 325 to 350 °C (620 to 660 °F), or through the reaction:

$$(C_2H_5)_2\,Te + (CH_3)_2Cd + nH_2 \rightarrow CdTe + \text{hydrocarbons} \qquad \textbf{(Eq 33)}$$

which takes place at substrate temperatures between 150 and 250 °C (300 and 480 °F) under the activation of an excimer laser (Ref 159).

Mercury telluride can be grown by using plasma-enhanced CVD, with dimethylmercury (DMHg) and dimethyltellurium (DMTe) as the mercury and tellurium sources, respectively. Williams et al. demonstrated a growth rate of 4 μm/h (160 μin./h) at a deposition temperature of 85 °C (185 °F), a pressure of 65 Pa (0.5 torr) and an RF power of 2 W at 15 MHz (Ref 160).

For HgCdTe, the selection of MOCVD growth temperature is a problem. The most commonly used tellurium precursor, diethyltellurium (DETe), pyrolyzes effectively only at a temperature of approximately 410 °C (770 °F). This is higher than the pyrolysis temperature of dimethylcadmium (DMCd), the Group II alkyl commonly used. The high temperatures

require a very high mercury pressure, which is supplied by heating elemental mercury. The combination of a high mercury concentration and a high molecular weight leads to convection cells in the vapor. It also results in the creation of large concentrations of mercury vacancies, which act as acceptors. Finally, the self-diffusion coefficients at 400 °C (750 °F) are large, precluding the growth of superlattice structures with abrupt interfaces. Lowering the growth temperature becomes the major consideration of the growth of HgCdTe. This material has been grown at 440 °C (825 °F) on GaAs and InSb substrates by using DETe and DMCd (Ref 161).

Group IV Semiconductor Growth Parameters

Silicon is the foundation of the present electronics industry. Epitaxial layers are used routinely in high-performance CMOS and bipolar technologies. Not surprisingly, the CVD process for silicon is the most mature. Germanium is another important Group IV semiconductor. Because both of these materials are grown from either chloride or hydride sources, they are categorized as CVD, rather than MOCVD, processes.

Epitaxial silicon (Si) layers can be grown at atmospheric pressure in the temperature range of 1050 to 1250 °C (1920 to 2280 °F), using either silicon tetrachloride ($SiCl_4$) or dichlorosilane (SiH_2Cl_2) as the source gas. Because this growth method is a high-temperature process, it is conducted during the initial stages of integrated-circuit manufacture. Lowering the deposition temperature minimizes dopant redistribution via solid-stage diffusion. Autodoping (the evaporation of dopants for the substrate and subsequent incorporation into the epitaxial layer) is reduced by operating at low temperatures and reduced pressures (Ref 162). Enhanced control of vertical dopant profiles permits the growth of thinner layers, which are necessary to achieve higher levels of integration. To achieve low-temperature growth, researchers have used lower-pressure processing and plasma-enhanced CVD (PECVD) methods, as well as silane (SiH_4) as a source gas.

The deposition temperature can be reduced to 825 °C (1520 °F) by using SiH_2Cl_2 in the pressure range of 1 to 3 kPa (8 to 25 torr) (Ref 163). By using SiH_4 as the source gas and utilizing very low pressures of 0.13 to 2.0 Pa (1 to 15 mtorr) to prevent parasitic reactions, epitaxial silicon can be deposited in the temperature range of 750 to 800 °C (1380 to 1470 °F) (Ref 164, 165). The growth temperature can be reduced to approximately 600 °C (1110 °F) by using a plasma-enhanced process (Ref 166). A review of PECVD methods is given by Reif and Kern (Ref 167).

Single-crystal germanium (Ge) can be grown by hydrogen reduction of the chloride in the temperature range of 600 to 900 °C (1110 to 1650 °F), according to the reaction (Ref 168):

$$GeCl_4 + 2H_2 \rightarrow Ge + 4\ HCl \qquad \textbf{(Eq 34)}$$

It is more widely grown by the decomposition of germane (GeH_4), usually at atmospheric pressure and at temperatures ranging from 600 to 900 °C (1110 to 1650 °F), according to the reaction:

$$GeH_4 \rightarrow Ge + 2H_2 \qquad \textbf{(Eq 35)}$$

Under low pressure (<130 Pa, or 1 torr), crystalline germanium can be grown in the temperature range of 350 to 400 °C (660 to 750 °F), using the above reaction (Ref 169).

Germanium also can be grown by using low-pressure MOCVD, with tetrapropylgermanium, $Ge(C_3H_7)_4$, and tetraethylgermanium, $Ge(C_2H_5)_4$, as the precursor and helium or hydrogen as the carrier gas. Growth temperatures range from 575 to 700 °C (1070 to 1290 °F) (Ref 170).

Silicon carbide (SiC) can be grown by the reaction of silane with a hydrocarbon such as propane or benzene, as expressed by the reactions:

$$3SiH_4 + C_3H_8 \rightarrow 3SiC + 10\ H_2 \qquad \textbf{(Eq 36)}$$

$$6SiH_4 + C_6H_6 \rightarrow 6SiC + 15\ H_2 \qquad \textbf{(Eq 37)}$$

The reaction temperature is about 800 °C (1470 °F), with a pressure of 1.3 KPa (10 torr) (Ref 171). The decomposition of methyl silane (Ch_3SiH_3) can be used to produce amorphous silicon carbide at 800 °C (1470 °F) and crystalline silicon carbide at 900 °C (1650 °F) (Ref 172).

References cited in this section

18. M. Razeghi, J.P. Duchemin, J.C. Portal, L. Dmowski, G. Remeni, R.J. Nicholas, and A. Briggs, *Appl. Phys. Lett.,* Vol 48, 1986, p 712
28. S.R. Kurtz, J.M. Olson, and A. Kibbler, *J. Electron. Mater.,* Vol 18, 1989, p 15
29. C.H. Chen, C.A. Larsen, and G.B. Stringfellow, *Appl. Phys. Lett.,* Vol 50, 1987, p 218
30. A. Brauers, M. Weyers, and P. Balk, *Chemtronics,* Vol 4, 1989, p 8
48. G.B. Stringfellow, *Organometallic Vapor-Phase Epitaxy: Theory and Practice,* Academic Press, 1989, p 8, 18
50. G.B. Stringfellow, *Semiconductors and Semimetals,* Vol 22A, W.T. Tsang, Ed., Academic Press, 1985, p 209
52. M. Razeghi, *The MOCVD Challenge,* A. Hilger, 1989, p 14
70. D.I. Fotiadis, M. Boekholt, K.F. Jensen, and W. Richter, *J. Cryst. Growth,* Vol 100, 1990, p 577
76. F.J. Callahan, *Swagelok Tube Fitting and Installation Manual,* 1985
77. L. Hollan, M. Boulon, and J.P. Chane, *J. Electron. Mater.,* Vol 10, 1981, p 193
78. N.J. Mason and P.J. Walker, *J. Cryst. Growth,* Vol 107, 1991, p 181
79. J.S. Roberts, N.J. Mason, and M. Robinson, *J. Crystal Growth,* Vol 68, 1984, p 422
80. C. Blaauw, C. Mincr, B. Emrnerstorfer, A.J. SpringThorpe, and M. Gallant, *Can. J. Phys.,* Vol 63, 1985, p 664
81. G. Landgren, S.G. Andersson, J.Y. Anderson, L. Samuelson, P. Silverberg, and P. Tolkien, *J. Crystal Growth,* Vol 77, 1986, p 67
82. E.J. Thrush, J.E.A. Whiteway, G. Wale-Evans, D.R. Wight, and A.G. Cullis, *J. Cryst. Growth,* Vol 68, 1984, p 412
83. R.J.M. Griffiths, N.G. Chew, A.G. Cullis, and G.C. Joyce, *Electron. Lett.,* Vol 19, 1983, p 319
84. L.J. Giling, *J. Electrochem. Soc.,* Vol 129, 1982, p 634
85. C. Blaauw, B. Emmerstorfer, and A.T. SpringThorpe, *J. Cryst. Growth,* Vol 84, 1987, p 431
86. J. van de Ven, H.G. Schoot, and L.J. Giling, *J. Appl. Phys.,* Vol 60, 1986, p 1648
87. J. van de Ven, G.J.M. Rutten, M.J. Raaymakers, and L.J. Giling, *J. Crystal Growth,* Vol 76, 1986, p 352
88. C. Goodings, N.J. Mason, P.J. Walker, and D. Jebb, *J. Cryst. Growth,* Vol 96, 1989, p 13
89. Yu.N. Makarov and A.I. Zhmakin, *J. Crystal Growth,* Vol 94, 1989, p 537
90. D. Schmitz, G. Strauch, H. Jürgensen, and M. Heyen, *J. Crystal Growth,* Vol 107, 1991, p 188
91. P.M. Frijink, *J. Crystal Growth,* Vol 93, 1988, p 207
92. E. Woelk and H. Beneking, *J. Cryst. Growth,* Vol 93, 1988, p 216
93. G.S. Tompa, M.A. McKee, C. Beckham, P.A. Zawadski, J.M. Colabella, P.D. Reinert, K. Capuder, R.A. Stall, and P.E. Norris, *J. Cryst. Growth,* Vol 92, 1988
94. A. Mircea, A. Ougazzaden, P. Daste, Y. Gao, C. Kazmierski, J.-C. Bouley, and A. Carenco, *J. Cryst. Growth,* Vol 92, 1988, p 235
95. M. Mpaskoutas, C. Morhaïm, J.N. Patillon, and J.P. Andréo, *J. Cryst. Growth,* Vol 107, 1991, p 192
96. M.J. Ludowise, *J. Appl. Phys.,* Vol 58 (No. 8), 1985, p R33
97. T.F. Kuech, E. Veuhoff, T.S. Kuan, V. Deline, and R. Potemski, *J. Cryst. Growth,* Vol 77, 1986, p 257
98. C. Plass, H. Heinecke, O. Kayser, H. Luth, and P. Balk, *J. Cryst. Growth,* Vol 88, 1988, p 455
99. J. Knauf, D. Schmitz, G. Strauch, H. Jurgensen, and M. Heyen, *J. Cryst. Growth,* Vol 93, 1988, p 34
100. G.B. Stringfellow, *J. Cryst. Growth,* Vol 55, 1981, p 42
101. R. Bhat, M.A. Koza, C.C. Chang, A. Schwarz, and T.D. Harris, *J. Cryst. Growth,* Vol 77, 1986, p 7
102. B.C. Harrison and E.H. Tompkins, *Inorg. Chem.,* Vol 1, 1962, p 951

103. K.W. Benz, H. Renz, J. Wiedlein, and N.H. Pilkuhn, *J. Electron. Mater.,* Vol 10, 1981, p 185
104. R.H. Moss and J.S. Evans, *J. Cryst. Growth,* Vol 55, 1981, p 129
105. R. Bath, M.A. Koza, and B.J. Skromme, *Appl. Phys. Lett.,* Vol 50, 1987, p 1386
106. M.K. Lee, K.C. Huang, D.S. Wuu, H.H. Tung, and K.Y. Yu, *J. Cryst. Growth,* Vol 93, 1988, p 539
107. P. Wolfram, F.W. Reier, D. Franke, and H. Schumann, *J. Cryst. Growth,* Vol 96, 1989, p 691
108. G. Laube, U. Kohier, J. Weidlein, F. Schol, K. Streubel, R.J. Dieter, N. Karl, and M. Gerdon, *J. Cryst. Growth,* Vol 93, 1985, p 45
109. K. Streubel, F. Scholz, G. Laube, R.J. Dieter, E. Zielinski, and F. Keppler, *J. Cryst. Growth,* Vol 93, 1988, p 347
110. R.H. Moss, private communication, 1985
111. T.S. Moss and S. Mahajan, *Handbook on Semiconductors,* Vol 3(a), North Holland, 1994, p 183
112. F.A. Maury and G. Constant, *J. Cryst. Growth,* Vol 62, 1983, p 568
113. F.A. Maury, A. El Hammadi, and G. Constant, *J. Cryst. Growth,* Vol 68, 1984, p 88
114. F.A. Maury, G. Constant, P. Fontaine, and J.P. Biberian, *J. Cryst. Growth,* Vol 78, 1986, p 185
115. F.A. Maury and A. El Hammadi, *J. Cryst. Growth,* Vol 91, 1988a, p 97
116. F.A. Maury and A. El Hammadi, *J. Cryst. Growth,* Vol 91, 1988b, p 105
117. K. Mori, M. Yoshida, and A. Usui, *Inst. Phys. Conf. Ser. 91,* 1988, p 187
118. C. Sasaoka, M. Yoshida, and A. Usui, *Jpn. J. Appl. Phys. Lett.,* Vol 27, 1988, p L190
119. K.L. Hess and R.J. Riccio, *J. Cryst. Growth,* Vol 77, 1966, p 95
120. G.B. Stringfellow, *J. Electron. Mater.,* Vol 17, 1989b, p 327
121. T.H. Chui, W.T. Tsang, E.F. Schubert, and E. Agyekum, *Appl. Phys. Lett.,* Vol 51, 1987, p 1109
122. A. Brauers, O. Kayser, R. Kall, H. Heinecki, P. Balk, and H. Hofmann, *J. Cryst. Growth,* Vol 93, 1988, p 7
123. L.M. Fraas, P.S. McLeod, R.E. Weiss, L.D. Partain, and J.A. Capc, *J. Appl. Phys.,* Vol 62, 1987, p 299
124. R.M. Lum, J.K. Klingert, and M.G. Lamont, *J. Cryst. Growth,* Vol 89, 1988a, p 137
125. S. Fujita, M. Imaizumi, S. Araki, Y. Takeda, and A. Sasaki, *J. Cryst. Growth,* Vol 93, 1988, p 1
126. R.M. Lum, J.K. Klingert, A.S. Wynn, and M.G. Larnont, *Appl. Phys. Lett.,* Vol 52, 1988b, p 1475
127. G. Haacke, S.P. Watkins, H. and Burnhard, *Appl. Phys. Lett.,* Vol 54, 1989, p 2029
128. H. Tanaka, T. Kikkawa, K. Kasai, and J. Komeno, *Jpn. J. Appl. Phys.,* Vol 28, 1989, p L901
129. R.H. Lum, J.K. Klingert, and M.G. Lamon, *Appl. Phys. Lett.,* Vol 50, 1987, p 284
130. C.H. Chen, E.H. Reihlen, and G.B. Stringfellow, *J. Cryst. Growth,* Vol 96, 1989, p 497
131. R. Bath, *J. Electron. Mater.,* Vol 14, 1985, p 433
132. K.W. Benz, H. Haspeklo, and R. Bosch, *J. Phys., Coll. CS,* Suppl. 43, 1982, p C5-393
133. M. Naitoh, T. Soga, T. Jimbo, and M. Umeno, *J. Cryst. Growth,* Vol 93, 1988, p 52
134. C.H. Chen, C.A. Larsen, G.B. Stringfellow, D.W. Brown, and A.J. Robertson, *J. Cryst. Growth,* Vol 77, 1986, p 11
135. R.R. Saxena, J.E. Fouquet, V.M. Sardi, and R.L. Moon, *Appl. Phys. Lett.,* Vol 53, 1988, p 26
136. F.G. Kellert, J.S. Whelan, and K.T. Chan, *J. Electron. Mater.,* Vol 18, 1989, p 355
137. M. Razeghi, F. Omnes, J. Nagle, M. Defour, D. Acher, and P. Bove, *Appl. Phys. Lett.,* Vol 55, 1989b, p 1677
138. D. Kisker, J.N. Miller, and G.B. Stringfellow, *Appl. Phys. Lett.,* Vol 40, 1982, p 614
139. G.B. Stringfellow and G. Hom, *Appl. Phys. Lett.,* Vol 34, 1979, p 794
140. M.J. Tsai, M.M. Tashima, and R.L. Moon, *J. Electron. Mater.,* Vol 13, 1984, p 437
141. T.F. Kuech, E. Veuhoff, D.J. Wolford, and J.A. Bradley, *Inst. Phys. Conf. Ser. 74,* 1985, p 181
142. M. Razeghi, X.G. He, J. Diaz, J. Hoff, M. Erdtmann, and E. Kolev, *Proc. SPIE,* 1994

143. C.J. Sun and M. Razeghi, *Appl. Phys. Lett.,* Vol 63, 1993, p 973
144. P. Kung, C.J. Sun, A. Saxler, H. Ohsato, and M. Razeghi, *J. Appl. Phys.,* Vol 75, 1994 p 4515
145. C. Besikci, Y.H. Choi, R. Sudharsanan, and M. Razeghi, *J Appl. Phys.,* Vol 73, 1993, p 5009
146. Y.H. Choi, C. Besikci, R. Sudharsanan, and M. Razeghi, *Appl. Phys. Lett.,* Vol 63, 1993, p 361
147. H. Beneking and H. Roehle, *J. Cryst. Growth,* Vol 55, 1981, p 79
148. H. Manasevit and K. Hess, *J. Electrochem. Soc.,* Vol 126, 1979, p 2031
149. H. Manasevit and K. Hess, *J. Electrochem. Soc.,* Vol 120, 1973, p 135
150. C. Cooper, M. Ludovik, and V. Achi, and R. Moon, *Electron. Lett.,* Vol 16, 1980, p 892
151. B. Baliga and S. Gandhi, *J. Electrochem. Soc.,* 1975, p 683
152. L. Aina and M. Mattingly, *Appl. Phys. Lett.,* Vol 51, 1987, p 1637
153. R.M. Biefeld, *J. Cryst. Growth,* Vol 75, 1986, p 255
154. T. Fukui and Y. Horikoshi, *Jpn. J. Appl. Phys.,* Vol 19, 1980, p L551
155. T. Yasuda, Y. Koyama, J. Wakitani, J. Yoshino, and H. Kukimoto, *Jpn. J. Appl. Phys.,* Vol 28, 1989, p L1628
156. T. Yasuda, K. Hara, and H. Kukimoto, *J. Cryst. Growth,* Vol 77, 1986, p 485
157. H. Mitsubashi, I. Mitshishi, and H. Kukimoto, *Jpn. J. Appl. Phys.,* Vol 24, 1989, p L864
158. S. Chu, T. Chu, K. Han, Y. Liu, and M. Mantravadi, *Proc. 10th Int. Conf. CVD,* Electrochemical Society, 1987, p 982
159. R.L. Gentilman, B. Bibendetto, R. Tustison, and J. Pappis, *Chemically Vapor Deposited Coatings,* H. Pierson, Ed., American Ceramic Society, 1981, p 47
160. L.M. Williams, P.Y. Lu, C.H. Wang, J.M. Partsey, and S.N.G. Chu, *Appl. Phys. Lett.,* Vol 21, 1987, p 1738
161. W.E. Hoke, P.J. Lemonias, and Traczewski, *Appl. Phys. Lett.,* Vol 44, 1984, p 1046
162. E. Krullman and W.L. Engl, *IEEE Trans. Electron. Dev.,* Vol ED-29, 1982, p 491
163. J. Borland and C. Drowley, *Solid State Technol.,* Aug, 1985, p 141
164. J.H. Comfort, L.M. Gaverick, and R. Reif, *J. Appl. Phys.,* Vol 62, 1987, p 3388
165. L.M. Gaverick, J.H. Comfort, T.R. Yew, R. Reif, F.A. Baiocchi, and H.S. Luftman, *J. Appl. Phys.,* Vol 62, 1987, p 3398
166. J.H. Comfort and R. Reif, *J. Electrochem. Soc.,* Vol 136 (No. 8), 1989, p 2386
167. R. Reif and W. Kern, *Thin Film Processes II,* W. Kern and J. Vossen, Ed., Academic Press, 1991, p 525
168. E.F. Cave and B.R. Czorny, *RCA Review,* Vol 24, 1963, p 523
169. J. Murota, A. Kobayashi, M. Kato, N. Mikoshiba, and S. Ono, *Proc. 11th Conf. CVD,* Electrochemical Society, 1990, p 325
170. R. Morancho, G. Constant, C. Gallon, J. Boucham, P. Mazerolles, and C. Bernard, *Proc. 5th European Conf. on CVD,* Sweden, 1985, p 526
171. H. Komiyama, H. Oyamada, S. Tanaka, and Y. Shimogaki, *Proc. 11th Int. Conf. on CVD,* K. Spear and G. Gullen, Ed., Electrochemical Society, 1990, p 361
172. P. Angelini, *Diss. Abst. Int.,* Vol 46, 1986, p 170

Plasma-Enhanced Chemical Vapor Deposition

Prabha K. Tedrow, Consultant; Rafael Reif, Massachusetts Institute of Technology

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Introduction

PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION (PECVD), also known as plasma-assisted CVD, is an important technique used for depositing films of a wide variety of crystalline and noncrystalline materials. Examples of

films that are commonly deposited using the PECVD process are noncrystalline materials such as oxides, nitrides, and oxynitrides of silicon (Ref 1), and crystalline materials such as polycrystalline silicon (Ref 2, 3, 4), epitaxial silicon (Ref 5, 6, 7), and refractory metals and their silicides. All of these materials are extensively used in microelectronic device fabrication, and PECVD is a critical process step in the fabrication of modern silicon devices. PECVD is also used in depositing optical coatings and other crystalline compounds such as titanium nitride, which is used in highly wear-resistant coatings on cutting tools (Ref 8).

Thermally driven atmospheric-pressure and low-pressure chemical vapor deposition (APCVD and LPCVD, respectively) are well understood and established methods for depositing films in integrated circuit (IC) fabrication technology (see the article "Chemical Vapor Deposition of Semiconductor Materials" in this Volume). However, the deposition temperatures in a thermally driven CVD process can be quite high (e.g., 700 to 900 °C, or 1300 to 1650 °F, for LPCVD silicon nitride deposition) (Ref 1, 9) and thus are detrimental to modern silicon devices. Plasma enhancement of the CVD process makes it possible to lower the deposition temperature significantly (e.g., to 250 to 300 °C, or 480 to 570 °F, for PECVD of silicon nitride) (Ref 1, 9) while maintaining a reasonable rate of deposition and film quality. Thus, some of the advantages of PECVD are that:

- Films can be deposited on substrates that would be unstable at higher temperatures (e.g., intermetallic dielectric layers deposited on aluminum or the encapsulation of ICs).
- Lower-temperature film deposition in microelectronic circuits allows precise control of dopant migration. The dimensions of modern microelectronic devices are getting smaller, increasing the importance of this control.

This article discusses application of the PECVD process in the deposition of amorphous and crystalline films from the point of view of microelectronic device fabrication. Plasma enhancement of the CVD process is discussed briefly, followed by a description of various types of PECVD reactors. Deposition techniques and the properties of some of the amorphous and crystalline films deposited by the PECVD process for IC fabrication are also described.

References

1. B. Gorowitz, T.B. Gorczyca, and R.J. Saia, in *Solid State Technology,* Vol 28 (No. 6), 1985, p 197
2. T.I. Kamins and K.L. Chiang, in *J. Electrochem. Soc.,* Vol 129, 1982, p 2326, 2331
3. W.R. Burger, T.J. Donahue, and R. Reif, in *VLSI Science and Technology,* C.J. Dell'Oca and W.M. Bullis, Ed., The Electrochemical Society, 1982, p 87
4. J.-J. Hajjar, R. Reif, and D. Adler, in *J. Electronic Materials,* Vol 15, 1986, p 279
5. S. Suzuki and T. Itoh, in *J. Appl. Phys.,* Vol 54, 1983, p 1466
6. S.R. Shanfield and R. Reif, in *The Electrochem. Soc. Extended Abstracts,* Vol 83-1, Abs. 144, 1983, p 230
7. J.H. Comfort, L.M. Garverick, and R. Reif, in *J. Appl. Phys.,* Vol 62, 1987, p 3388
8. N. Kikuchi, Y. Oosawa, and A. Nishiyama, in *Proceedings of the Ninth International Conference on Chemical Vapor Deposition,* McD. Robinson, C.W. Cullen, C.H.J. van den Brekel, and J.M. Blocher, Jr., Ed., The Electrochemical Society, 1984, p 728
9. A.C. Adams, *Solid State Technology,* in Vol 26 (No. 4), 1983, p 135; also in *VLSI Technology,* S. Sze, Ed., McGraw-Hill, 1983, Chapter 3

Process Description

In a thermally driven CVD process, component elements of the film to be deposited are introduced into the reaction chamber via gaseous precursor reactants. The reactants are mass-transported to the surface of the hot substrate, where they are adsorbed. If the substrate is heated to an appropriate temperature for the desired chemical reaction to take place, films of the material to be deposited form on the substrate surface while the reaction byproducts are pumped out of the system. Thus the quality and the rate of film deposition are a function of, among other things, reactor geometry, partial pressures of the reactants, and the substrate temperature. Although the thermally driven CVD process is thermodynamically quite well understood and is widely used for the deposition of some films (e.g., undoped

polycrystalline silicon), high deposition temperatures could be quite prohibitive for other applications (e.g., deposition of intermetallic dielectrics).

In the PECVD process, the gaseous precursors are most commonly subjected to time-varying electric fields of frequencies in the range of 50 kHz to 13.5 MHz. In some designs, microwave frequencies are also used. The electric field initially reacts primarily with the free electrons present in the gas. Although the electric field also reacts with the ions, these species remain initially unaffected because of their higher mass. The electrons undergo elastic and inelastic collisions with the gas molecules, but the electrons do not lose much energy during the elastic collisions because they are much lighter than the gas molecules. Loss of electronic energy during inelastic collisions with the gas molecules occurs only if the electrons, accelerated by the electric field, acquire energy that is higher than the threshold energies for excitation and ionization for a particular gas species (e.g., 11.56 eV for excitation and 15.8 eV for ionization of argon) (Ref 10). The inelastic collisions between these energetic electrons and gas molecules generate highly reactive species such as excited neutrals, free radicals, and ions, as well as more electrons. By this mechanism, the energy of the electrons is used to create reactive and charged species, while the gas temperature does not increase substantially.

In the PECVD environment, only a fraction of the precursor species in the gas phase undergo electron impact ionization and excitation, thereby generating the reactive species. The latter have a lower energy barrier to physical and chemical reactions than the parent species and consequently react at lower temperatures. Thus in the PECVD process, these reactive species lead to lower deposition temperatures and higher deposition rates than are possible with only thermally driven CVD. In film growth with the PECVD process, in addition to the unchanged parent species, these highly reactive species also diffuse to the surface of the substrate, where they are adsorbed and undergo a sequence of processes similar to that of thermal CVD. But these reactive species follow an alternate deposition pathway that proceeds parallel to the thermal pathway, because:

- The reactive species created during the inelastic collisions of gas molecules with energetic electrons have a sticking coefficient closer to unity (Ref 10); that is, once they reach the surface of the substrate, they tend not to escape.
- The activation energy for chemical dissociation is typically lower for these plasma-enhanced reactions (Fig. 1).

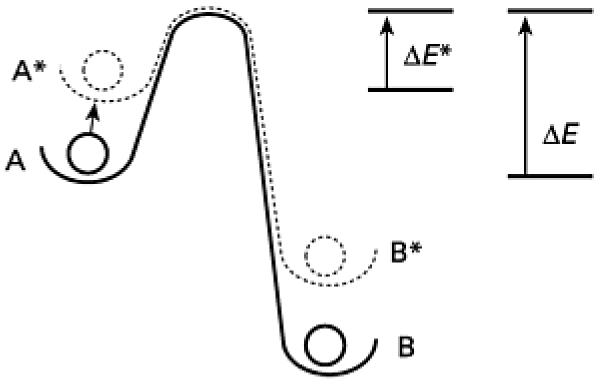


Fig. 1 Activation energy diagram for thermally driven (solid line) and plasma-enhanced (dashed line) chemical vapor deposition reactions. A and B, initial and final energy states, respectively, for the thermally driven reaction; ΔE, activation energy; A*, B*, ΔE*, corresponding parameters for the plasma-enhanced reaction. Source: Ref 11

Some heat is needed to drive the reaction over E*, but as shown in Fig. 1, this energy is typically lower than the energy needed for a purely thermally driven reaction to proceed at a reasonable rate. If the substrate is kept at a temperature such that the deposition proceeds at a very slow rate without the plasma but at a reasonable rate once the plasma is switched on, a plasma can be used as a "switch" to turn the deposition reaction on and off (Ref 12). Switching the plasma on and off can be used to start and stop the deposition process. Extremely abrupt layers can be grown by this technique, because the time required for the plasma to switch is equivalent to that between gas molecule collisions (e.g., 1 ms at 1 torr) (Ref 13). The thermal energy in a PECVD process, in addition to driving the surface reaction, is also needed for desorption of

the reaction byproducts, minimizing adsorption and the inclusion of undesired gases in the deposited film, thereby lowering film contamination.

Typically, radio-frequency (rf) glow discharges used for the deposition of thin films operate at frequencies between 50 kHz to 13.56 MHz and at pressures of 0.1 to 2.0 torr. The plasma density (i.e., the density of ions and free electrons) is in the range of 10^8 to 10^{12} cm^{-3}. The degree of ionization is 10^{-4}. Typical average electron energies are in the range of 1 to 3 eV, but the fastest electrons may reach energies as high as 10 to 30 eV (Ref 14).

In a PECVD deposition system, many factors can affect the growth, composition, and the properties of deposited films, in addition to conditions such as the substrate temperature, reactor geometry, and reactant partial pressures, which are important in thermally driven CVD film growth. Some of these factors are plasma power, frequency, electrode spacing, and substrate positioning. In these plasma glow discharges, the PECVD environment is not in thermal equilibrium because the average electron energies are much higher than the ion energies. Consequently, thermodynamic calculations cannot reliably predict the product of a PECVD reaction (Ref 13).

References cited in this section

10. M. Rand, in *J. Vac. Sci. Technol.,* Vol 16, 1979, p 420
11. R. Reif, in *Handbook of Plasma Processing Technology,* S. Rossnagel, J. Cuomo, and W. Westwood, Ed., Noyes Publications, 1990, Chapter 10
12. A.D. Huelsman, L. Zien, and R. Reif, in *Appl. Phys. Lett.,* Vol 52, 1988, p 726
13. R. Reif and W. Kern, Plasma Enhanced Chemical Vapor Deposition, *Thin Film Processes II,* Academic Press, Inc., 1991
14. J.R. Hollahan and A.T. Bell, Ed., *Techniques and Applications of Plasma Chemistry,* John Wiley, 1974

Types of PECVD Systems

As with thermal CVD reactors, PECVD systems can be either the hot-wall type, in which the reactor walls, the substrate, and the reactant gases are all at the same temperature, or the cold-wall type, in which only the substrate is heated to the desired temperature. In addition, PECVD reactors can be of direct or remote plasma type, where consideration is given to the plasma generation and what is coupled to this plasma. Numerous articles in the published literature (Ref 15, 16, 17, 18, 19, 20, 21) describe in detail the different geometries of commercial PECVD reactors and their use in the deposition of specific films.

In a direct PECVD system, all the reactant gases as well as the substrate are exposed to the rf plasma glow. A schematic of a direct plasma cold-wall reactor is shown in Fig. 2. The upper electrode is connected to the high-frequency rf power generator through an impedance-matching network. The reactants are introduced through the upper electrode, which is perforated, and directly enter the plasma region. The gases are pumped out at the bottom of the chamber. The lower electrode is a continuous plate and has a resistive heating element to heat the substrates. Substrates (wafers) are placed on the lower electrode and are thus immersed in the plasma as well as heated to the desired temperature of deposition.

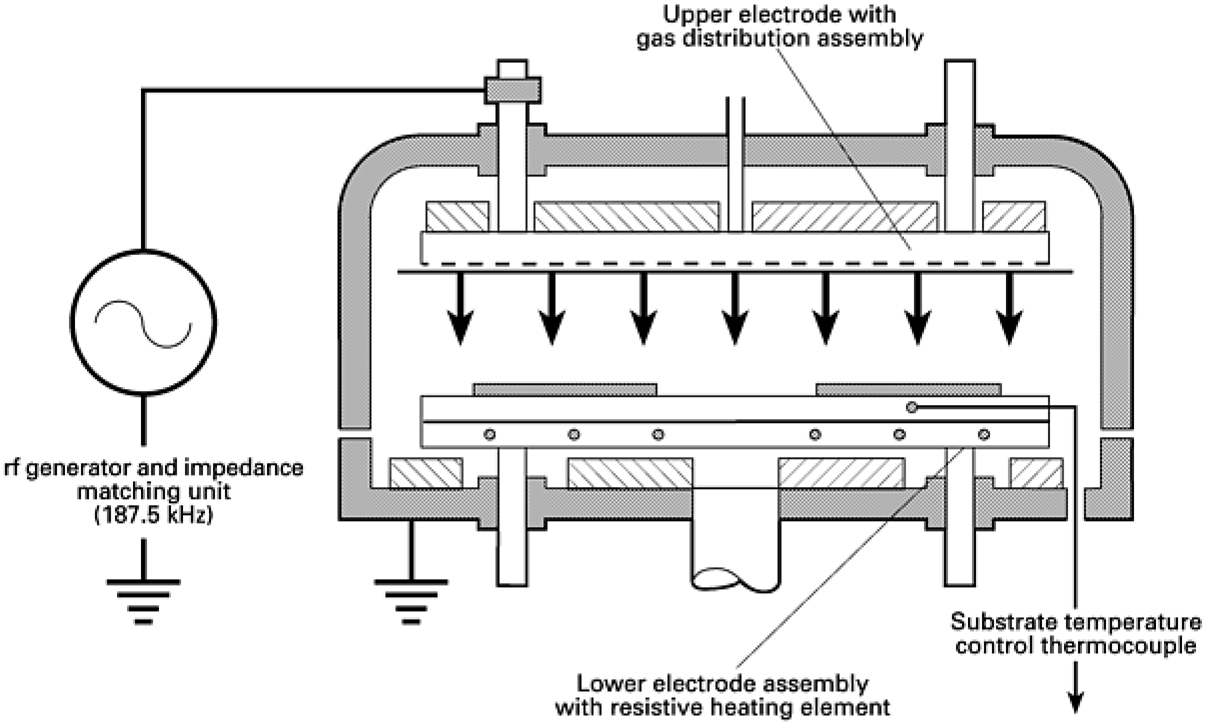


Fig. 2 Schematic of a direct plasma cold-wall reactor. Source: Ref 17, 22

Remote PECVD Systems. In a direct PECVD system, the substrate is exposed to the plasma discharge environment, which may cause radiation damage in the film being deposited. In a remote PECVD system, the substrate is removed from the plasma glow, and the reactant gases may be selectively excited by the plasma. The excited species are then carried to the substrate surface, where they react with other adsorbed gaseous reactants and the desired chemical reaction for deposition takes place. Keeping the substrate out of the plasma glow eliminates the deleterious effects of radiation. Moreover, this technique allows independent optimization of plasma, reactant gas chemistries, and wafer parameters.

One example of a remote PECVD system is shown in Fig. 3. This reactor was designed and built at the Massachusetts Institute of Technology (Ref 23) for metallo-organic CVD (i.e., CVD where some of the source gases are metallo-organic compounds) of gallium arsenide. The reactor consists of three vertically aligned concentric regions. The group III source gases enter through the center tube, the group V source gases enter between the inner and center tubes, and the reaction byproducts are exhausted between the inner and outer tubes. The substrate rests horizontally on a SiC-coated graphite disk, which is heated from below by a 750 W quartz halogen lamp with an elliptical reflector. The reactor can be equipped with internal electrodes fabricated of either aluminum or tantalum that can be connected via feedthroughs to an external power source to generate the plasma. The electrode configuration consists of an aluminum cylinder, 5 cm (2 in.) in diameter and 4 cm (1.6 in.) long, placed parallel to the gas stream. The distance between the wafer and the plasma can be varied by moving the electrode up or down in the inner quartz tube. In this design, the substrate receives a uniform distribution of plasma species and uniform infrared heat.

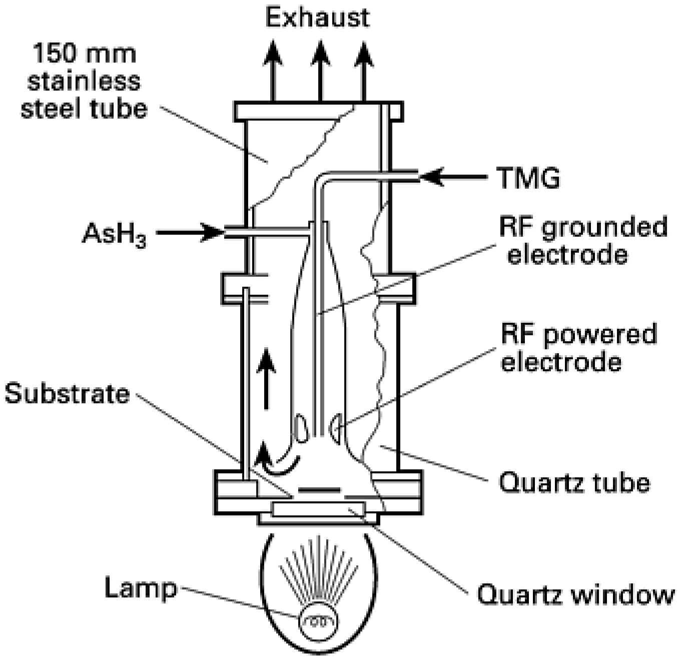


Fig. 3 Schematic of a remote plasma-enhanced chemical vapor deposition reactor for depositing compound semiconductor films. TMG, trimethylgallium. Source: Ref 23

Hybrid PECVD systems are a combination of the direct and remote PECVD systems. One example of such a system is a reactor designed for the deposition of amorphous hydrogenated silicon (Ref 24). In this reactor, one of the electrodes is replaced by a grid and the substrate is positioned directly under it. The substrate is thus shielded from the direct plasma glow while the reactant gases are subjected to the plasma discharge.

In some PECVD systems, microwave power is used to generate plasma. The plasma is excited by the resonance of microwaves and electrons through a microwave discharge across a magnetic field of 800 to 1200 G. This process, called electron cyclotron resonance, allows the film to grow at high rates of deposition at very low gas pressures (!10^{-4} torr) and at very low temperatures (<275 °C, or 525 °F) (Ref 25). The plasma is contained magnetically in the system and the deposition occurs outside the glow region, while all the gases are subject to plasma excitation.

References cited in this section

15. A.R. Reinberg, in *The Electrochem. Soc. Extended Abstracts,* Vol 74-1, Abs. No. 6, 1974
16. W. Kern, in *Microelectronic Materials and Processes,* C.R. Levey, Ed., NATO ASI Series E, Vol 164, Kluwer Academic Publishers, 1989, Chapter 5; see also *Semiconductor International,* Vol 8 (No. 7), 1985, p 121
17. A. Kiermasz, A.A. Chambers, and A. McQuarrie, in *Research and Development,* Vol 29 (No. 12), 1987, p 71
18. R.S. Rosler and G.M. Engle, *Solid State Technol.,* Vol 24 (No. 4), 1981, p 172
19. A.D. Weiss, *Semiconductor International,* Vol 6, July 1983, p 88
20. Novellus Systems Inc., San Jose, CA
21. E.R. van de Ven, I.-W. Connick, and A.S. Harrus, in *Proceedings of the Seventh International IEEE Multi-Level Interconnection Conference* (Santa Clara, CA), Institute of Electrical and Electronics Engineers, June 1990, p 194
22. Electrotech, Hauppauge, NY
23. A.D. Huelsman and R. Reif, in *J. Vac. Sci. Technol. A,* Vol 7, 1989, p 2554

24. A. Matsuda and K. Tanaka, Investigation of the Growth Kinetics of Glow-Discharge Hydrogenerated Amorphous Silicon Using a Radial Separation Technique, *J. Appl. Phys.,* Vol 60, 1986, p 2351
25. W.R. Snow, in *Proceedings of the Tenth International Conference on Chemical Vapor Deposition,* G.W. Cullen, Ed., The Electrochemical Society, Inc., 1987, p 810

PECVD of Dielectric Films

One of the most important uses of PECVD is in the deposition of dielectric films used in microelectronic device fabrication. The ability to deposit films of a dielectric such as silicon nitride, silicon oxide, or silicon oxynitride at lower temperatures is critical in the manufacture of modern very-large-scale integration (VLSI) chips. Fabrication of devices with smaller dimensions requires precise control of dopant movement during the multistep processing sequences. In addition, deposition of dielectrics used in intermetallic layers and/or chip encapsulations also requires low-temperature depositions.

Silicon nitride films provide an excellent barrier against alkali ions and moisture and are thus the material of choice as a final passivation and coating layer for ICs. The PECVD technique makes it possible to deposit silicon nitride films at temperatures in the range of 250 to 400 °C (480 to 750 °F), which is low enough to be deposited over device wafers with aluminum metallization and interconnects. Silicon nitride films deposited by the PECVD process are generally represented as $Si_xN_yH_z$ because they are not stoichiometric and contain bonded hydrogen. The films can be deposited by using silane (SiH_4) and ammonia (NH_3) as source gases for silicon and nitrogen, respectively. The depositions are normally carried out at pressures of 0.2 to 3 torr, and film growth rates at these pressures are about 200 to 500 Å/min. These films contain 15 to 30 at.% H bonded to either silicon or nitrogen (Ref 9, 26, 27).

Another choice of reactant gases can be silane and nitrogen (N_2). In this case, the deposition rates are low and the films tend to be silicon-rich. The SiH_4-N_2 chemistry tends to yield films that have less hydrogen and an excess of nitrogen, and that have poorer step coverage of the underlying metal.

Film properties such as refractive index, stress, and optical absorption edge are greatly affected by the concentration and chemical bonding of the hydrogen in the film. Other film properties (e.g., electric breakdown strength, etch rates in hydrofluoric acid, diffusion barrier to alkali ions and moisture, and stress) are also functions of the film composition and are very sensitive to the reactor geometry and deposition conditions.

Both bonded hydrogen and a high level of stress are harmful to the chips on which the films are deposited. Hydrogen tends to escape from the films when further processing is done at temperatures higher than the deposition temperature, and this can change the electrical properties of underlying devices (Ref 28). Stress in the PECVD nitride films can vary from 10^{10} dyn/cm^2, compressive, to 10^{10} dyn/cm^2, tensile. Excessive stress can cause the films to crack and peel (Ref 29). It is possible to choose the stress type and control the stress level by selecting the right deposition conditions (Ref 21).

Silicon oxide films are used as intermetallic dielectric layers in microelectronic circuits. Some of the important advantages that PECVD silicon oxide films offer are that:

- The deposition temperatures are low (200 to 300 °C, or 390 to 570 °F), so that PECVD silicon oxide films can be deposited over low-melting-point metals such as aluminum.
- The dielectric constant of PECVD oxide is relatively low (4 to 6, versus 6 to 9 for silicon nitride films) (Ref 30).
- The dry etch rate of PECVD oxide films is much higher than that of thermal CVD films.

The last factor is used to advantage in the process called planarization. During IC device fabrication, the surface needs to be planarized at some point before the next processing step. One method involves depositing the PECVD oxide film over the processed wafer, followed by deposition and flow of photoresist. The photoresist and the oxide films are then dry etched. The etch rate of the PECVD oxide may be 20 to 40% higher than that of thermal oxide. This high etch rate allows the planarization process to succeed, because the latter depends on having equal etch rates of photoresist and oxide (Ref 31).

Properties of PECVD silicon oxide films are a function of deposition conditions, reactor geometry, and the reaction chemistry (but to a lesser degree than in PECVD silicon nitride films) (Ref 13). Some of the source gas combinations that can be used for the deposition of PECVD silicon oxide films are (Ref 1, 32):

- SiH_4, used as the silicon source, and nitrous oxide (N_2O), used as the source of nitrogen. SiH_4 is usually diluted with argon.
- SiH_4 diluted with oxygen (alone or in combination with N_2O)
- Tetraethylorthosilicate (TEOS) as the source of silicon in an O_2-N_2 ambient

The SiH_4-N_2O process tends to yield films with better uniformity and less particle contamination. Hydrogen occurs in PECVD silicon oxide films in the bonded form as Si-H, Si-O-H, or H-O-H in concentrations ranging from 2 to 9 wt% (Ref 30). The hydrogen in oxide films is less of a problem than in PECVD nitride films. If the films are heated substantially beyond their deposition temperatures, the hydrogen in the films escapes by outdiffusion, whereas the PECVD silicon nitride films may be destroyed by blistering because they are relatively impermeable.

Some of the properties of silicon oxide films deposited by PECVD process are:

- Compressive stress, 0.07 to 2.4×10^9 dyn/cm^2
- Breakdown strength, 2 to 6×10^6 V/cm
- Resistivity, 10^{13} to 10^{17} $\Omega \cdot$ cm

Effects of deposition variables on the properties of PECVD silicon oxide films are reported in Ref 33, 34, 35, 36.

Silicon oxynitride films combine some of the best properties of PECVD silicon nitride and oxide films. Deposition of silicon oxynitride film is based on SiH_4 (diluted with helium), NH_3, and N_2O as reactants in various ratios at 300 °C (570 °F) (Ref 37). Properties such as stress, dielectric constant, and resistance to the diffusion of sodium ions and moisture can be modified by changing the gas flow ratios during film growth. The presence of oxygen in these films lowers the values of properties such as stress and dielectric constant, whereas the presence of nitrogen increases the impermeability to sodium ions and moisture (Ref 13). PECVD oxynitride films are also used in the planarization process, where the difference in etch rates of oxynitrides, photoresist, and nitride films is used advantageously (Ref 1).

References cited in this section

1. B. Gorowitz, T.B. Gorczyca, and R.J. Saia, in *Solid State Technology,* Vol 28 (No. 6), 1985, p 197
9. A.C. Adams, *Solid State Technology,* in Vol 26 (No. 4), 1983, p 135; also in *VLSI Technology,* S. Sze, Ed., McGraw-Hill, 1983, Chapter 3
13. R. Reif and W. Kern, Plasma Enhanced Chemical Vapor Deposition, *Thin Film Processes II,* Academic Press, Inc., 1991
21. E.R. van de Ven, I.-W. Connick, and A.S. Harrus, in *Proceedings of the Seventh International IEEE Multi-Level Interconnection Conference* (Santa Clara, CA), Institute of Electrical and Electronics Engineers, June 1990, p 194
26. A.K. Sinha, in *Solid State Technol.,* Vol 23 (No. 4), 1980, p 133
27. J.L. Vossen, in *J. Electrochem. Soc.,* Vol 126, 1979, p 319
28. S.J. Fijita, N.S. Zhon, H. Toyoshima, T. Ohishi, and A. Sasaki, in *IEDM Tech. Digest,* Vol 84, 1984, p 630
29. W. Kern and R.S. Rosler, in *J. Vac. Sci. Technol.,* Vol 14 (No. 5), Sept/Oct 1977, p 1082
30. A.C. Adams, in *Reduced Temperature Processing for VLSI,* R. Reif and G.R. Srinivasan, Ed., The Electrochemical Society, 1986, p 111
31. A.C. Adams and C.D. Capio, in *J. Electrochem. Soc.,* Vol 128, 1981, p 423
32. I.T. Emesh, G. D'Asti, J.S. Mercier, and P. Leung, in *J. Electrochem. Soc.,* Vol 136, 1989, p 3404

33. E.P.G.T. van den Ven, in *Solid State Technol.,* Vol 24 (No. 4), 1981, p 167
34. J.R. Hollahan, in *J. Electrochem. Soc.,* Vol 126, 1979, p 930
35. A.C. Adams, F.B. Alexander, C.D. Capio, and T.E. Smith, in *J. Electrochem. Soc.,* Vol 128, 1981, p 1545
36. A.C. Adams, in *Reduced Temperature Processing for VLSI,* R. Reif and G.R. Srinivasan, Ed., The Electrochemical Society, 1986, p 111
37. V.S. Nguyen, S. Burton, and P. Pan, in *J. Electrochem. Soc.,* Vol 131, 1984, p 2349

PECVD of Amorphous and Polycrystalline Silicon Films

Amorphous Silicon Films. The PECVD process is extensively used to deposit amorphous silicon films. Amorphous hydrogenated silicon (a-Si:H) films are deposited by the PECVD process by the decomposition of monosilane, disilane, or chlorosilane in a glow discharge plasma at temperatures in the range of 200 to 300 °C (390 to 570 °F) (Ref 38). The amorphous-to-polycrystalline transition temperature is sensitive to reactor design and deposition conditions and has to be controlled carefully. The a-Si:H films have important applications in the fabrication of solar cells (Ref 39), as photoreceptors in photolithography, and in Vidicon-type photoconductive image tubes (Ref 40).

Polycrystalline Silicon Films. Polycrystalline silicon is used as the gate electrode in metal-oxide semiconductor devices and as the emitter in bipolar devices. It is also used as interconnect material in ICs. In commercial manufacturing of ICs, polycrystalline silicon is deposited by thermally driven LPCVD at 625 °C (1150 °F). The PECVD process is rarely used for polycrystalline silicon film deposition, because deposited polycrystalline silicon films are intrinsic and have very high resistivity. Most applications in the microelectronic industry require the polycrystalline films to be highly conductive, which is achieved by doping the films after deposition. The number of processing steps can be reduced if the films are doped in situ. Application of PECVD for in-situ doping of polycrystalline silicon films is being explored. Thickness, uniformity, and deposition rates are very much affected when relatively high concentrations of dopant species are introduced in the LPCVD reactor during film growth. When PECVD is used to dope the polycrystalline silicon films in situ, the conductivity of these films can be modulated by six orders of magnitude for both p-type (by adding diborane) and n-type (by adding arsine) (Ref 41).

In other applications of polycrystalline silicon films, for example in the fabrication of thin-film transistors, PECVD is very desirable. Thin-film transistors are being explored for use in flat-panel displays and require much lower deposition temperatures, which can be achieved by PECVD. In addition, the growth rate of PECVD polycrystalline silicon films is less sensitive to the deposition temperature (Ref 4), as shown in Fig. 4, and so uniform film deposition requires less stringent control of the wafer temperature.

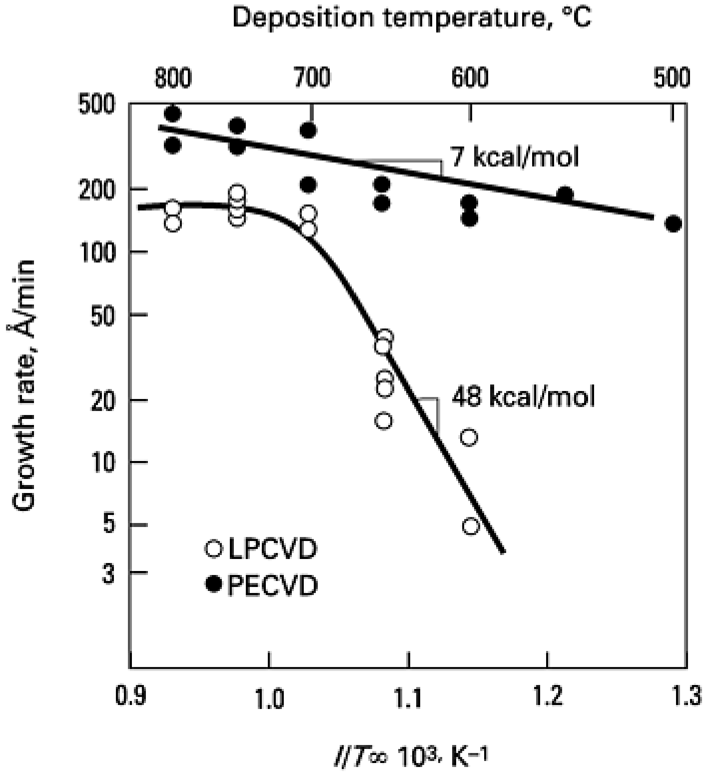


Fig. 4 Arrhenius plots of growth rates of polycrystalline silicon films deposited on oxidized silicon wafers with and without plasma enhancement. LPCVD, low-pressure chemical deposition; PECVD, plasma-enhanced chemical vapor deposition. Source: Ref 41

Epitaxial Films. In microelectronic devices, epitaxial films have extensive applications in both bipolar technology (as subcollector) and complementary metal-oxide semiconductor technology (to prevent latch-up). They are commercially deposited by APCVD at 1050 to 1200 °C (1920 to 2190 ° F) (Ref 42). Other deposition techniques can be used to deposit epitaxial silicon films at temperatures lower than in LPCVD, namely, molecular beam epitaxy (Ref 43), ion beam epitaxy (Ref 44), ultrahigh-vacuum CVD (Ref 45), and photo-enhanced CVD (Ref 46). The PECVD process is another exciting option for depositing homoepitaxial or heteroepitaxial films at lower temperatures. PECVD offers other potential advantages, such as flexibility in the deposition of in-situ doped films (Ref 47).

Deposition of silicon epitaxial films with and without plasma enhancement has been reported (Ref 48). The films were deposited in a very-low-pressure CVD system at temperatures as low as 650 °C (1200 °F) with SiH_4 as the source gas. A schematic of this reactor, which was designed and built at the Massachusetts Institute of Technology, is shown in Fig. 5. The substrate or wafer sits vertically on a graphite susceptor and faces a bank of infrared lamps, which heat both the wafer and the susceptor to the desired deposition temperature. The reactant gases can be pure SiH_4 for intrinsic deposition or SiH_4 mixed with other reactants (e.g., arsine or diborane) for epitaxial deposition of doped silicon. The gases enter the reactor from the top and are pumped out at the bottom. The reactor could be evacuated to a hydrocarbon-free base pressure about 10^{-8} torr, and epitaxial films are deposited at operating pressures of 1 to 100 mtorr. Plasma powers from 2.5 to 100 W could be used at a frequency of 13.56 MHz. In this reactor, a direct-current power supply was also used to bias the susceptor relative to ground and to decouple the substrate biasing from rf plasma power or electrode self-bias. At low plasma power (2.5 W) and in the temperature range of 750 to 800 °C (1380 to 1470 °F), the plasma-enhanced depositions were 20% faster, and at higher power (20 W), an additional 10% increase in the growth rate was observed.

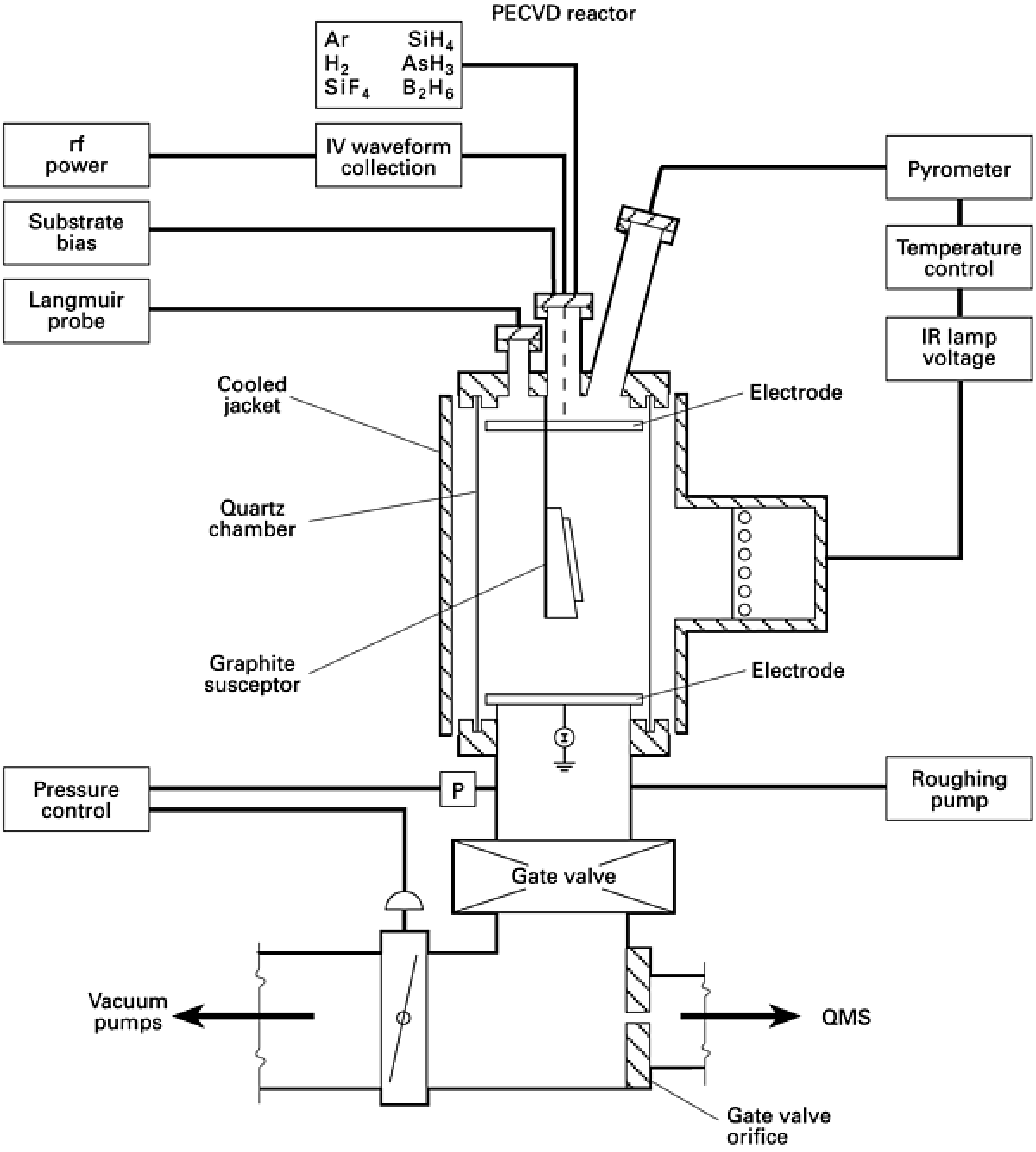


Fig. 5 Reactor for plasma-enhanced chemical vapor deposition of epitaxial silicon films. QMS, quadruple mass spectrometer. Source: Ref 48

Conductive Films. The deposition of refractory metals and their silicides with the PECVD process has been a subject of investigation by many researchers (Ref 49, 50, 51, 52). Refractory metals such as tungsten and molybdenum and their silicides--for example, tungsten silicide (WSi_2), molybdenum silicide ($MoSi_2$), and titanium silicide ($TiSi_2$)--have resistivities greater than that of aluminum but much less than that of doped polycrystalline silicon. Typical resistivities of the refractory metals are !15 μΩ· cm, while those of the refractory metal silicides have a range of 16 to 40 μΩ· cm (as compared to aluminum, which has a resistivity of 2.6 μΩ· cm, and doped polycrystalline silicon, which has a resistivity of about 500 μΩ· cm). When aluminum is used as the interconnect material in ICs, all the postaluminum processing steps have to be kept below about 450 °C (840 °F) (aluminum melts at about 600 °C, or 1220 °F). The refractory metals and their silicides are compatible with higher-temperature processing steps and can be used as interconnects or gates (in conjunction with polycrystalline silicon or alone). They are most commonly deposited by thermally driven CVD (Ref 13).

The resistivities of both the refractory metals and their silicides are very sensitive to factors such as impurities, which can be trapped in the film during the PECVD process, and grain size. When the PECVD process is used to deposit films of refractory metals or their silicides, even though the actual deposition temperatures can be as low as 400 °C (750 °F), a high-temperature postdeposition anneal is always necessary to bring down the resistivity. This high-temperature annealing step also presumably helps in the outdiffusion of impurities, in increasing the grain size, and in the annealing-out of radiation-induced defects in the films created during the PECVD process.

Refractory metal films are usually deposited at 400 °C (750 °F) with metal halides as the source gases (Ref 49, 50), for example, tungsten hexafluoride (WF_6) for tungsten deposition, and molybdenum pentachloride ($MoCl_5$) and H_2 for molybdenum deposition. Deposition of refractory metal silicides is carried out by introducing a silicon source (e.g., SiH_4) along with the metal halides into the reaction chamber. Usually an inert gas is also used to dilute the mixture. Table 1 gives a description of source gases, deposition temperatures, and the required postdeposition anneals when various refractory metal films and their silicides are deposited by the PECVD process.

Table 1 Plasma-enhanced chemical vapor deposition of refractory metal films

Material	Reactant gases	Deposition temperature		Post-deposition anneal	References
		°C	°F		
W	WF_6, H_2	350-400	660-750	1000 °C (1830 °F) for 30 min	49, 50
WSi	WF_6 + SiH_4 diluted with He	230	450	1000 °C (1830 °F) for 60 min in N_2	52
Mo	$MoCl_5$, H_2	170-430	340-800	800 °C (1470 °F) for 30 min in N_2	53
$MoSi_2$	$MoCl_5$, SiH_4 + Ar	400	750	1000 °C (1830 °F) for 20 min in N_2	51
$TaSi_2$	$TaCl_5$, SiH_2Cl_2 + H_2	580	1080	900 °C (1650 °F) for 60 min in Ar	54

References cited in this section

4. J.-J. Hajjar, R. Reif, and D. Adler, in *J. Electronic Materials,* Vol 15, 1986, p 279
13. R. Reif and W. Kern, Plasma Enhanced Chemical Vapor Deposition, *Thin Film Processes II,* Academic Press, Inc., 1991
38. H. Fritzsche, in *Thin Solid Films,* Vol 90, 1982, p 119
39. D.E. Carlson, in *Solid Energy Mat.,* Vol 3, 1980, p 503
40. I. Shimizu, T. Komatsu, K. Saito, and E. Inoue, in *J. Non-Cryst. Solids,* Vol 35-36, 1980, p 773
41. J-J. Hajjar and R. Reif, in *J. Electrochem. Soc.,* Vol 137, 1990, p 2888
42. J.O. Borland and C. Drowley, in *Solid State Technol.,* Vol 28 (No. 8), 1985, p 141
43. Y. Ota, in *J. Appl. Phys.,* Vol 51, 1980, p 1102
44. P.C. Zalm and L.J. Beckers, in *Appl. Phys. Lett.,* Vol 41, 1982, p 167
45. B.S. Meyerson, in *Appl. Phys. Lett.,* Vol 48, 1986, p 797
46. A. Ishitani, Y. Ohshita, K. Tanigaki, K. Takada, and S. Itoh, in *J. Appl. Phys.,* Vol 61, 1987, p 2224

47. J.H. Comfort and R. Reif, in *J. Appl. Phys.,* Vol 65, 1989, p 1053, 1067
48. T.J. Donahue and R. Reif, in *J. Appl. Phys.,* Vol 19, Supplement 19-1, 1979, p 647
49. J.K. Chu, C.C. Tang, and D.W. Hess, in *Appl. Phys. Lett.,* Vol 41, 1982, p 75
50. C.C. Tang, J.K. Chu, and D.W. Hess, in *Solid State Technol.,* Vol 26 (No. 3), 1983, p 125
51. A. Tabuchi, S. Inoue, M. Maeda, and M. Takagi, in *Proceedings of the 23rd Symposium on Semiconductors and IC Technology of the Electrochemical Society of Japan,* 1-2 Dec 1982, p 60
52. K. Akitmoto and K. Watanabe, in *Appl. Phys. Lett.,* Vol 39, 1981, p 445
53. S. Inoue, N. Toyokura, T. Nakamura, M. Maeda, and M. Takagi, in *J. Electrochem. Soc.,* Vol 130, 1983, p 1603
54. K. Hieber, M. Stolz, and C. Wieczorik, in *Proceedings of the Ninth International Conference on Chemical Vapor Deposition,* McD. Robinson, C.H.J. van den Brekel, G.W. Cullen, and J.M. Blocher, Jr., Ed., The Electrochemical Society, 1984, p 205
55. T. Hara, Y. Ishizawa, H.M. Wu, D.G. Hemmes, and R.S. Rosler, in *Proceedings of the Tenth International Conference on Chemical Vapor Deposition,* G.W. Cullen and J. Blocher, Jr., Ed., The Electrochemical Society, 1987, p 867

Growth and Growth-Related Properties of Films Formed by Physical Vapor Deposition

Donald M. Mattox, IP Industries

Introduction

THE PROPERTIES of atomistically deposited films depend strongly on the material being deposited, the substrate surface chemistry and morphology, the surface preparation process, and the details of the deposition process and the deposition parameters. The origin of the unique properties of physical vapor deposition (PVD) film can be understood by understanding the film formation process.

The formation of a useful and commercially attractive engineered surface using any PVD process (vacuum deposition, sputter deposition, or ion plating) involves several stages:

1. Choice of the substrate ("real surface") and development of an appropriate surface preparation process
2. Selection of the film material(s) to produce the surface properties required
3. Choice of the PVD process to provide reproducible properties, compatibility with subsequent processing, and long-term stability
4. Development of the fabrication process parameters, parameter limits, and the monitoring/control techniques
5. Development of appropriate characterization techniques to determine the film properties and stability of the product
6. Creation of written specifications and manufacturing processing instructions to cover the substrate material, surface preparation, deposition process, and characterization procedures

The properties of a film of a material formed by any PVD process depends on four factors:

- *Substrate surface condition*--e.g., surface morphology (roughness, inclusions, particulate contamination), surface chemistry (surface composition, contaminants), mechanical properties, surface flaws, outgassing, preferential nucleation sites, and the stability of the surface
- *Details of the deposition process and system geometry*--e.g., angle-of-incidence distribution of the depositing adatom flux, substrate temperature, deposition rate, gaseous contamination, and concurrent energetic particle bombardment (flux, particle mass, energy)
- *Details of film growth on the substrate surface*--e.g., substrate temperature, nucleation, interface

formation, interfacial flaw generation, energy input to the growing film, surface mobility of the depositing adatoms, growth morphology of the film, gas entrapment, reaction with deposition ambient (including reactive deposition processes), and changes in the film properties during deposition
- *Postdeposition processing and reactions*--e.g., reaction of film surface with the ambient, thermal or mechanical cycling, corrosion, interfacial degradation, burnishing of soft surfaces, shot peening, and overcoating ("topcoat")

In order for the film to have reproducible properties, each of these factors must be reproducible.

Technological (Real) Surfaces

Technological surfaces or *engineering surfaces* are terms that are used to describe the real surfaces of engineering materials. These layers, along with the underlying bulk material, are the real substrate that must be altered to produce the desired surface properties. Invariably the real surface differs chemically from the bulk material by having surface layers of reacted and adsorbed material such as oxides and hydrocarbons. The surface chemistry, morphology, and mechanical properties of the real surface can be very important to the adhesion and film formation process. The underlying bulk material can be important to the performance of the surface. For example, a wear coating on a soft substrate will not function well if, under load, it is fractured by the deformation of the underlying substrate. Also, good film adhesion cannot be obtained when the substrate surface is mechanically weak, because failure can occur in the near-surface material. The bulk material can influence the surface preparation and the deposition process by continual outgassing and outdiffusion of internal constituents.

Some of the surface properties that affect the formation and properties of the deposited film are:

- *Surface chemistry*--affects the adatom-surface reaction and nucleation density. Chemistry can affect the stability of the interface formed by the deposition.
- *Contamination* (particulate and film, local or uniform)--affects surface chemistry and nucleation of the adatoms on the surface. Particulate contamination generates pinholes in the deposited film.
- *Surface morphology*--affects the angle-of-incidence of the depositing atoms and thus the film growth. Geometrical shadowing of the surface from the depositing adatom flux reduces surface coverage. Surface morphology can affect the film properties and stability.
- *Mechanical properties*--affects film adhesion and deformation under load
- *Outgassing and outdiffusion*--affects nucleation and film contamination
- *Homogeneity of the surface*--affects uniformity of film properties over the surface

In particular, the surface morphology can have an important effect on the film properties. Figure 1 shows the effect of surface morphology and particulate contamination on surface coverage and pinhole formation. Also, the surface morphology can affect the average angle-of-incidence of the adatom flux, which has a large effect on the development of the columnar morphology in atomistically deposited films.

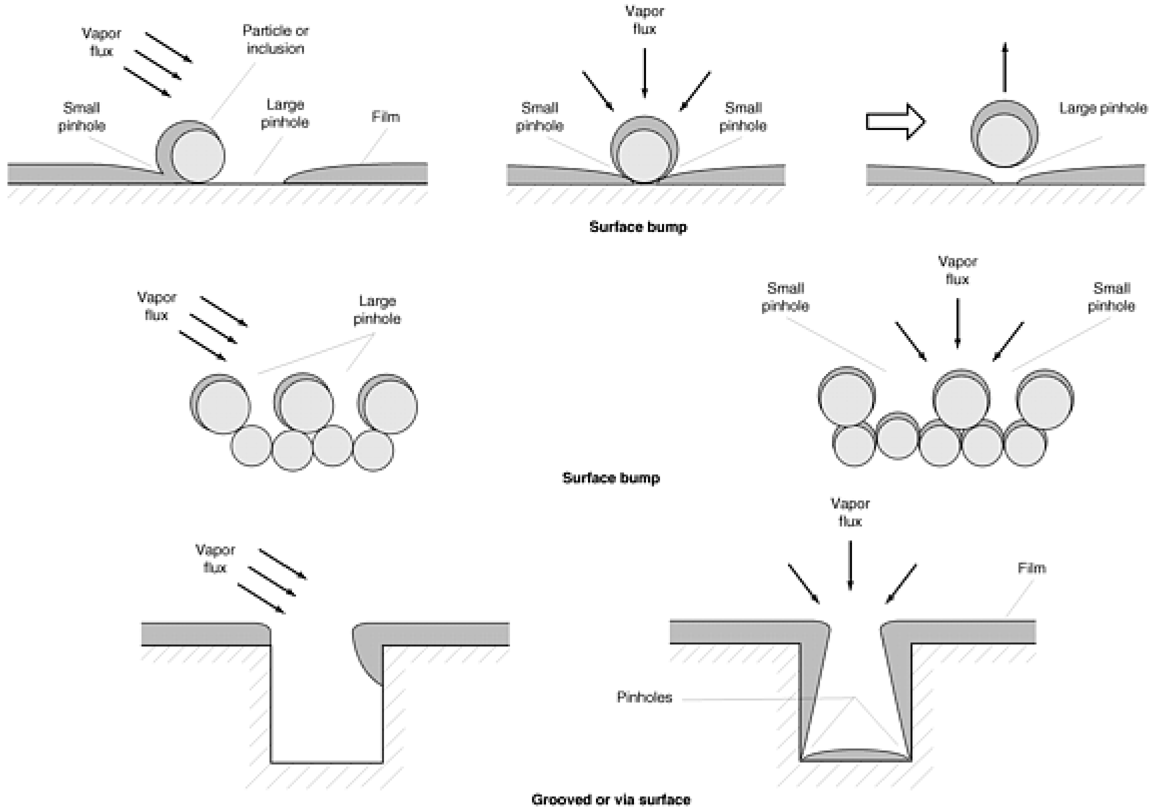


Fig. 1 Surface morphology effects on pinhole formation

The nature of the real surface depends on its formation, handling, and storage history. In order to have reproducible film properties, the substrate surface must be reproducible. This reproducibility is attained by careful specification of the substrate material, careful incoming inspection procedures, careful surface preparation, and appropriate handling and storage of the material.

Surface preparation is the process of preparing a surface for the film/coating deposition process (Ref 1). Surface preparation may mean cleaning (removal of contaminants), but it can also include surface treatments to change the properties of the surface in a desirable way, such as roughening or smoothing the surface, making a harder surface by plasma treatment (i.e., plasma nitriding) or shot peening, or "activating" the surface, such as the oxygen plasma treatment of a polymer surface. Often surface preparation consists of two distinct stages. The first is "external cleaning," which takes place outside the deposition system in a controlled environment. This processing environment is designed to control recontamination after cleaning. For example, to control recontamination by particulates, a filtered air "cleanroom" is used. External cleaning can consist of both "gross cleaning," which removes a portion of the substrate surface material, and "specific cleaning," which removes specific contaminants such as hydrocarbons or salts. The second stage of surface preparation is "in situ cleaning," which is performed in the deposition system. For example, hydrocarbon contamination can be removed from some surfaces by exposing them to an oxygen plasma in the deposition system.

Care must be taken to ensure that the surface preparation process does not change the surface in an undesirable or uncontrolled manner, such as selective leaching of one phase of a two-phase surface. One objective of any surface preparation procedure is to produce as homogeneous a surface as possible. Reproducible surface preparation, as well as associated handling and storage techniques, are obtained by having appropriate specifications for the process, handling, and storage procedures used. In addition, recontamination of the prepared surface in the deposition chamber and by the deposition process is a major consideration.

Reference cited in this section

1. D.M. Mattox, Surface Preparation for Film and Coating Deposition Processes, Chapter 3, *Deposition*

Processes for Films and Coating, 2nd ed., R. Bunshah, Ed., Noyes Publications, 1994

Atomistic Film Growth

Atomistic film growth occurs as a result of the condensation of atoms ("adatoms") on a surface. The stages of film formation are:

1. Vaporization of the material (adatoms) to be deposited
2. Transport of the material to the substrate
3. Condensation and nucleation of the adatoms
4. Nuclei growth
5. Interface formation
6. Film growth--nucleation and reaction with previously deposited material
7. Changes in structure during the deposition process--interface and film
8. Postdeposition changes due to postdeposition treatments, exposure to the ambient, subsequent processing steps, in-storage changes, or in-service changes

All of these stages are important in determining the properties of the deposited film material (Ref 2, 3, 4, 5).

Vaporization

In physical vapor deposition, vapors can be formed by thermal and nonthermal techniques. Thermal techniques require heating, such as vacuum evaporation and sublimation (see the article "Vacuum Deposition, Reactive Evaporation, and Gas Evaporation" in this Volume). Nonthermal vaporization includes sputtering (see the article "Sputter Deposition" in this Volume), arc vaporization, laser ablation, and others.

Transport

The vaporized material can be transported through a vacuum, gas, or plasma. The vacuum environment allows control of the contamination in the ambient environment to any desired level. The gaseous environment may thermalize energetic particles and cause vapor phase nucleation, depending on the gas density (see the article "Vacuum Deposition, Reactive Evaporation, and Gas Evaporation" in this Volume). The plasma environment "activates" reactive species, making them more chemically reactive.

Condensation and Nucleation

Atoms that impinge on a surface in a vacuum environment either are reflected immediately, reevaporate after a residence time, or condense on the surface. The ratio of the condensing atoms to the impinging atoms is called the *sticking coefficient*. If the atoms do not immediately react with the surface, they will have some degree of surface mobility over the surface before they condense. Re-evaporation is a function of the bonding energy between the adatom and the surface, the surface temperature, and the flux of mobile adatoms. For example, the deposition of cadmium on a steel surface having a temperature greater than about 200 °C (390 °F) will result in total re-evaporation of the cadmium.

Surface Mobility. The mobility of an atom on a surface will depend on the energy of the atom, atom-surface interactions (chemical bonding), and the temperature of the surface. The mobility on a surface can vary due to changes in chemistry or crystallography. The different crystallographic planes of a surface have different surface free energies that affect the surface diffusion. For example, for face-centered cubic metals the surface free energy of the (111) surface is less than that of the (100) surface, and the surface mobility of an adatom is generally higher on the (111) surface than on the (100) surface. This means that different crystallographic planes will grow at different rates during adatom condensation. Various techniques have been developed to study surface mobility and the surface diffusion rate of adatoms on a surface (Ref 6, 7).

The surface mobility of adatoms can be an important factor in surface coverage. For example, the surface coverage of a silicon device is improved by depositing an Al/Cu metallization on a TiN barrier layer at 500 °C (930 °F). The Al/Cu has a higher surface mobility on the TiN surface than on the silicon surface and is able to completely fill a 0.5 μm diameter

by 0.8 μm deep "via" holes. Also, by direct current magnetron sputter-depositing the Al-5Ga eutectic alloy at 300 °C (570 °F), "via" holes with aspect ratios of up to 4:1 have been successfully filled.

Nucleation. Atoms condense on a surface by losing energy. They lose energy by:

- Making and breaking chemical bonds with the substrate surface atoms
- Finding preferential nucleation sites (e.g., lattice defects, atomic steps, impurities)
- Colliding with other diffusing surface atoms (same species)
- Colliding or reacting with adsorbed surfacespecies

Nucleation by Surface Reaction. The condensing atoms react with the surface to form atom-to-atom chemical bonds. The chemical bonding may be by metallic (homopolar) bonding where the atoms share orbital electrons, by electrostatic (coulombic, heteropolar) bonding where ions are formed due to electron loss/gain, or by electrostatic attraction (van der Waals forces) due to polarization of molecules. If the atom-atom interaction is strong, surface mobility is low and each surface atom can act as a nucleation site. If the reaction is strong, the atom is said to be *chemisorbed*. In some cases the chemisorbed adatom displaces the surface atoms, giving rise to a "pseudomorphic" surface structure.

The bonding energy of atoms to surfaces can be studied by thermal desorption techniques. The chemisorption energy for some materials on clean surfaces are:

Material	Energy, eV
Rb on W	2.6
Cs on W	2.8
B on W	6.1
N_2 on Fe	3.0
Ni on Mo	2.1
Ag on Mo	1.5
Au on W	3.0
O_2 on Mo	7.5

Note: 1 eV/atom = 23 kcal/mole.

Source: Ref 8

The bonding between a metal atom and an oxide surface is proportional to the metal-oxygen free energy of formation, with the best adhesion produced by the formation of an intermediate oxide interfacial layer. In many instances the surface composition can differ significantly from that of the bulk of the material, and/or the surface can have an nonhomogeneous

composition. Examples are the glass-bonded (Si-O) sintered, alumina ceramics shown in Fig. 2. Film atoms prefer to nucleate and react with the glassy Si-O phase, and if this material is leached from the surface during surface preparation, the film adhesion suffers (Ref 9). Preferential sputtering of a compound or alloy substrate surface can change the surface chemistry. For instance, preferential sputtering of an Al_2O_3 surface removes oxygen, leaving an aluminum-rich surface (Ref 10). Surface contamination can greatly influence the nucleation density, interfacial reactions, and nuclei orientation. When a two-phase binary alloy is deposited, the two materials may react differently with the surface, resulting in segregation on the surface.

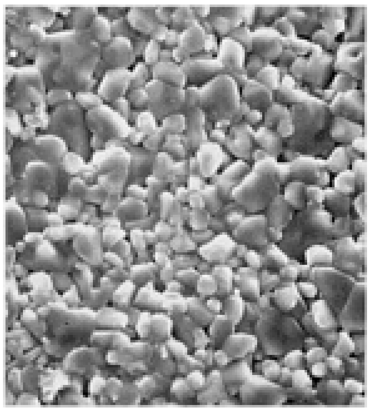


Fig. 2 Surface morphology of an as-sintered 96% alumina ceramic such as is used in hybrid circuitry. 1000×

Nucleation at Preferential Nucleation Sites. If the adatom-surface interaction is weak, the adatom will have a high surface mobility and will condense at preferential nucleation sites where there is stronger bonding due either to a change in chemistry (element or electronic) or an increase in coordination number (e.g., at a step). Preferential nucleation sites can be:

- Morphological surface discontinuities such as steps or scratches
- Lattice defects in the surface such as point defects or grain boundaries
- Foreign atoms in the surface
- Charge sites in insulator surfaces
- Surface areas that have a different chemistry or crystallographic orientation

Steps on a surface can act as preferential nucleation sites. For example, gold deposited on cleaved single-crystal NaCl or KCl shows preferential nucleation on cleavage steps. Steps on Si (100) and GaAs (100) surfaces can be produced by polishing at an angle of several degrees to a crystal plane. This procedure produces an "off-cut" or "vicinal" surface (Ref 11) comprised of a series of closely spaced steps. These steps aid in dense nucleation for epitaxial growth of GaAs on Si and Al_xGa_{1-x} As on GaAs. Scratches on the substrate surface provide nucleation sites in the deposition of diamond films.

Lattice defects can act as preferential nucleation sites. For example, amorphous carbon films have a high density of defects that act as nucleation sites for gold deposition. When depositing adatoms on electrically insulating substrates, charge sites on the surface can act as preferential nucleation sites. Electron irradiation, ultraviolet radiation (UV), and ion bombardment can be used to create charge sites.

Nucleation by Collision. Mobile surface adatoms can nucleate by collision with other mobile surface species to form stable nuclei. Thus the nucleation density can depend on the deposition (arrival) rate. For example, in the deposition of silver on lead it has been shown that at a deposition rate of 0.1 nm/min, the silver is completely re-evaporated, while at 10 nm/min, the atoms are completely condensed. When depositing silver on glass, improved adhesion can be obtained by a rapid initial deposition rate, followed by a lower rate to build up the thickness.

Nucleation by Reaction with Adsorbed Atoms. Mobile surface species can react with adsorbed surface species such as oxygen. For example, chromium deposition after oxygen plasma cleaning of glass generally results in improved

adhesion compared to a glass surface that has not been oxygen-plasma cleaned. This is probably due to the adsorption of oxygen on glass, which increases the nucleation density of deposited gold (Ref 12). The adsorption of reactive species can also have an important effect in reactive deposition processes (Ref 13).

Nucleation of Unstable Surfaces. Some surfaces are unstable and change their nature when atoms are added to the surface. For example, the adatom may interact with the surface lattice and cause atomic rearrangement such that a pseudomorphic surface is formed that presents a different surface to atoms subsequently deposited (Ref 8). Some polymers, particularly glassy polymers (i.e., those above their glass transition temperatures), have surfaces that are unstable and into which the depositing adatom will sink and possibly even nucleate below the polymer surface (Ref 14). Polyethylene and polypropylene are examples of polymers that are glassy at room temperature.

Nucleation Density. In general, the number of nuclei per unit area, or "nucleation density," should be high in order to form a dense film and obtain complete surface coverage at low film thickness. The nucleation density and growth behavior can vary with different substrate locations due to phase distribution, surface morphology, or crystallographic orientation of the substrate surface. The variation of nucleation density and subsequent film growth can result in film property variations over the surface.

Characterization of Nucleation Density. The relative and absolute nucleation density can be determined by a number of techniques (Ref 15), including:

- Optical density of the deposited film as a function of mass deposited
- Behavior of the thermal coefficient of resistivity (TCR) as a function of mass deposited
- Transmission electron microscopy (TEM) and ultrahigh vacuum TEM
- Auger electron spectroscopy (AES)
- Low-energy electron diffraction (LEED)
- Reflection high-energy electron diffraction (RHEED)
- Work function change as a function of mass deposited
- Scanning electron microscopy (SEM)
- Scanning tunneling microscopy (STM) (Ref 16)
- Atomic force microscopy (AFM)
- Photon tunneling microscopy (PTM) (Ref 17)

Optical Adsorption. On transparent substrate materials, the optical density of a film formed by depositing a given amount of material can be used to measure the comparative nucleation density. The optical density (OD) is defined as: OD = log [(% visual light transmitted through the substrate)/(% visual light transmitted through a metallized substrate)]. A good electrical conductor having a high nucleation density is optically opaque to the human eye when the film thickness is about 1000 Å (100 nm). A comparison of optical densities is often a good "quick check" on process reproducibility.

The temperature coefficient of resistance (TCR) of very thin metal films on electrically insulating substrates depends on the growth of the nuclei. Isolated nuclei result in a negative TCR (increasing temperature/decreasing resistance) due to thermally activated tunneling conduction between nuclei. Connected nuclei, which form a continuous film, have a positive TCR as would be expected in a metal. Thus TCR measurements can be used to provide an indication of nucleation density and growth mode by determining the nature of the TCR as a function of mass deposited.

Surface Analytical Techniques. Using low-energy electron diffraction (LEED) it has been shown that very low coverages of contamination can inhibit interfacial reaction and epitaxial growth. The field ion microscope has been used to field-evaporate deposited material and observe the "recovered" substrate surface. Using this technique to study the deposition of copper on tungsten, it was shown that electroplating results in interfacial mixing similar to that produced by high-temperature vacuum deposition processing.

Modification of Nucleation Density. There are a number of ways to modify the nucleation of depositing atoms on substrate surfaces, including:

- Change deposition temperature (increasing temperature can increase reaction with surface and increases

surface mobility; decreasing temperature can decrease surface mobility)

- Increase deposition rate to increase collision probability of diffusing species
- Change surface chemistry to make the surface more reactive
- "Sensitizing" the surface by the addition of "nucleating agents"
- Generate nucleation sites on the surface (lattice defects, charge sites on insulators) by mechanically disrupting the surface to produce defects and disturb contaminant layers ("mechanical activation"), using ion bombardment to produce lattice defects (Ref 18), incorporating species by ion implantation or chemical substitution, or using electron bombardment or photon bombardment (Ref 19) to charge centers on insulator surfaces
- Produce codeposition or absorption of reactive species
- Change surface roughness
- Create a new surface--"basecoat" or "glue layer"

Adsorption and Codeposition or Reactive Species. Adsorbed or codeposited reactive species can affect the surface chemistry and thus the nucleation of the deposited species. The presence of adsorbed oxygen or oxygen in a plasma or bombarding oxygen ion beam during deposition has been shown to aid in the adhesion of gold (Ref 20) and oxygen-active film materials (Ref 21) to oxide substrates. The increased adhesion is attributed to the increased nucleation density. In the case of a plasma system such as plasma-enhanced chemical vapor deposition (PECVD), the radicals, unique species, and excited species formed in the plasma may play an important role in adsorption and deposition from a gaseous precursor. For example, in the deposition of silicon from silane by PECVD, it has been proposed that the formation of disilane and trisilane in the plasma and its adsorption on the surface, along with low-energy particle bombardment, is important to the low-temperature, high-rate deposition of amorphous silicon (Ref 22).

Surface roughness can also play an important role in nucleation. The typical 94% alumina used in microelectronics has a surface roughness that looks like a field of boulders several microns in diameter (see Fig. 2). Deposition on such a surface results in a high nucleation density on the tops of the "boulders" and a lower nucleation density on the sides and in the pores. Flowed glass surfaces, on the other hand, are smooth and the nucleation density can be uniform over the surface.

Establishing a New Surface. In the extreme case, a new surface layer ("glue layer," basecoat) can be used to provide a better surface for the deposition of the desired material. This is often done in the metallization systems used in micro-electronics and for interconnects in integrated circuit technology. In these cases a material is deposited on the oxide/semiconductor surface that forms a desirable oxide interface (e.g., titanium or chromium). Then a surface layer is deposited that alloys with the first layer and provides the desired property (e.g., gold, copper, silver). The new surface can also be used to smooth or "planarize" the initial surface (e.g., a "flowed" basecoat layer).

Growth of Nuclei

When atoms condense they form nuclei. If the surface is of the same material as the depositing atoms, the process is called *homogeneous nucleation*; if they are of different materials, the process is call *heterogeneous nucleation*. In semiconductor terminology, heterogeneous nucleation forms *heterojunctions*. Three types of nucleation mechanisms have been identified; they differ according to nature of interaction between the deposited atoms and the substrate material (Ref 23): (a) the van der Merwe mechanism leading to a monolayer-;by-monolayer growth; (b) the Volmer-;Weber (V-;W) mechanism, characterized by a three-dimensional nucleation and growth; and (c) the Stranski-Krastanov (S-K) mechanism, where an altered surface layer is formed by reaction with the deposited material to generate a strained or pseudomorphic structure, followed by nucleation on this altered layer. The S-K nucleation is common with metal-on-metal deposition and at low temperatures where the surface mobility is low. The conditions for these types of growth is generally given in terms of thermodynamics and surface energy considerations.

Often the adsorption is accompanied by surface reconstruction, surface lattice strain, or surface lattice relaxation, which change the lattice atom spacing or the surface crystallography to give a pseudomorphic structure. The interaction of the depositing material with the surface can form a structure on which subsequent depositing atoms nucleate and grow in a manner different from that of the initially depositing material. This may alter the subsequent film structure. For example, the unique beta-tantalum structured films are stabilized by deposition on an as-grown tantalum silicide interfacial material.

Nuclei Coalescence and Agglomeration. The nuclei grow by collecting atoms that diffuse over the surface. Isolated nuclei grow laterally and vertically on the surface to form a continuous film (Ref 24). The higher the nucleation density, the less the amount of material needed to form a continuous film. The principal growth mode of the nuclei may be laterally over the substrate surface ("wetting growth"), or the nuclei may prefer to grow in a vertical mode ("dewetting growth"). Examples of wetting growth are: gold on copper and chromium, iron on W-O surfaces, and titanium on SiO_2. Examples of dewetting growth are nickel and copper on W-O surfaces, and gold on carbon, Al_2O_3, and SiO_2. Growth and coalescence of the nuclei can leave interfacial voids or structural discontinuities at the interface, particularly if there is no chemical interaction between the nuclei and the substrate material and dewetting growth occurs.

In cases where there is little chemical interaction between the nucleating atoms and the substrate, the isolated nuclei grow together, giving the so-called island-channel-continuous film growth stages. Before coalescence the nuclei can have a "liquid-like" behavior that allows them to rotate and align themselves crystallographically with each other, giving an oriented (epitaxial) overgrowth.

Agglomeration of nuclei occurs when the temperature of the nuclei is high enough to allow atomic diffusion and rearrangement such that the nuclei "ball-up" to minimize the surface area. Agglomeration of evaporated gold films is increased at high deposition rates, at high substrate temperatures, and in high-rate electron beam evaporation. Gold is often used for replication in electron microscopy, and agglomeration of pure gold can be a problem; therefore, gold alloys such as 60Au:40Pd are used to reduce the agglomeration tendencies and provide better replication. Agglomeration can occur after deposition if there is appreciable columnar growth (high surface area) in the film and the film is heated.

Where there is strong interaction between the adatoms and the substrate but little diffusion or compound formation with the substrate, the crystal orientation of the deposited material can be influenced by the substrate crystallographic orientation, producing a preferential crystallographic orientation in the nuclei. This type of oriented overgrowth is called *epitaxial growth.* Lattice mismatch between the nuclei and the substrate at the interface can be accommodated by lattice strain or by the formation of "misfit" dislocation networks, and under proper conditions a single crystal epitaxial film can be grown. This is often the goal in molecular beam epitaxy (MBE) and chemical vapor deposition (CVD) of semiconductor thin films. In the growth of semiconductor materials it is desirable to form an interface that is defect-free so that electronically active sites are not generated. Such an interface can be formed if there is lattice parameter matching between the deposited material and the substrate, or if the deposited material is thin enough to allow lattice strains to accommodate the lattice mismatch without producing dislocation networks. This latter condition produces a "strained layer superlattice" structure (Ref 25).

At the other extreme of growth are amorphous materials where rapid quenching, bond saturation, limited surface diffusion, and the lack of substrate influence results in a highly disordered material. Comparison between amorphous materials formed by coevaporation and those formed by rapid quenching show some indication of a lower degree of short range ordering in the codeposited material, as indicated by the lower crystallization temperature and lower activation energy for crystallization than in the low-temperature deposited films. Amorphous conductive materials, such as $W_{75}Si_{25}$, have been proposed as a diffusion barrier film in semiconductor metallization. Because amorphous films have no grain boundaries, they are expected to show lower diffusion rates than films that have grain boundaries, in that grain boundary diffusion rates are generally higher than bulk diffusion rates.

Heating by Condensation. At high deposition rates, the condensation energy can produce appreciable substrate heating. When a thermally vaporized atom condenses on a surface it releases energy from several sources, including:

- *Heat of vaporization or sublimation* (enthalpy of vaporization)--a few electron volts per atom
- *Energy to cool to ambient*--depends on heat capacity and temperature change
- *Energy associated with reaction*, which may be exothermic, where heat is released, or endothermic, where heat is adsorbed--heat of reaction (Table 1)
- *Energy released on solution*--heat of solution

Table 1 Heats of reaction

Material	Heat, kcal/mole

Ni_2Si	-11
NiSi	-18
Pt_2Si	-11
PtSi	-15
$ZrSi_2$	-35
Ta_2O_5	-500
Al_2O_3	-399
V_2O_3	-290
Cr_2O_3	-270
TiO_2	-218
WO_3	-200
MoO_3	-180
Cu_2O	-40
SiC	-15
Au in Si	-2.3[(a)]
Ni_3C	+16
Au_2O_3	+19

(a) Heat of solution

The thermal vaporization energy for gold from tungsten is about 3 eV per atom, and the kinetic energy of the vaporized atom is about 0.3 eV per atom. Thus the kinetic energy is only a small part of the energy being released during deposition. However, it has been shown, using mechanical velocity filters, that the kinetic energy of the depositing gold particles is important to the film structure, properties, and annealing behavior.

If the depositing atom has greater than thermal energy, due either to being vaporized by sputtering (and not "thermalized" during transport from source to substrate), or to being accelerated as an ion (film ion), the kinetic energy that it releases will be greater than thermal. If the depositing species is excited or ionized, it also releases the excitation energy or the ionization energy. In these situations the energy released also includes excess kinetic energy, excitation energy (if an excited species), or ionization energy (if an ionized species).

Interface Formation

The depositing film material can diffuse and react with the substrate to form an "interfacial region." The material in the interfacial region has been called the "interphase material," and its properties are important to the adhesion, electrical, and electronic properties of film-;substrate systems. The type and extent of the interfacial region can change as the deposition process proceeds or be modified by postdeposition treatments. Interfacial regions are categorized as (Ref 26):

- Abrupt
- Mechanical (specific type of the abrupt interface)
- Diffusion
- Compound (also requires diffusion)
- Pseudodiffusion (physical mixing, ion implantation, recoil implantation)
- Reactively graded
- Combinations of the above

Figure 3 schematically shows the types of interfacial regions.

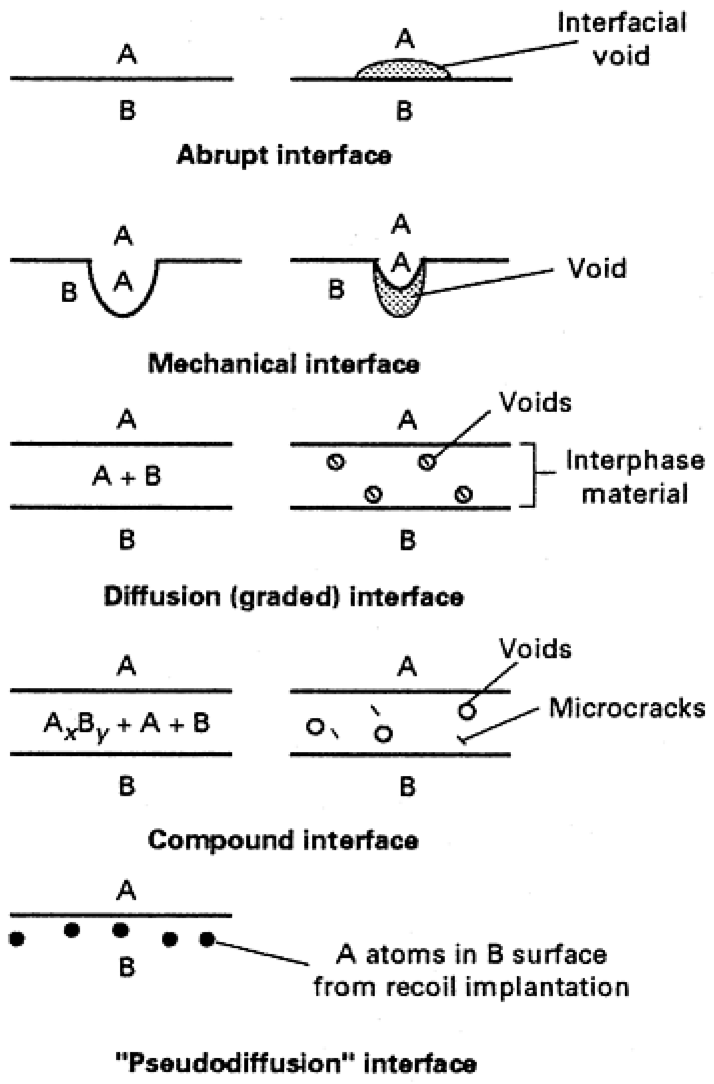


Fig. 3 Types of interfacial regions

The abrupt interface is characterized by an abrupt change from the film material to the substrate material in a distance of the order of the atomic spacing (i.e., 0.2 to 0.5 nm), with concurrent abrupt changes in material properties. This type of interface is formed when there is no bulk diffusion, and it generally signifies weak chemical reaction between the depositing atoms and the substrate, a low deposition temperature, surface contamination, or no solubility between film and substrate materials. The formation of this type of interfacial region generally means that the nucleation density is low and that the film will have to grow to appreciable thickness before it becomes continuous. This results in the formation of interfacial voids along the interface. Typically the adhesion in this system is low because of interfacial voids and an easy fracture path.

Mechanical Interlocking Abrupt Interface. The mechanical interface is an abrupt interface on a rough surface where the deposited material forms a conformal surface to the roughness and the rough surface is "filled in" to give mechanical interlocking. The strength of the interface depends on the mechanical properties of the materials. To fracture along the interface requires following a tortuous path with changing stress tensors, and the adhesion of the film to the surface can be high. Surfaces can be made rough or porous to increase the degree of mechanical interlocking. The adhesion of this couple is limited by the deformation and/or fracture properties of the materials involved. If the roughness is not filled in, the adhesion will be low due to the lack of contact and interfacial voids. The filling in of the roughness can be aided by having a dispersed adatom flux distribution, concurrent energetic particle bombardment, or high surface mobility of the deposited material.

The diffusion interface is characterized by a gradual change or gradation in composition across the interfacial region with no compound formation. The diffusion interface is formed when there is mutual solid solubility between the film and substrate material and the temperature and time are sufficient to allow diffusion to occur. This type of interfacial system is often found in metallic systems. Some systems, such as silver on iron and indium, or gallium on GaAs, have no solubility and an abrupt interface is formed. If contamination is present on the surface, diffusion can be suppressed.

The extent of diffusion in the interface depends on time and temperature. Differing diffusion rates of the film and substrate materials can create porosity in the interfacial material. Porosity formed by this mechanism is called *Kirkendall porosity*. This porosity can weaken the interfacial material and provide an easy fracture path for adhesion failure.

In some cases, diffusion barriers are used at the interface to reduce diffusion. For example, tungsten plus titanium or the electrically conductive nitride, TiN, is used as a diffusion barrier in silicon metallization to inhibit aluminum diffusion into the silicon during high-temperature processing. The presence of compound-forming species in the depositing material reduces the diffusion rate. Alternatively, the depositing material can be alloyed with substrate material to reduce diffusion rates.

In high-temperature processing the substrate material near the interface can be weakened by the diffusion of a constituent of the substrate into the depositing film material. For example, the diffusion of carbon from cemented carbide tools during CVD deposition of coating forms a weak eta phase at the interface. Conversely the diffusion from the substrate can result in increased adhesion. For example, it has been shown that in the deposition of carbides on oxide surfaces the oxygen intermixes and reacts with the carbide material, producing a "keying" action.

Compound Interface. Diffusion, along with chemical reaction, forms a compound interfacial region. The compounds formed are often brittle, and high stresses are often introduced due to the volumetric changes involved in forming the new phase(s). Sometimes these stresses are relieved by microcracking in the interfacial region, thus weakening the interphase material. The compound interface is generally conducive to good adhesion, but if the reaction region is too thick, the development of porosity and the formation of microcracked brittle compounds can lead to poor adhesion.

The compound interface is the type of interface found in reactive systems, such as oxygen-active metal films on oxide substrates (Ref 27), or in intermetallic-forming metal-on-metal systems such as Au-Al and Al-U. In the case of Au-Al, the interdiffusion and reaction forms both Kirkendall voids and a brittle intermetallic phase termed "purple plague" that causes easy bond failure (Ref 28).

Table 1 lists heats of reactions of various materials in forming compounds. An exothermic reaction is one in which heat is released and is indicated by a negative heat of formation. An endothermic reaction is one in which heat is taken up and is indicated by a positive heat of reaction. In some layered film systems there can be an exothermic reaction such that large amounts of heat are generated after the reaction has been "triggered." Such systems are Pd-Sn, Al-Pd, and Al-Zr, which have increasingly higher "triggering" temperatures. Multilayer composite structures of these materials can be used to rapidly release heat (Ref 29).

Interfacial Boundary. It should be remembered that diffusion and reaction can continue during the deposition process, particularly if an elevated deposition temperature and long times are used. For example, with aluminum on platinum an Al-Pt intermetallic is formed, and as the intermetallic layer thickness increases it removes the aluminum preferentially from grain boundaries at the Al/Al-Pt interface. This leads to void formation at the grain boundaries and the formation of "capillary voids."

As diffusion proceeds, the interfacial boundary becomes "rough." Rapid diffusion can occur at grain boundaries and dislocations, giving a "spiked" interfacial surface that aids in the bonding of some coatings to surfaces but can cause shorting in semiconductor junctions ("pipe diffusion"). Rapid heating and cooling can also limit diffusion and in ion plating, where heat is introduced directly into the surface, a cold substrate can be used. As a postdeposition process, heating by rapid thermal processing can be used to limit preferential diffusion along lattice defects.

The interphase material formed by diffusion and reaction often contains a graded composition with properties that vary throughout the layer. If the material becomes thick, it can develop high residual stress, voids, and microcracks that weaken the material and result in poor adhesion. The interphase material is important in film adhesion, contact resistance, and the electronic "interfacial states" of metal-semiconductor contacts.

In the extreme the film material can completely react with the substrate, thus forming a film of the interphase material. This is usually an effect of high substrate temperature during deposition or postdeposition processing. For example, it has been reported that sputter-deposited tungsten on silicon forms a silicide film that has the same properties as 900 °C (1650 °F) furnace-diffused tungsten-on-silicon silicide films. Platinum on silicon can also be completely reacted to form silicide electrodes on the silicon.

Metal-Polymer Interfaces. In the case of polymer surfaces, particularly glassy polymers, the depositing atoms can diffuse into the surface, then nucleate, forming nuclei of the material in the subsurface region. For example, in the deposition of copper on polyimide at low deposition rates (1 monolayer/min), copper nuclei are formed beneath the surface while chromium, which forms a chemical bond with the polymer chain, does not diffuse into the surface. The nucleation and chemical bonding of the adatoms to the polymer surface determine the adhesion strength (Ref 30).

Pseudodiffusion Interfaces. In deposition processes, an interface with a graded composition and materials properties can be formed by "grading" the deposition from one deposited material to the other. For example, in depositing Ti-Au or Ti-Cu metallization, the gold or copper deposition can begin before the titanium deposition has ended. This produces a graded interface similar to the diffusion interface, called a *pseudodiffusion interface*. This can be formed between insoluble materials, such as silver and iron, and at low temperatures where the phases do not segregate. This method of grading the interface also avoids the potential problem of oxidation of the titanium film before the gold or copper is deposited. If oxidation occurs, the adhesion between the titanium and the gold or copper layers will be poor. The pseudodiffusion type of interface can also be formed by "recoil implantation" during concurrent or subsequent ion bombardment.

Reactively Graded Interface. A compound-containing interfacial region that consists of a graded compound-matrix material can be formed by controlling the availability of reactive gases during reactive deposition. For example, a TiN hard coating can be deposited with a graded interfacial layer of Ti to TiN_x, to improve adhesion, by controlling the availability of the reactive nitrogen.

Characterization of Interfaces. Generally the interphase material is difficult to characterize because it usually consists of a small amount of material buried under a relatively thick film. In 1988 the National Science Foundation conducted a workshop on adhesion, and one of the principal determinations was that the properties of the interphase material were poorly characterized and understood (Ref 31).

In some cases the compositional profile of the interfacial region can be determined using Auger electron spectroscopy in combination with sputter etching or Rutherford backscatter spectrometry (Ref 15). Cross section TEM can be used with proper care not to introduce artifacts due to sample preparation.

Modification of Interfacial Regions. Interface composition, structure, and extent can be modified by:

- Substrate surface cleaning and surface preparation
- Changing the substrate temperature and deposition time
- Introducing energy into the surface region during deposition by concurrent ion bombardment, laser heating, and so on

Surface preparation is an important factor in interface formation in that the interface reactions can be drastically modified by the presence of strongly bound contaminants such as oxygen, carbon, and nitrogen, whereas weakly bound contaminants such as H_2O, CO, and hydrogen, can be displaced from the surface during deposition.

Ion bombardment, before and during deposition, can introduce defects into the surface region, and diffusion can be enhanced by mechanisms similar to those found in "radiation enhanced diffusion." For example, in the aluminum metallization of silicon it has been shown that there is little diffusion of aluminum into silicon during high-temperature processing if the silicon surface is undamaged. However, extensive diffusion occurs if the surface is damaged by ion bombardment.

Film Growth

Films grow by the continuous nucleation of depositing atoms on previously deposited material. The film growth, as well as the nucleation mode, determines many film properties, such as density, surface area, surface morphology, and grain size. Important aspects of film growth are:

- Continual burial of the surface under newly depositing material
- Substrate surface roughness--initially, and as the film develops
- Surface temperature--initially, and as the film develops
- Adatom surface mobility
- Geometrical shadowing effects (angle-of-incidence effects)
- Reaction and mass transport during deposition, such as segregation effects and void agglomeration

Developing Surface Roughness. On an atomistic scale, surface morphology can vary from very smooth, such as that of a flowed glass surface, to very rough, such as is found with sintered materials (see Fig. 2). Generally, as the film grows the surface roughness increases because some features or crystallographic planes grow faster than others. The roughness may not be uniform over the surface, or there can be local areas of roughness due to scratches, vias, embedded particles, particulate contamination, and so on that lead to variations of the film properties in these areas.

Structure-Zone Model (SZM). Typically the film near the interface is influenced by the substrate and/or interface material, and it takes an appreciable thickness before the film establishes a particular growth mode. After a growth mode has been established, the film morphology can be described by a structure zone model (SZM). The SZM was first applied to vacuum-deposited coatings by Movchan and Demchishin in 1969 (Ref 32). Later the SZM was extended to sputter-deposited films by Thornton (Ref 33), as shown in Fig. 4, and was later modified by Meissier (Ref 34) to include point defect agglomeration and void coarsening with thickness. The details of the condensation processes that determine the film morphology at low temperatures where atom mobility is low are not well understood, although there are a number of factors involved, including:

In vacuum:

- Angle-of-incidence of the adatom flux effects (i.e., geometrical shadowing)
- Ratio of the deposition temperature (in K) to the melting temperature (in K) of the film material
- Energy released on condensation
- Adatom surface mobility on surfaces and crystallographic planes
- Surface roughness
- Deposition rate
- Void coalescence
- Mass transport and grain growth during deposition

In sputter deposition and ion plating (Ref 13):

- Adsorption of inert and/or reactive gaseous species on the surface
- Gas scattering of vaporized particles
- Concurrent bombardment by high-energy particles, which can be from reflected high-energy neutrals from the sputtering target that are not thermalized by collisions in the gas phase, accelerated negative ions from the sputtering target, accelerated positive ions from a plasma, or energetic neutrals formed by charge exchange processes

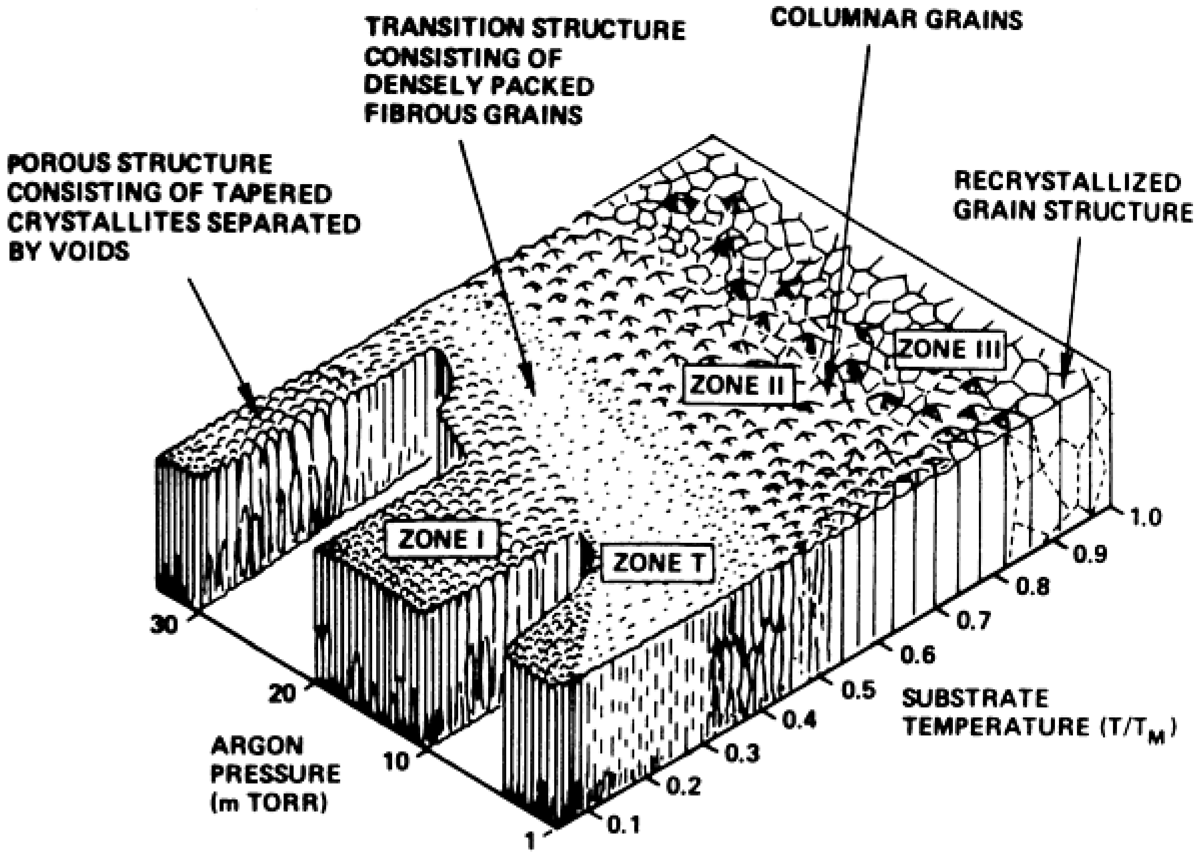


Fig. 4 Structure-zone model for sputter-deposited films (Ref 33)

The morphology of the depositing film is determined by the surface roughness and the surface mobility of the depositing atoms, with geometrical shadowing and surface diffusion competing to determine the morphology of the depositing material. When the surface is rough, the peaks receive the adatom flux from all directions, and if the surface mobility of the adatoms is low, the peaks grow faster than the valleys due to geometrical shadowing. This shadowing effect is exacerbated if the adatom flux is off-normal so that the valleys are in "deeper shadows" than when the flux is normal to the surface. Adsorbed gaseous species decrease the adatom surface mobility, while concurrent energetic particle bombardment can increase or decrease the surface mobility.

SZM Zone 1. In Zone 1 of the Movchan and Demchishin model and in the Thornton model, the adatom surface diffusion is insufficient to overcome the geometrical shadowing by the surface features. This results in open boundaries between the columns that are formed. This morphology produces a film with a high surface area and a film surface that has a "mossy" appearance. Higher gas pressures extend this zone to higher temperatures due to gas scattering, and surface mobilities decrease due to gas adsorption and collisions on the surface. The columnar morphology that develops has been computer modeled for depositing spheres (Ref 35). The columns can have different shapes such as round columns for aluminum (as shown in Fig. 5) and platelets for beryllium. The columns are not single grains. The columns can be microns in size, but the grain size can be less than 1000 Å (100 nm) or even amorphous within the columns. Because the columnar growth is strictly a function of surface geometry and adatom surface mobility, amorphous as well as crystalline materials show the columnar growth mode.

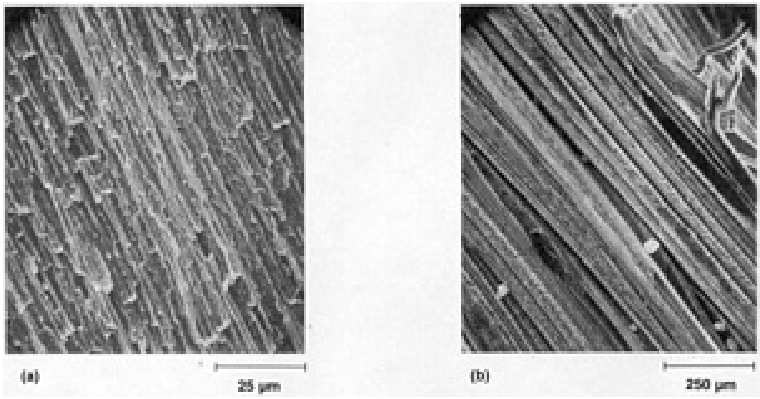


Fig. 5 Columnar morphologies of (a) sputter-deposited stainless steel and (b) vacuum-deposited aluminum films

The development of the columnar morphology begins very early in the film growth stage and generally becomes prominent after about 100 nm of thickness. For example, in the sputter deposition of MoS_2 solid film lubricants, the growth is such that, irrespective of the thickness of the deposited film, during wear, all the columns shear off at their base, leaving a surface layer of about 200 nm thickness. Another example is the vacuum deposition or sputter deposition of CoCr, a magnetic recording material that is very sensitive to film growth. The film consists of columnar grains with the hexagonal close-packed (hcp) *c*-axis, which is the easy magnetization direction, perpendicular to the substrate surface. TEM studies of the growth of sputter-deposited CoCr on NaCl at 100 °C (212 °F) show the following stages of columnar morphology development as a function of film thickness (Ref 36):

- Less than 5 nm: Poor crystal quality--substrate effects
- 10 nm: Good hcp with clear grain boundaries--grain size 2 to 8 nm, various crystallographic orientations
- 80 nm: Well-developed columnar grain orientation
- 100 nm: *c*-axis becomes perpendicular to growth direction, grain size 15 to 25 nm

Angle-of Incidence Effects. The columnar growth is exacerbated by oblique deposition flux orientations because now the valleys get no flux. The oblique angle of incidence can be due to a rough surface, a surface with features such as steps, scratches, or vias, or an off-normal deposition on a relatively smooth surface. For an off-normal incident flux, the columns do not grow normal to the surface but grow toward the adatom source with a change in column shape. The off-normal growth gives an even more open morphology with a lower density than that of the normal-deposited columnar morphology. The off-normal incidence can vary over the surface due to local surface morphologies such as that of a sintered material (see Fig. 2), scratches, via sidewalls, particulates, steps (Ref 37), etc. Figure 6 shows a "nodule" in a sputter-deposited chromium film that developed on particulate contamination on the substrate surface.

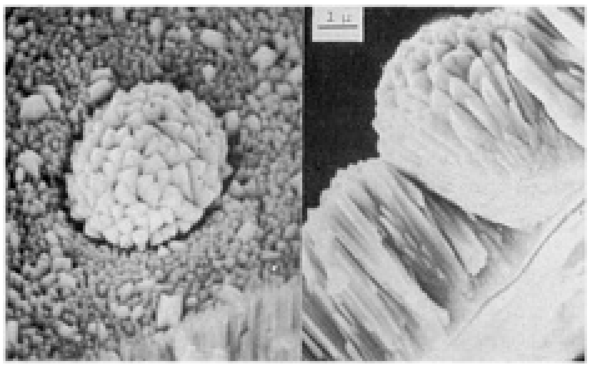


Fig. 6 Picture of a "nodule" in a thick sputter-deposited chromium film

Angle-of-incidence effects can be apparent when the substrate is moved in front of the vaporization source, as in the case of the use of a pallet fixture. In this case the angle of incidence starts very low, goes through normal incidence, then exits at a low angle of incidence. The initial growth at high angle can influence the growth at normal incidence.

SZM Zone T. In the zone model for sputter-deposited films, Thornton introduced the zone T. In zone T the coating has a fibrous morphology and is considered to be a transition from zone 1 to zone 2. The formation of the zone T material is due to the energetic bombardment from reflected high-energy neutrals from the sputtering target at low gas pressures. These energetic high-energy neutrals erode the peaks and fill in the valleys to some extent.

SZM Zone 2. In zone 2 the growth process is dominated by adatom surface diffusion. In this region, surface diffusion during deposition allows the densification of the intercolumnar boundaries. However, the basic columnar morphology remains. The grain size increases and the surface features tend to be faceted.

SZM Zone 3. In zone 3, bulk diffusion allows recrystallization, grain growth, and densification. Often the highly modified columnar morphology is detectable, with the columns being single crystals of material.

Surface Morphology Effects on Film Morphology. A columnar morphology will develop on a smooth substrate surface as it roughens with film thickness during growth. If the surface is not smooth, the variation in the angle of incidence and the general roughness will produce a more complex morphology and generally a less dense film than on a smooth surface. For example, a film grown on the surface shown in Fig. 2 will consist of a "microcolumnar" morphology of columns grown in films on each of the individual "boulders" and a "macrocolumnar morphology" resulting from shadowing effects by the boulders. The result will be a very complicated morphology that will depend on the surface morphology. If the surface has some morphology pattern, such as the patterned metallization on a smooth silicon wafer, the angle of incidence will vary with position on the surface, and differing film properties with position can be expected over the surface. For example, the film on the sidewall of a via can be expected to be less dense than the surface facing the vapor source directly (Ref 37). This effect is easily demonstrated using chemical etch rate tests. It is important to remember that the film growth can vary over the surface due to surface inhomogeneities, angle-of-incidence variation, and variations in the process variables.

Particulates on the surface present very local changes in surface morphology, and local features develop such as those shown in Fig. 6. These features are poorly bonded to the film and the surface and easily come out, leaving a pinhole in the film. The resulting pinhole will be larger than the initiating particulate. This "pinhole flaking" from film deposited on surfaces and fixtures in the deposition system can be a major source of particulate contamination in the deposition system. It is particularly evident when the surfaces and fixtures have been cleaned by glass bead blasting and glass chards have been embedded in the surfaces.

Residual Gas Effects on Film Growth. Residual gases in the deposition system can influence the growth, structure, morphology, and properties of the deposited films. The origins of these effects are poorly understood, but some portion can be attributed to changing the surface mobility of the adatom. In the case of reactive deposition, the residual gas partial pressure is high and has a major effect on the surface mobility and the development of columnar morphologies at high deposition temperatures.

Changes in Microstructure and Morphology during Deposition

Film microstructure, morphology, and properties can be influenced by processes that occur after adatom condensation but during film growth. The processes that change the film properties include:

- Mass transport, such as growth of the interfacial region and crystal defect formation and void coalescence
- Recrystallization and grain growth
- Phase precipitation and growth
- Chemical reaction of codeposited species

- Stress annealing

Many of these changes are time- and temperature-dependent and therefore depend on the thermal history of the film during deposition. This thermal history depends on the deposition temperature, condensation energy release, deposition rate, deposition time, thermal conductivity of the film and substrate materials, heat removal mechanisms, and so on.

Modification of Film Morphology. The film morphology and microstructure can be modified during growth. Methods of modifying the columnar growth include continuous or periodic:

- Bulk or surface heating by laser or radiant heating
- Codeposition of alloying species
- Reaction with ambient gaseous species
- Changing angle of incidence of adatom flux
- Mechanical disruption of the growth
- Changing deposition rate
- Changing gas pressure
- Bombardment by massive energetic particles

Heating. Increasing the deposition (substrate) temperature changes the film morphology, as shown in Fig. 4. Surface heating by a laser or by a radiant heat source can change the surface mobility of the adatom, thereby changing the growth mode of the deposited material.

Codeposition of Alloying, Impurity, or Dopant Species. Codeposition of alloying species can change the surface mobility and thus the film morphology. Alloying species that lower the melting point of the deposited material are particularly effective.

Impurities are small amounts of material incorporated into the structure unintentionally. The addition of small amounts of an impurity can have a significant influence on the microstructure and properties of the growing film. Small amounts of nitrogen in aluminum films change the electromigration properties. Residual gases present during deposition can affect film stress.

Dopants are small amounts of materials that are deliberately incorporated into the structure to affect microstructure or film properties. For example, the inclusion of gold, nickel, or cobalt (5 wt%) in sputter-deposited MoS_2 films for solid film lubricants produces "compact" films that are physically stronger to greater thicknesses than MoS_2 films sputtered without the additions.

Periodic Injection of Reactive Gas. Periodic reaction of the surface of the growing film with ambient species generates a new surface chemistry. This can force the adatoms to renucleate on the "foreign" surface, thereby changing the film morphology. For example, the periodic injection of oxygen during aluminum deposition suppresses the columnar growth morphology (Ref 38). The same effect is seen for nitrogen on beryllium films. The effect is similar to the "brightening agents" used in electrodeposition.

The angle of incidence of the adatom flux is important to the growth of the columnar morphology. The angle of incidence can be modified by proper fixturing and position control. Generally it is not possible to optimize the angle of incidence for all surface features.

Mechanical Disruption during Deposition. Mechanical disruption of the growing surface can be used to change the columnar morphology. Periodic mechanical brushing of a surface during deposition has been used to densify and eliminate porosity in sputter-deposited aluminum films and in CVD-tungsten deposits.

Changing Gas Pressure during Deposition. For gaseous environments, where vapor phase collision processes are important, changes in the ambient pressure change the scattering and thermalization of the adatom flux, and, in the case of sputter deposition, the flux and energy of reflected high-energy neutrals. These factors are important in determining the film morphology, stress (Ref 39), and other properties.

Concurrent Massive Energetic Particle Bombardment. In ion plating, the growing film is subjected to continuous or periodic energetic particle bombardment during deposition. When massive energetic particles bombard a surface, they release their energy rapidly by physical collisions with the near-surface atoms. These physical collisions cause a number of effects, some of which modify the columnar morphology of the growing film. These effects include:

- Sputtering and redeposition
- Input of "heat" into the surface and the near-surface region
- Increased or decreased surface mobility of the depositing atoms
- Generation of point defects that act as nucleation sites

Typically, a film sputtering rate of 20 to 40% of the deposition rate or an energy input of about 20 eV per depositing atom is necessary to completely disrupt the columnar growth process.

References cited in this section

2. C.A. Neugebauer, Condensation, Nucleation and Growth of Thin Films, Chapter 8, *Handbook of Thin Film Technology,* L.I. Maissel and R. Glang, McGraw-Hill, 1970
3. J.E. Greene, Film Growth and Structure of PVD Deposits, Chapter 13, *Deposition Processes for Films and Coating,* 2nd ed., R. Bunshah, Ed., Noyes Publications, 1994
4. J.A. Thornton, High Rate Thick Film Growth, *Ann. Rev. Mater. Sci.,* Vol 7, 1977, p 239
5. J.A. Venables, Nucleation and Growth Processes in Thin Film Formation, *J. Vac. Sci. Technol. B,* Vol 4, 1986, p 870
6. A.G. Naumovets and Y.S. Vedula, Surface Diffusion of Adsorbates, *Surf. Sci. Rep.,* Vol 4 (No. 7/8), 1984, p 365
7. V.T. Binh, Ed., *Surface Mobilities on Solid Materials--Fundamental Concepts and Applications,* NATO ASI Series, Series B: Physics, Vol 86, Plenum Press, 1983
8. G. Somorjai, *Principles of Surface Chemistry,* Wiley, 1969
9. R.C. Sundahl, Relationship between Substrate Surface Chemistry and Adhesion of Thin Films, *J. Vac. Sci. Technol.,* Vol 9 (No. 1), 1971, p 181
10. R. Kelly, Bombardment-Induced Compositional Changes with Alloys, Oxides, Oxysalts and Halides, Chapter 4, *Handbook of Plasma Processing Technology Fundamentals, Etching, Deposition and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes Publications, 1990, p 91
11. J.E. Griffith and G.P. Kochanski, The Atomic Structure of Vicinal Si(001) and Ge(001), *Crit. Rev. Solid State Mater. Sci.,* Vol 16 (No. 4), 1990, p 255
12. G.G. Paulson and A.L. Friedberg, Coalescence and Agglomeration of Gold Films, *Thin Solid Films,* Vol 5, 1970, p 47
13. D.M. Mattox, Surface Effects in Reactive Ion Plating, *Appl. Surf. Sci.,* Vol 48/49, 1991, p 540, and references therein
14. F.K. LeGoues, B.D. Silverman, and P.S. Ho, The Microstructure of Metal-Polyimide Interfaces, *J. Vac. Sci. Technol. A,* Vol 6, 1988, p 2200
15. *Materials Characterization,* 9th ed., Vol 10, *Metals Handbook,* 1986, ASM International
16. H. Neddermeyer, STM Studies of Nucleation and the Initial Stages of Film Growth, *Crit. Rev. Solid State Mater. Sci.,* Vol 16 (No. 5), 1990, p 309
17. J.M. Guerra, Photon Tunneling Microscopy, *Appl. Optics,* Vol 29 (No. 26), 1990, p 3741
18. J.E. Greene, T. Motooka, J.-E. Sundgren, D. Lubbens, S. Gorbatkin, and S.A. Barnett, The Role of Ion/Surface Interactions and Photo-Induced Reactions during Film Growth from the Vapor Phase, *Nucl. Instrum. Methods Phys. Res. B,* Vol 27, 1987, p 226, and references therein

19. J.E. Greene, T. Motooka, J.-E. Sundgren, A. Rockett, S. Gorbatkin, D. Lubben, and S.A. Barnett, A Review of the Present Understanding of the Role of Ion/Surface Interactions and in Photo-Induced Reactions during Vapor Phase Crystal Growth, *J. Cryst. Growth,* Vol 79, 1986, p 19
20. A.M. Klumb, C.R. Aita, and N.C. Tran, Sputter Deposition of Gold in Rare-Gas (Ar,Ne)-O_2 Discharges, *J. Vac. Sci. Technol. A,* Vol 7 (No. 3), 1989, p 1697, and references therein
21. P.H. Holloway, Gold/Chromium Metallization for Electronic Devices, *Solid State Technol.,* Vol 23 (No. 2), 1980, p 109, and references therein
22. S. Veprek and M. Heintz, The Mechanism of Plasma-Induced Deposition of Amorphous Silicon from Silane, *Plasma Chem. Plasma Process.,* Vol 10 (No. 1), 1990, p 3
23. J.A. Venables, G.D.T. Spiller, and M. Hanbucker, Nucleation and Growth of Thin Films, *Rep. Prog. Phys.,* Vol 47, 1984, p 399
24. M.A. Listvan, Determination of the Time Dependence of Domain Growth by Direct Observation of Small Metal Clusters, *Surf. Sci.,* Vol 173, 1986, p 294
25. C. Mailhoit and D.C. Smith, Strained-Layer Semiconductor Superlattices, *Crit. Rev. Solid State Mater. Sci.,* Vol 16 (No. 2), 1989, p 131
26. D.M. Mattox, Thin Film Adhesion and Adhesive Failure--A Perspective, *ASTM Proc. Conf. Adhesion Measurement of Thin Films, Thick Films and Bulk Coatings,* STP 640, ASTM, 1978, p 54
27. D.M. Mattox, Thin Film Metallization of Oxides in Microelectronics, *Thin Solid Films,* Vol 18, 1973, p 173
28. E. Philofsky, Intermetallic Formation in Gold Aluminum Systems, *Solid State Electronics,* Vol 13 (No. 10), 1970, p 1391
29. F. Bordeaus and A.R. Yavari, Ultra Rapid Heating by Spontaneous Mixing Reactions in Metal-Metal Multilayer Composites, *J. Mater. Res.,* Vol 5 (No. 8), 1990, p 1656
30. R.W. Burger and L.J. Gerenser, Understanding the Formation and Properties of Metal/Polymer Interfaces via Spectroscopic Studies of Chemical Bonding, *Society of Vacuum Coaters Ann. Tech. Conf. Proc.,* SVC Publications, 1991, p 162
31. G.G. Fuller and K.L. Mittal, Ed., *Opportunities and Research Needs in Adhesion Science and Technology,* National Science Foundation Workshop on Adhesion, 14-16 Oct 1987 (Lake Tahoe, CA), Hitex Publication, 1988
32. B.A. Movchan and A.V. Demchishin, Study of the Structure and Properties of Thick Vacuum Condensates of Nickel, Titanium, Tungsten, Aluminum Oxide and Zirconium Oxide, *Phys. Met. Metallogr. (USSR),* Vol 28, 1969, p 83
33. J.A. Thornton, High Rate Thick Film Growth, *Ann. Rev. Mater. Sci.,* Vol 7, 1977, p 239
34. R. Messier, A.P. Giri, and R.A. Roy, Revised Structure Zone Model for Thin Film Physical Structure, *J. Vac. Sci. Technol. A,* Vol 2, 1984, p 500
35. R.N. Tait, T. Smy, and M.J. Brett, Modeling and Characterization of Columnar Growth in Evaporated Films, *Thin Solid Films,* Vol 226 (No. 2), 1993, p 196
36. M. Futamoto, Y. Honds, H. Kakibayashi, T. Shimotsu, and Y. Uesaka, Microstructure of CoCr Thin Films Prepared by Sputtering, *Jpn. J. Appl. Phys.,* 1985, p L460
37. R.N. Tait, T. Smy, and M.J. Brett, Simulation and Measurement of Density Variation in Mo Films Sputter Deposited over Oxide Steps, *J. Vac. Sci. Technol. A,* Vol 8 (No. 3), 1990, p 1593
38. R.W. Springer and D.S. Catlett, Structure and Mechanical Properties of Al/Al_xO_y Vacuum Deposited Laminates, *Thin Solid Films,* Vol 54, 1978, p 197
39. R.E. Cuthrell, D.M. Mattox, C.R. Peeples, P.L. Dreike, and K.P. Lamppa, Residual Stress, Stress Anisotropy, Stress Control and Resistivity in Post Cathode Magnetron Sputter-Deposited Molybdenum Films, *J. Vac. Sci. Technol. A,* Vol 6, 1988, p 2914

Reactive Deposition

Reactive deposition is the formation of a film of a compound, either by codeposition and reaction of the constituents or by the reaction of a deposited species with the ambient gaseous environment. If the reacting species form a volatile compound, etching results. If the reaction results in a nonvolatile species, a compound film is formed (Ref 40).

Codeposition of reactive species does not necessarily mean that they will chemically react to form a compound. For example, a mixture of titanium and carbon may not have any TiC, or it may be partially TiC and the rest an unreacted mixture of titanium and carbon, substoichiometric TiC_{1-x}, or TiC with excess titanium or carbon, each of which will have different properties. Generally, for low-temperature deposition, the best situation for reactive deposition is where one of the reacting species is condensable and the other is gaseous (e.g., titanium plus nitrogen). If both are condensable (e.g., titanium plus carbon), the best deposition condition is to have a high substrate temperature to promote reaction or use postdeposition heat treatment to promote reaction. Reactively deposited films of oxides and nitrides are commonly used in the optics, electronics, decorative, and mechanical applications, with TiN being one of the more common film materials.

There are a number of techniques for performing reactive atomistic film deposition. The simplest way is to thermally evaporate the material in a partial pressure of a reactive gas in the process called *reactive evaporation* (see the article "Vacuum Deposition, Reactive Evaporation, and Gas Evaporation" in this Volume). This generally gives poor-quality films because the materials are not completely reacted and the high gas pressures necessary for reaction result in gas phase collision and vapor phase nucleation, giving a low-density deposit. Better-quality films are obtained by promoting the chemical reaction by some means, such as activating the reactive gas or using concurrent energetic particle bombardment to promote the chemical reaction (Ref 13).

Reactive Species

Molecular Species. Typically gaseous reactive species are in the molecular form (i.e., N_2, O_2, H_2, etc.). The molecular species is less chemically reactive than the atomic species of the gas.

Activated Reactive Species. The gaseous reactive species can be "activated" to make them more chemically reactive and/or more readily adsorbed on surfaces (Ref 13). The reactivity of the species can be increased by adding internal energy to form "excited species," by fragmenting the species to form uncharged "radicals," such as O, N, or F, by forming ions, which are charged species such as O^+, N_2^+, or N^+, or by forming a new volatile reactive species, such as ozone (O_3) from O_2 + O or Si_2H_6 from SiH_4. Activation is most often done in a direct current, radio frequency, or microwave plasma, in a plasma arc, or by radiation adsorption (e.g., "photoexcitation") from a source such as a mercury vapor lamp or an excimer laser. Such activation is done in reactive sputter deposition, reactive ion plating, PECVD, and activated reactive evaporation. Activation of the gaseous species can also be done using other means, such as the hot filament decomposition of NH_4, F_2, and H_2.

A plasma provides a very complicated chemical environment that can give reactive deposition processes that are not normally expected. For example, the sputter deposition of gold on oxide surfaces in an oxygen-containing plasma gives rise to very adherent gold films. It has been shown that the deposition of gold in an oxygen plasma gives rise to Au-O bonding. This may be due to the formation of activated oxygen species in the plasma or the formation of a more readily adsorbed reactive species (i.e., O_3) (Ref 41, 42).

Reaction Probability

In reactive deposition, the depositing material is continually being buried and the time available for reaction is limited. The probability of chemical reaction of the growing film surface depends on a number of factors, including:

- Temperature of the surface
- Chemical reactivity of the species
- Extent of prior reaction on the surface (e.g., whether the surface composition is $TiN_{0.1}$ or $TiN_{0.95}$)
- Relative fluxes of condensing species and incident gaseous species (i.e., the "availability" of the reactive species)
- Residence time (adsorption) of reactive species on the surface
- Radiation by electrons capable of stimulating chemical reactions on the surface
- Radiation by photons capable of stimulating photochemical reactions
- Energy of the incident reactive species
- Concurrent bombardment by energetic species not involved in the reaction (e.g., concurrent argon ion bombardment during titanium plus nitrogen deposition)

In many cases, surface reaction occurs first at active sites on a surface providing a nonhomogeneous growth mode. The extent to which this occurs in reactive deposition is not known.

Adsorption on a Surface. For an ambient pressure of 10^{-3} torr (0.13 Pa) and 25 °C (77 °F), gaseous particles will impinge on a surface at about 10^3 monolayers/s, compared to a typical atomistic deposition rate of 10 or so monolayers per second. The impinging species may be reflected with little residence time, or they may be adsorbed with an appreciable residence time (Ref 42). Adsorbed species will be available for reaction for a longer period of time than the reflected species. The adsorption probability and adsorbed film thickness will depend on a number of factors, such as the impinging species, nature of the surface, adsorption sites, and so on. For instance, it has been shown that atomic oxygen on silicon will adsorb with a higher probability and to a greater thickness than molecular oxygen and that ozone (O_3) is strongly adsorbed on Al_2O_3, whereas O_2 is not (Ref 41). It has also been shown that the surface stoichiometry affects the adsorption. For example, stoichiometric TiO_2 surfaces do not adsorb oxygen but substoichiometric surfaces do, with the amount depending on the degree of substoichiometry. In plasma CVD of silicon from silane (SiH_4), it has been shown that the disilane species formed in a plasma has a high adsorption probability and is important in the deposition of the silicon at low temperatures (Ref 22). Oxygen molecules will react with a pure aluminum film, but nitrogen molecules will not react. The probability that the oxygen molecules will react with the aluminum decreases as the aluminum reacts with the oxygen molecules and the oxygen coverage increases.

Reaction Extent. The extent of the reaction before the surface is buried also depends on the factors listed above. For example, in the case of atomic oxygen on silicon surfaces, the reaction probability will decrease monotonically with coverage through several monolayer coverages. If the material can form a series of compounds (e.g., TiN, T_2N) the probability of reaction is further decreased as the extent of reaction increases, making it more difficult to form the higher compound (i.e., TiN will be more difficult to form than the Ti_2N).

Reactant Availability. The degree of reaction of codepositing species depends on the availability of the reactive species; therefore, the relative fluxes of the reactants are important. This gives rise to the "loading factor," which means that there is a relationship between the surface area for reaction (deposited film area) and the amount of reaction gas available.

Stoichiometry. Many materials form a series of stable compounds that have different crystal structures. For example, titanium and oxygen form TiO, Ti_2O_3, TiO_2 (brookite), TiO_2 (anatase), and TiO_2 (rutile). By controlling the availability of the reactive gas, the stoichiometry of the resulting film material can be controlled. The stoichiometry of the material can be changed during the deposition by changing the reactant gas availability.

Reactively Graded Interface. The composition of the reactively deposited material can be controlled by controlling the availability of the reactive species. This allows the gradation of composition from an elemental phase to the compound phase. For example, in the deposition of titanium nitride TiN, the deposition may start by having no nitrogen available, so as to deposit pure titanium, and then increase the nitrogen availability so as to grade the composition to TiN. This technique is often helpful in obtaining good adhesion of compound films to surfaces. Another example is the deposition of a nitride on an oxide where the deposited material is graded from an oxide through an oxynitride composition to the nitride by controlling the availability of both oxygen and nitrogen.

Free electrons can enhance chemical reactions in the vapor phase and on a surface. Electron energies of about 50 eV are the most effective. The effect of electrons on reactive deposition is relatively unknown.

Photon radiation can enhance chemical reactions by exciting the reacting species (photoexcitation), thereby providing internal energy to aid in chemical reactions (Ref 18).

Energetic Inert Particle Bombardment Effects. The reactivity between codeposited or adsorbed species can be increased by using concurrent energetic particle bombardment by a reactive species or with an inert species that does not enter into the reaction. Concurrent energetic particle bombardment during reactive film deposition has been shown to have a substantial effect on the composition, structure, and properties of compound films (Ref 43, 44). In general, the bombardment:

- Introduces heat into the surface
- Generates defects that can act as adsorption and reaction sites
- Dissociates adsorbed molecular species
- Produces secondary electrons that can assist chemical reactions

- Selectively desorbs or sputters unreacted or weakly bound species

This process has been termed "bombardment-enhanced chemical reaction" (Ref 44). It is of interest to note that Coburn and Winters attribute the major portion of bombardment-enhanced etching of silicon with fluorine to the development of the volatile high-fluoride compound (SiF_4) (i.e., more complete reaction) under bombardment conditions. Periodic bombardment of a depositing species by energetic reactive species can accomplish many of the same effects (Ref 45). For example, oxide films can be formed by depositing several monolayers of aluminum, then alternately bombarding the film with energetic oxygen ions and depositing more aluminum to form an aluminum oxide film.

Beam Deposition Using Activated Species. Ions of an activated species can be produced in a separate source, accelerated, and then used to bombard the depositing material in a vacuum environment to give "reactive ion beam" deposition. For particle energies greater than a few tens of electron volts, the energetic particle will physically penetrate into the surface, thereby increasing its "residence time." For example, it has been shown that for N_2^+, ions having an energy of 500 eV impinging on a depositing aluminum film, all of the nitrogen will react with the aluminum up to a N:Al deposition ratio of 1:1 (Ref 46).

Deposition of Composite Materials

Composite materials are materials that consist of several phases in the form of either layers or phases dispersed in a matrix.

Layered Composites. In many applications, multilayer film structures are used. One of the most common uses is to produce an adhesion layer next to the substrate with the functional layer(s) on top, such as the Ti-Au metallization on oxides. In some cases several layers are used. Examples are Ti-Pd-Au (Ref 47, 48), where the palladium inhibits corrosion, and the Ti-Pd-Cu-Au metallization, where the copper acts as an economical electrical conductor and the gold is present to prevent surface reaction.

Dispersed Phase Composites. Dispersed phase materials can be formed by codepositing insoluble materials. If the temperature is high enough for mass transport, the phases will separate, resulting in a two-phase material. Composite materials can also be formed by codepositing materials where the phase formed by reaction is dispersed in a matrix of the unreacted material (Ref 49). For example, a reactive material such as titanium can be codeposited with a less reactive material such as nickel in a reactive environment of oxygen or carbon to give dispersed phases of oxides (TiO_2) or carbides (TiC) in nickel. Composite films can be formed by a minor constituent reacting with the major constituent to form an intermetallic phase that is dispersed in the major phase. For example, in the Al-2Cu metallization, on heating, the Al_2Cu phase will precipitate to form a dispersion in the aluminum. This precipitate phase then acts as segregation sites for voids formed due to film stress. In cases where two or more materials are depositing at the same time on nonreactive surfaces, there may be changes in composition in the early stages of nucleation due to differing segregation effects.

The presence of second-phase materials in a film can lead to galvanic corrosion problems when an electrolyte is present. For example, Al-Al_2Cu composite films have been found to be more susceptible to intergranular and pitting corrosion than pure aluminum films (Ref 50). The Al_2Cu acts as a cathode (-0.73 volts) while the aluminum acts as the anode (-0.85 volts). The corrosion effects become more important with increasing copper concentration, so the copper in the Al-Cu metallization is limited to 2 to 4% when a homogeneous distribution of the Al-Cu particles is desirable.

Composite materials of metal particles in a polymer matrix can be formed by deposition of the metallic phase during plasma polymerization. Such a composite film has been shown to have a better wear durability than the polymer film alone (Ref 51) and to have interesting optical properties.

Deposition of Intermetallic Materials

Intermetallic compounds are formed from relatively electropositive and electronegative metals that chemically bond to form compounds with a specific composition and crystalline structure. Intermetallic films are often formed by depositing the film material on a hot surface so that the adatoms diffuse and react with the surface material, converting it into a silicide, aluminide, or whatever. Very corrosion-resistant intermetallic materials can be formed by codeposition processes at high temperatures. These include the very chemically stable compounds Mo_5Ru_3 and W_3Ru_2 (Ref 52) and $ZrPt_3$ and $ZrIr_3$, which are d-orbital bonded intermetallic compounds (Ref 53).

"Amphoteric" metals are those that may gain or lose electrons, that is, act as either an acid (electron donor) or a base (electron acceptor) in chemical reactions.

References cited in this section

13. D.M. Mattox, Surface Effects in Reactive Ion Plating, *Appl. Surf. Sci.,* Vol 48/49, 1991, p 540, and references therein
18. J.E. Greene, T. Motooka, J.-E. Sundgren, D. Lubbens, S. Gorbatkin, and S.A. Barnett, The Role of Ion/Surface Interactions and Photo-Induced Reactions during Film Growth from the Vapor Phase, *Nucl. Instrum. Methods Phys. Res. B,* Vol 27, 1987, p 226, and references therein
22. S. Veprek and M. Heintz, The Mechanism of Plasma-Induced Deposition of Amorphous Silicon from Silane, *Plasma Chem. Plasma Process.,* Vol 10 (No. 1), 1990, p 3
40. W.D. Westwood, Reactive Sputter Deposition, Chapter 9, *Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Noyes Publications, 1990, p 233
41. A.O. Klimovskii, A.V. Bavin, V.S. Tkalich, and A.A. Lisachenko, Interaction of Ozone with Gamma-Al_2O_3 Surface, *React. Kinet. Catal. Lett.,* Vol 23 (No. 1-2), 1983, p 95-98 (trans. from Russian)
42. P.A. Dowben, A Review of the Halogen Adsorption Process on Metal Surfaces, *Crit. Rev. Solid State Mater. Sci.,* Vol 13 (No. 3), 1987, p 191
43. J.E. Greene and S.A. Barnett, Ion-Surface Interactions during Vapor Phase Crystal Growth by Sputtering, MBE and Plasma-Enhanced CVD: Applications to Semiconductors: Critical Review, *J. Vac. Sci. Technol.,* Vol 21 (No. 2), 1982, p 285
44. G.A. Lincoln, M.W. Geis, S. Pang, and N. Efremow, Large Area Ion Beam Assisted Etching of GaAs with High Etch Rates and Controlled Anisotropy, *J. Vac. Sci. Technol. B,* Vol 1, 1983, p 1043
45. S. Schiller, U. Heisig, and K. Goedicke, Alternating Ion Plating--A Method of High Rate Ion Vapor Deposition, *J. Vac. Sci. Technol.,* Vol 12 (No. 4), 1975, p 858
46. J.M.E. Harper, J.J. Cuomo, and H.T.G. Hentzell, Quantitative Ion Beam Process for the Deposition of Compound Thin Films, *Appl. Phys. Lett.,* Vol 43, 1983, p 547
47. J.D. Speight and M.J. Bill, Observations on the Aging of Ti-Based Metallizations in Air/HCl Environments, *Thin Solid Films,* Vol 15, 1973, p 325
48. D.J. Sharp, Corrosion Inhibition in Sputter-Deposited Thin-Film Systems using an Intermediary Layer of Palladium, *J. Vac. Sci. Technol.,* Vol 16 (No. 2), 1979, p 204
49. B.V. Movchan, Composite Materials Deposited from the Vapour Phase under Vacuum, *Surf. Coat. Technol.,* Vol 46 (No. 1), 1991, p 1
50. S. Thomas and H.M. Berg, Micro-Corrosion of Al-Cu Bonding Pads, *IEEE/IRPS,* 1985, p 153
51. H. Biedwermann and L. Martinu, Plasma Polymer-Metal Composite Films, Chapter 4, *Plasma Deposition, Treatment and Etching of Polymers,* R. d'Agostino, Ed., Academic Press, 1990
52. L.R. Testardi, W.A. Royer, D.D. Bacon, A.R. Storm, and J.H. Wernick, Exceptional Hardness and Corrosion Resistance of Mo_5Ru_3 and W_3Ru_2 Films, *Metall. Trans.,* Vol 4, 1973, p 2195
53. L. Brewer, A Most Striking Confirmation of the Engel Metallic Correlation, *Acta Metall.,* Vol 15, 1967, p 553

Postdeposition Processing

Postdeposition heating of films can be done in a furnace, by flash lamp heating such as is used in RTP techniques, or by laser irradiation. In the extreme, the heating can be used to melt and "reflow" the film to planarize the surface.

Postdeposition heating can create film stresses due to differences in the coefficient of thermal expansion between the film and substrate and between different phases in the film. These stresses can result in plastic deformation of the film or substrate material, create stress-related changes in the film properties such as voids (Ref 54), or create interfacial fractures.

Diffusion. Heating is used to promote mass transport so as to anneal the residual stress and defect structure in deposited films. For example, it has been shown that glass films exhibit strain points far lower than those of the bulk material (Ref 55), that grain growth can take place in sputter-deposited copper films at very low temperatures (Ref 56), and that stress relief in TiB_2 films occurs far below the annealing temperature of the bulk material. Postdeposition heating has been shown to modify the structure and electrical properties of deposited SiO_2 films. These effects are probably due to the residual film stress and high defect concentrations in the deposited films.

Postdeposition heat treatments can be used to induce grain growth or phase changes, but care must be taken because the changes can result in increased film stress or fracture. The substrate material and structure can influence the kinetics of the phase change by influencing the nucleation of the new phase. Postdeposition heating rarely allows densification of columnar films, because the surfaces of the columnar structure react with the ambient and the surface layers that are formed prevent the diffusion needed for densification. Typically, heating during deposition or in situ heating in the deposition chamber is more effective in densifying deposits than ex situ heating.

Agglomeration. Postdeposition heating can cause the film structure to agglomerate into islands generating porosity and changing the optical and electrical properties of the films (Ref 57). Agglomeration also occurs by grain boundary grooving of the film material (Ref 58).

Heating with Reaction and Diffusion. Postdeposition heat treatments are used to promote reaction between unreacted codeposited materials and to promote reaction of the deposited material with an ambient gas. For instance, it is common practice to heat deposited high-temperature oxide superconductor films in an oxygen atmosphere to improve their performance, and transparent, electrically conductive indium-tin-oxide films are heated in "forming gas" to increase their electrical conductivity. Heating can also cause the formation of internal dispersed phases (e.g., Ni-B, Cu-Al) to give dispersion strengthening.

Heating is used to alloy the deposited material with the substrate surface. Postdeposition diffusion and reaction can form a more extensive interfacial region and induce compound formation in semiconductor metallization. Postdeposition heating and diffusion can be used to completely convert the deposited material to interfacial material. For example, a platinum film on silicon can be heated to form a platinum silicide layer. Postdeposition interdiffusion can result in the failure of metallized semiconductor devices by diffusion and shorting of the junctions.

Alloying and reaction between films and substrates can be limited by:

- Deposition of refractory metal diffusion barriers such as tungsten or W-Ti alloy
- Deposition of electrically conductive diffusion barrier layers of compounds such as carbide (e.g., TiC), nitrides (e.g., TiN), or silicides (Ref 59)
- Formation of compounds that act as diffusion barriers when the film and substrate materials react
- Doping of the film or substrate materials with a material that retards mass-transport (e.g., rare earth metals in aluminum)
- Rapidly heating and cooling the surface region

Melting. The XeCl (308 nm) excimer laser has been used to melt and planarize thin films of gold, copper, and aluminum on silicon devices with submicron features.

Postdeposition ion bombardment using reactive or nonreactive bombarding species can be used to change the composition or properties of the film material or to increase the interfacial adhesion by interfacial mixing or "stitching" (Ref 60).

To "recoil mix" or "stitch" an interface, the films must be rather thin (<100 nm) and the ion energies are selected to give the peak range just beyond the interface. In recoil mixing at an interface, if the materials involved are miscible, the ion mixing results in interfacial reaction and diffusion. If the materials are not miscible, the interfacial region is not mixed but the adhesion is increased. Generally adhesion improvement is dose dependent, with the best result being for doses of 10^{15} to 10^{17} ions/cm^2, while excessive bombardment induces interfacial voids. Part of the observed increase in adhesion may be due to the elimination of interfacial voids by "forward sputtering."

Deformation. In the case of films of soft materials, the film structure can be densified and porosity closed by postdeposition burnishing (Ref 61) or shot peening of the surface. For example, the MCrAl (where M can be a metal of various types) films deposited on turbine blades are routinely shot peened to increase their corrosion resistance.

Chemical and Electrochemical Treatments. Deposited films may be subjected to various chemical and electrochemical treatments to convert all or part of the film to another material. For example, aluminum films can be anodized (Ref 62) or chemically converted by a chromate conversion process for increased corrosion resistance.

Pore Filling. Porosity of the deposited films is often a limiting factor in their use. Various techniques may be used to fill the pores in the film. For example, electrophoretic deposition of polymer particles has been used to selectively fill the pores in a dielectric film on a conductive substrate (Ref 62), and corrosion of the substrate through the pores has been used to plug the pores with corrosion products.

Topcoats are often applied to deposited films to increase abrasion and corrosion resistance. An example of a fluid topcoat is the dip-coated polysiloxane coating used on aluminum-coated polycarbonate automotive headlight reflectors.

Fluid Topcoats. Often deposited coatings are overcoated with a thin (<1μm) protective film of highly cross-linked polymeric material. Many topcoat materials require heat for curing. The heating is necessary to remove the solvents and cross-link the polymeric materials. Due to environmental concerns this type of topcoat material is being modified to give a higher "solids content" (i.e., less solvent will be released into the environment). Another class of polymeric topcoat materials are the organo-siloxanes, which consist of an organic host polymer containing siloxane coupling agents and colloidal silica. The coatings can be applied by spraying, spinning, or dip coating and can be cross-linked by UV radiation or electron irradiation (e.g., UV-curable acrylics).

Plasma-Deposited Topcoats. Some topcoat material can be deposited by plasma polymerization. For example, plasma polymerization of polysiloxane is used to form organo-silicon coatings, which are sometimes heat treated in oxygen to increase the Si-O content of the films. The plasma-polymerized organo-silicon films have excellent surface coverage ability and are hydrophobic, hard, and relatively pinhole-free. The films are being used as clear protective topcoats on optical reflective films. Plasma-deposited organo-carbon films are used as conductive films.

References cited in this section

54. F.G. Yost, D.E. Amos, and A.D. Romig, Stress Driven Diffusion Voiding of Aluminum Conductor Lines, *Proc. IEEE/IRPS '89,* 1989, p 193
55. G.J. Kominiak and D.M. Mattox, Physical Properties of Thick Sputter-Deposited Glass Films, *J. Electrochem. Soc.,* Vol 120, 1973, p 1535
56. J.W. Patten, E.D. McClanahan, and J.W. Johnson, Room-Temperature Recrystallization in Thick Bias-Sputtered Copper Deposits, *J. Appl. Phys.,* Vol 42, 1971, p 4371
57. R.R. Zito, W.S. Bickel, and W.M. Bailey, The Physical and Optical Properties of Agglomerated Gold Films, *Thin Solid Films,* Vol 114, 1984, p 241
58. Y.-K. Chao, S.K. Kurinec, I. Toor, H. Shillingford, and P.H. Holloway, Porosity in Thin Ni/Au Metallization Layers, *J. Vac. Sci. Technol. A,* Vol 5, 1987, p 337
59. M.-A. Nicolet, Diffusion Barriers in Thin Films, *Thin Solid Films,* Vol 52, 1978, p 415
60. J.E.E. Baglin, Ion Beam Effects on Thin Film Adhesion, Chapter 15, *Ion Beam Modification of Insulators,* P. Mazzoldi and G. Arnold, Ed., Elsevier, 1987
61. A.T. English and P.A. Turner, Use of Vibratory Finishing for Occlusion of Pinholes and for Surface Smoothing in Thin Films on Ceramic Substrates, *Plating,* Sept 1972, p 851
62. J.K.G. Panitz, D.J. Sharp, and F.E. Martinez, Electrophoretic Coatings for Capacitor Applications, *Plat. Surf. Finish,* Vol 75, 1988, p 23

Growth-Related Film Properties

Films deposited by PVD processes invariably have properties that differ from those of the bulk materials (Ref 63). For this reason the specific film properties should be determined for films made with controlled and reproducible materials

and processes. The columnar morphology and the residual film stress developed during film growth are important to a number of the film properties and the stability of the deposited film structure, including:

- *Density*--mechanical deformation, electrical resistivity
- *Porosity*--corrosion rate, etch rate
- *Surface area and morphology*--contaminant adsorption, optical reflectivity, electrical resistivity

Residual Film Stress

Invariably, atomistically deposited films have a residual film stress that can be tensile or compressive and that can approach the yield or fracture strength of the materials involved. Generally, vacuum-deposited films and sputter-deposited films prepared at a high sputtering gas pressure have a tensile stress that can be anisotropic with off-normal angle-of-incidence depositions. Compressive stresses are generally encountered in films deposited under conditions where there is concurrent high-energy particle bombardment, such as in ion plating and in low-pressure sputtering where high-energy reflected neutrals from the target bombard the growing film (Ref 39). Figure 7 shows the residual film stresses generated in one direction in the film during postcathode magnetron sputter deposition of molybdenum. The film stress is anisotropic and is related to the configuration of the sputtering cathode. At low pressures, where there is bombardment by high-energy reflected neutrals, the stress is compressive. At higher pressures the stress is tensile, and at even higher pressures, where the morphology is more columnar and the film density is lower, the stress decreases. The origin of these stresses is poorly understood, though several phenomenological models have been proposed (Ref 64).

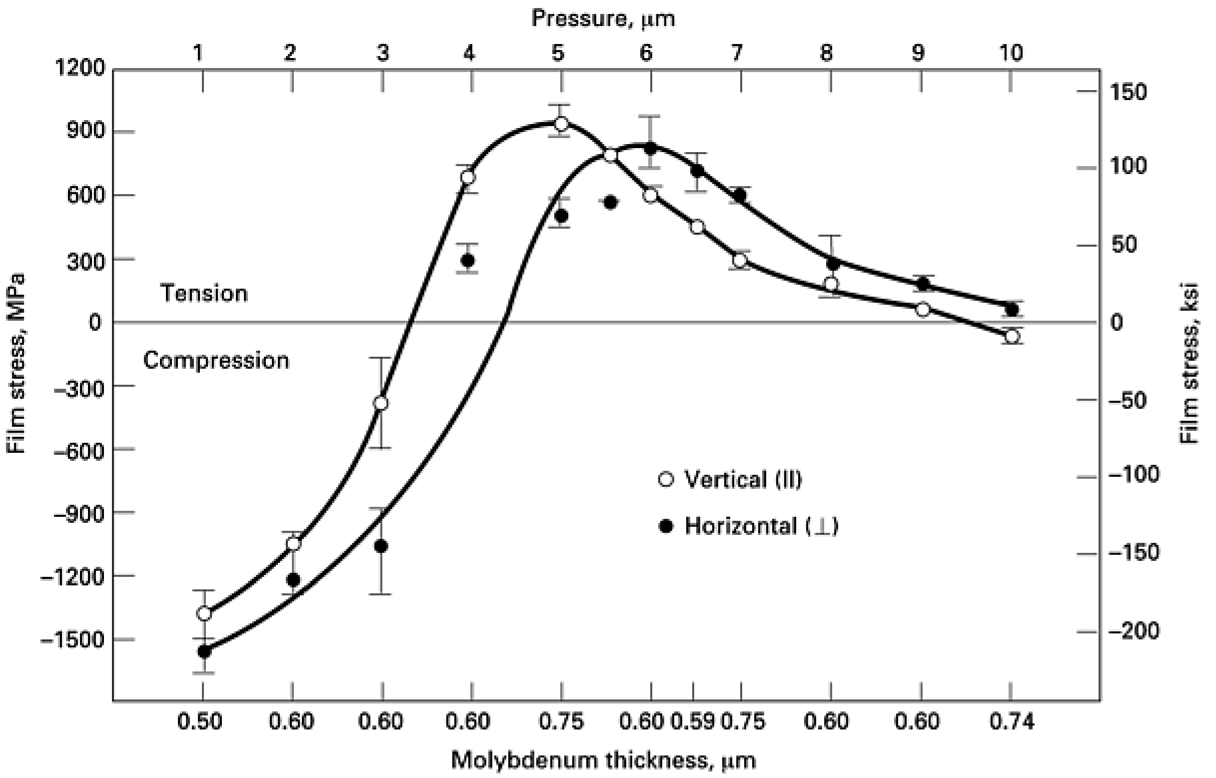


Fig. 7 Film stress as a function of gas pressure in postcathode magnetron sputter-deposited molybdenum films (Ref 39)

Tensile stresses can be developed when the growth mechanism does not allow the depositing atoms to attain their lowest energy positions. The Klockholm-Berry model is based on a constrained shrinkage of deposited material resulting in lattice parameters greater than normal. The grain boundary model attributes the stress to the development of grain boundary material. It has been proposed that the coalescence of lattice defects into "microvoids" causes the tensile stresses. It has been shown that the mechanical properties of the grain material are important to the resulting stresses and that impurity incorporation and reaction with the depositing film material can also be important factors in the stress

generation. Tensile stresses can also be generated by phase changes and recrystallization, which result in volumetric shrinkage.

For high-temperature deposition conditions, the differences in the coefficients of thermal expansion of the substrate and film material can produce thermal (shrinkage) stresses that put the film in tension or in compression, depending on which material has the greater thermal expansion.

Film stress can change with film thickness. Stress gradients can exist in the deposited film due to the growth mode and differing thermal histories of the various layers of the film. These stresses can give the outermost layer of the film a tensile stress compared to the rest of the film. This film stress profile leads to "curling" of a film when it is detached from the substrate. If the adhesion failure is such that some of the substrate material remains attached to the film, the film can curl because of the constrained surface. Local stresses can be found in films where there is nonhomogeneous growth, such as over steps and defects in the substrate.

On a thin substrate that is in the form of a thin, long beam, the sum of all these stresses in the film causes the "beam" to bend. From the degree of bending and the material properties, the film stress can be calculated. The force on a substrate due to the film stress is a function of the film thickness. Film stress can also be determined by x-ray diffraction measurements of lattice strain, but this does not fully take into account boundary effects. The film morphology affects the stress buildup with a columnar morphology resulting in a low total stress.

Film stress and the resulting force and shear stresses are important factors in the adhesion and stability of films. High isotropic compressive film stresses produce "blistering" of the film from the surface in "worm-track" patterns. High isotropic tensile film stresses produce microcracking of the film. The cracks tend to meet orthogonally and form polygon "islands" or "chips" such as are seen in dried "mudflats" (Ref 65). Because the interface is constrained, the mudflat islands will tend to curl at the edges. If the compressive stresses are highly anisotropic, the "worm-track" pattern changes to line-shape blisters. If the tensile stresses are highly anisotropic, the "mud-flatting" pattern changes to linear cracks. If the adhesion between the film and the substrate is high, the stress can cause fracture in the film or substrate material. The film buckling or cracking can be time-dependent and can also depend on the moisture available in the ambient environment. This time/environment-related failure is called *static fatigue* (Ref 66). Fractures and fracture patterns in films can be detected by the use of fluorescent tracers. Generally, residual film stress should be minimized to prevent failure.

Modification of Film Stress. There are several methods of modifying the mechanical stresses developed in films during growth:

- Limiting the thickness of the stressed film
- Using concurrent energetic particle bombardment during deposition to maintain a near-zero-stress condition (Ref 67)
- Periodically alternating the concurrent bombardment conditions (Ref 39)
- Periodically adding alloying or reacting materials
- Mixing materials
- Deliberately generating an open columnar morphology that cannot transmit a stress

Limiting the film thickness is generally the most easily accomplished approach. As a "rule-of-thumb," the thickness of high-modulus materials such as chromium and tungsten should be limited to less than 50 nm to avoid excessive residual stress. If the film thickness is to exceed that value, some technique for stress monitoring and control should be developed.

One technique to control film stress is to use concurrent ion bombardment during deposition to create compressive stress to offset the tensile stress (Ref 67). By carefully controlling the bombardment parameters it is possible to find a zero-stress condition. Unfortunately this condition is usually very dependent on the process parameters and the proper conditions are hard to control and maintain. A more flexible technique is to alternately deposit layers having tensile and compressive stresses that offset each other (Ref 39). This can be done by varying the concurrent bombardment from the reflected high-energy neutrals in low-pressure sputter deposition, bombardment from a plasma or bombardment from an ion gun.

Adhesion

Adhesion is a fundamental requirement of almost all film systems. It is determined by the nature of the stresses that appear at the interface and the energy needed to propagate a fracture and/or cause deformation. Film adhesion is intimately connected with the film and substrate properties as well as the properties of the interfacial (interphase) materials (Ref 26). Good adhesion is promoted by high fracture toughness of the interface and the near-surface material, presence of fracture blunting and deflecting features, low stresses and stress gradients, absence of fracture-initiating features, and an absence of operational adhesion-degradation mechanisms.

Poor adhesion can be attributable to low degree of chemical bonding, poor interfacial contact, low fracture toughness (brittle materials, flaws), high residual film stresses, fracture-initiating features, and/or operational adhesion-degradation mechanisms. Poor adhesion may be localized so as to give local failure (i.e., pinholes). In many systems where direct adhesion is difficult to attain, an intermediate material is introduced onto the substrate surface to bond to both the substrate and the film material. Substrate surface roughness can improve or degrade the adhesion, depending on the ability of the deposition technique to fill in the surface roughness and the film morphology generated. The generation of a good interface is also important to other properties such as thermal transport and electrical contact resistance. The lack or loss of adhesion is often called *deadhesion*.

Modeling of Adhesion. The principal models used for explaining adhesion are:

- Surface energy reduction, wettability, and spreading--commonly used with polymer bonding
- Interfacial fracture and deformation--used in inorganic systems (Ref 26)

In the latter case the fracture toughness or fracture energy is the relevant physical parameter. This depends on the stress at the interface and the properties of the interface, the "interphase material," and the nearby material of the film and substrate. The failure modes for ductile materials will be quite different from those of brittle materials.

Causes of Deadhesion. The stresses that appear at the interface and can cause adhesion failure (deadhesion) include:

- *Mechanical*--tensile, shear, compressive, shock, fatigue
- *Chemical and electrochemical*--corrosion, solution
- *Thermal*/*time*--diffusion, reaction

These stresses can cause loss of adhesion at or near the interface by:

- Fracture and deformation at the interface--mechanical
- Generation or propagation of flaws in the interface region--mechanical, static fatigue
- Corrosion at the interface--chemical
- Dissolution of interfacial material--chemical
- Diffusion of material away from the interface--thermal (Ref 21)
- Diffusion of species to the interface--thermal
- Phase change of material at the interface giving flaws and stress--thermal, diffusion

These stresses can originate externally to the film from the environment, subsequent processing, storage, or use, or they can be internal to the film-substrate structure. In addition, residual ionic species in the film can cause interfacial corrosion if exposed to humidity, or dissolved mobile species, such as gases, can migrate to the interface, causing deadhesion.

Deadhesion due to Fracture. The loss of adhesion under mechanical stress (tensile, compressive, shear) occurs by deformation and fracture of material at or near the interface. The fracture mode (brittle or ductile) depends on the properties of the materials. The fracture path depends on the applied tensor stress, the presence of flaws, the interface configuration, "easy fracture paths," and the properties of the materials involved.

The fracture toughness (K_c) of a material is a measure of the energy necessary for fracture propagation and is thus an important adhesion parameter. In fracture, energy is adsorbed in the material and at the propagating crack tip by elastic deformation, plastic deformation, generation of defects, phase changes, and the generation of new surfaces. If this fracture

occurs at an interface or in the nearby material, then loss of adhesion (deadhesion) occurs. Fracture mechanics approaches to measuring, describing, modeling, and/or predicting thin film (or any interface) adhesion are few. Some work has been published on the fracture of thick film and thin film systems. Thouless (Ref 68) has described the problem of critical and subcritical crack growth in thin film systems. Very little has been done to elucidate the effects of environment (subcritical crack growth) and film properties (Ref 69) on fracture and adhesion of thin film systems.

The fracture toughness of a material depends on the material composition, the microstructure, the flaw concentration, and the nature of the applied stresses. If an interphase material has been formed in the interfacial region it will be involved in the fracture process. Such interphase material is formed by diffusion, by diffusion plus compound formation, and by physical processes such as physical mixing and recoil implantation. The interphase material may be weaker or stronger than the nearby film and/or substrate material. For example, carbon lost from high-carbon steel substrates by diffusion into the film material during high-temperature processing can weaken the substrate and strengthen the film material. A National Science Foundation workshop in 1987 determined that the properties of the "interphase" (interfacial) material are some of the critical concerns in quantifying, measuring, and modeling the adhesion failure process (Ref 31). At present there are few if any good characterization techniques for determining the properties of interfacial materials that affect adhesion, such as fracture toughness, deformation properties, interfacial stress, presence of microscopic flaws, or effects of degradation mechanisms.

When a fracture surface (crack) advances, energy is needed for the creation of new crack surfaces and the deformation processes around the crack tip. This energy is supplied by the applied stress and the internal strain energy stored in the film-substrate system (residual film stress). The path of crack propagation is determined by the mechanical properties of the materials and by the resolved tensor stresses (tensile and shear) on the crack tip. The crack may progress along a plane of weakness, through weak material, or it can be diverted into stronger materials by the resolved stress. The fracture path is also determined by the presence of features that can blunt or change the fracture propagation direction.

Interfacial Morphology Effects on Fracture. In atomistic film deposition, the nucleation of depositing atoms on a smooth surface is controlled by various factors such as surface chemistry and nucleation sites. If the film-substrate interface is smooth, then any interfacial growth defects, such as interfacial voids, will lie in a plane that will then be a plane of weakness or "easy fracture path" along which fracture will easily propagate.

If the surface is rough and the deposited film material "fills in" the roughness, the propagating fracture must take a circuitous path with the likelihood that the fracture will be arrested and have to be reinitiated, as in the case of fiber-reinforced composite materials. If the roughness is not "filled in," there will be weakness (voids and low contact area) built into the interfacial region. Therefore the nature of the substrate surface roughness and the ability of the deposition process to fill in this roughness is important to the development of good adhesion.

The energy necessary for fracture propagation (fracture energy) can be lessened by mechanisms that weaken the material at the crack tip or reduce the elastic-plastic deformation in the vicinity of the crack tip. These mechanisms can be dependent on the environment in the case of ionically bonded materials. If time is involved in reducing the strength of the crack tip, the loss of strength is called *static fatigue* (Ref 66). Static fatigue depends strongly on mechanical (stress) and environmental (chemical) effects, particularly moisture and hydrogen (Ref 70).

Brittle surfaces and interfaces can be strengthened by placing them in compressive stress. This can be done by chemically replacing some surface ions with larger ions (chemical strengthening), by ion implantation, by putting the interior of the bulk material into tensile stress, or by placing the film in a state of compressive stress.

Residual Film Stress Effects on Adhesion. Invariably, atomistically deposited films have a residual stress that can be either tensile or compressive and can approach the yield or fracture strength of the materials involved. These stresses can arise from high-temperature deposition when there are differences in the thermal coefficients of expansion between the film and substrate, thermal gradients formed in the depositing film, and/or stresses due to the growth of the film. These stresses can enhance or retard fracture propagation.

In thin-film systems, high residual stress can be relieved by plastic deformation, blistering of the film from the surface in the case of compressive stress, or by microcracking and flaking in the case of high tensile stresses. If the film adhesion is high or the strength of the surface or film is low, the actual fracture path can be in the substrate or film and not at the interface. In many cases, in order to obtain good adhesion the residual film stress must be minimized and controlled. In some cases, film adhesion can increase with time due to the relief of high residual film stress.

Localized regions of high intrinsic stress can be found in films due to growth discontinuities or defects such as pinholes, nodules, or surface features such as edges or inclusions. These stressed areas can lead to localized adhesion failure under applied stress, producing pinholes.

Static fatigue is the slow growth of a crack under ambient stress and environmental conditions (Ref 66). The static fatigue failure mode due to moisture can be accelerated by breathing on the films to condense moisture at the crack tip. This moisture condensation method is an easy method of quickly determining if the residual film stresses are high, if the adhesion is poor, and whether the stresses in a failed film are compressive or tensile.

Corrosion. Interfacial corrosion/dissolution occurs when chemical or electrochemical (galvanic) effects create a solid or soluble corrosion product at the interface. An example of the loss of adhesion due to corrosion effects is the degradation of Ti-Au metallization in an HCl environment. This electrochemical degradation can be prevented by the addition of a thin intermediate layer of palladium between the titanium and the gold. The presence of chloride ions is generally to be avoided; they are often present as residues from cleaning and processing steps. Corrosion products can aggravate failure by a "wedging" action at the crack tip, either by solid corrosion products or by gas accumulation.

The diffusion of material away from the interface can weaken the interface by producing voids or in the extreme the complete removal of a bonding layer. For example, in the case of Cr-Au metallization, heating the system to higher than 200 °C in air will cause the chromium to diffuse from the interface to the surface, where it is tied up as the oxide (Ref 21). If all of the chromium diffuses from the interface, the gold film will not adhere. This "out-diffusion" of the interfacial material is dependent on the gaseous ambient, and a nonoxidizing ambient reduces the diffusion. The incorporation of a small amount of oxygen in the gold during deposition (by deposition in an oxygen plasma) reduces the chromium diffusion rate and gives a more thermally stable metallization.

Diffusion to the Interface. Interfaces generally act as preferential condensation regions for diffusion species. Diffusion of species to the interface can weaken or strengthen the interface. The deposition process may have influence on this effect. For instance, plasma cleaning of glass surfaces prior to silver deposition has been shown to give a time-dependent improvement in the adhesion of the silver films after deposition. Precipitation of gas at the interface to form voids will reduce adhesion. The diffusion of hydrogen through a film to an interface where it precipitates has been used by the electroplating community as an adhesion test. Diffusion and precipitation of vacancies form voids at interfaces that can cause adhesion loss.

Diffusion of water vapor through a polymer film to the interface can lead to the degradation of metal-polymer adhesion (Ref 71). Interfacial mixing can improve the moisture degradation properties of polymer-metal film systems.

Interdiffusion and reaction at the interface can generate an undesirable interphase material that results in a loss of adhesion. For example, in Au-Al metallization, interdiffusion and reaction form both Kirkendall voids and a brittle intermetallic phase ($AuAl_2$), termed "purple plague," that causes loss of adhesion (Ref 28).

Film Morphology Effects on Adhesion. Film properties can influence the apparent adhesion of a film-substrate couple (Ref 72). The mechanical, microstructural, and morphological properties of the film material determine the ability of the material to transmit mechanical stress and to sustain internal stresses. For example, a columnar film morphology can exhibit good adhesion because each column is separately bonded to the substrate and the columns are poorly bonded to each other. The columnar morphology is generally not desirable because of its low density and high surface area.

Deliberate Nonadhering Coatings. In some situations, adhesion is not desirable. For example, one technique to form freestanding films or shapes is to deposit a coating on a mandrel and then separate the coating from the mandrel. The coating can be deposited on a substrate to which it will not adhere, or a "parting layer" (release layer) can be used (Ref 73). In the electrodeposition of freestanding copper or gold structures, stainless steel or carbon is often used as a mandrel, because the chromium oxide and carbon are good electrical conductors but copper and gold will not adhere to the oxide or carbon surface. Easily dissolved materials such as sodium chloride or polymers can be used as parting layer materials. In some cases, particularly for complex shapes, the mandrel must be completely dissolved to release the structure.

Film Density and Surface Area

The presence of porosity in the columnar structure, closed and open voids, and pinholes means that the film density is lower than that of the bulk material and that the surface area exposed to the ambient is much higher than the geometrical

surface area. This low density and high surface area influence many film properties, such as hardness, deformation, chemical etch rate, resistivity, and index of refraction.

Open porosity features pores that connect to the free surface and contribute to the surface area of the film. The coalescence of lattice defects along surfaces such as grain boundaries and the open space between the columns in the columnar microstructure are sources of such porosity. Process parameters that affect the growth of the columnar microstructure affect the film porosity. For example, the porosity of vacuum-deposited films can be varied by controlling the substrate surface roughness, angle of incidence of the adatom flux, or the gas pressure during deposition.

Through porosity is a special case of open porosity where the porosity is aligned in such a manner as to allow an open space to exist between the film surface and the substrate surface. Through porosity develops from the columnar growth, particularly on rough surfaces, and the growth on surface contaminants such as particulates (see Fig. 6). Such porosity causes pinholes in the film and allows corrosion of the substrate through the pinholes, electrical "opens" in patterned electrical circuits, optical transmission, and high surface diffusion rates from the interface to the film surface.

Crystallographic Orientation

The crystallographic orientation of the grains in the film is determined by the preferential growth of certain crystal planes over others. This orientation can be altered by epitaxial growth on a substrate or by concurrent energetic ion bombardment.

Even when single crystal films are not formed, it is often found that a preferential crystallographic orientation or texture develops in deposited films. This texturing can lead to nonisotropic film properties in materials that do not have cubic crystal forms.

Epitaxial Film Growth. *Epitaxy* is defined as the oriented overgrowth of film material and typically refers to the growth of single crystal films (Ref 74). *Homoepitaxy* is the epitaxial growth of a deposit on a substrate of the same material (e.g., doped Si on Si). *Heteroepitaxy* is the epitaxial growth of a deposit on a substrate of a different material (e.g., Au on Ag, GaAs on Si). Epitaxial growth requires some degree of mobility of the atoms and nuclei on the surface. An "epitaxial temperature" necessary for epitaxial growth in specific systems and under specific deposition conditions is sometimes specified.

Single crystal overgrowth can be accomplished with large mismatches in lattice parameters between the film and substrate, either by keeping the thickness of the deposited material small, so that the mismatch can be taken up by straining the film lattice without forming lattice defects ("strained layer superlattice"), or by using a "buffer" layer to grade the strains from the substrate to the film. For example, thick single crystal SiC layers can be grown on silicon by CVD techniques even though the lattice mismatch is large (20%). This is accomplished by forming a buffer layer by first carbonizing the silicon surface and grading the composition from the substrate to the film. However, in general, if the lattice mismatch is large, the interface has a high density of dislocations and the resulting film is polycrystalline.

Oriented growth can be enhanced by "seeding" of the substrate surface with oriented nuclei. Such "seeds" can be formed by depositing a small amount of material, heating the surface to form isolated oriented grains, and then using these grains as seeds for the deposition of an oriented film.

Energetic adatoms and low-energy ion bombardment during deposition can be used as partial substitutes for increased substrate temperature in the epitaxial growth process. Carefully controlled bombardment can lower the temperature at which epitaxy can be obtained. This is probably due to increased surface mobility of the adatoms. Ion beams of the depositing material (film ions) have also been used to deposit epitaxial films.

Lattice Defects and Voids

Lattice defects are point defects in the lattice and the microstructures, such as dislocations, that arise from coalescence of point defects or the relaxation of elastic strains. Voids are internal pores that do not connect to a free surface of the material and thus do not contribute to the surface area but do affect film properties such as density. During film growth, vacancies can agglomerate into "microvoids" in the crystal structure. Defects in the films can be reduced by:

- Increased substrate heating during deposition

- Controlled concurrent ion bombardment during deposition--use of low enough particle energies such that the bombarding species are not incorporated into the growing film

Point defects in the film can affect the electrical conductivity and electromigration in metallic films, and carrier mobility and lifetime in semiconductor materials. Generally, high-defect concentrations result in poor electromigration properties. Lattice defects have been shown to be important to the properties of the high-transition-temperature superconductor films.

Surface Coverage

Surface geometry affects the growth of films by shadowing the surfaces from the depositing flux of atoms. Steps, vias, and grooves are of particular importance, and in order to get conformal coverage over such surfaces, the deposition often must be done at an elevated temperature to increase surface mobility or by using backsputtering/redeposition. Off-normal incidence of the depositing flux makes conformal coverage more difficult. The ability of concurrent ion bombardment to improve step-coverage is of great interest in microelectronic fabrication. The improved coverage by concurrent ion bombardment is due to a number of factors, including:

- Forward sputtering (Ref 75)
- Gas scattering--randomizing of direction of adatom flux
- Backscattering of sputtered material
- Ionization and return of sputtered material

Graded Properties

There are a number of effects that lead to changes of film properties with thickness (graded properties). As previously discussed, the film growth mode is continually changing with thickness in the early stages of growth, particularly on rough surfaces. The initial deposition may have reacted with residual gases, giving a changing composition with thickness. In addition, the initially deposited material is being heated while the film is growing, thus allowing annealing during growth. The degree of this annealing differs with deposition time, deposition rate, thickness, and the thermal transport properties of the film and substrate material.

Postdeposition Changes (Stability) in Film Properties

High surface areas and high residual film stress are major factors in the change of film properties with time. The high surface areas allows corrosion and adsorption to play major roles in the stability of film properties. Residual stress represents stored energy that can give long-term stability problems.

Adhesion. In some cases, film adhesion can increase or decrease with time under ambient conditions. The increase in adhesion can be due to diffusion of reactive species to the interface or the relief of residual stresses. The film adhesion may decrease with time, and it can be due to static fatigue fracture at the interface due to residual stress, promoted by the presence of moisture, or to corrosion of the interface by ambient species.

Microstructure. High residual stress and high point defect concentrations can lead to time-dependent changes in the microstructure of the deposited material. This may lead to low-temperature grain growth and recrystallization in sputter-deposited copper and the generation of voids ("stress voiding") at room temperature.

Electromigration (Ref 76) and stress-induced void formation (Ref 54, 77) in aluminum metallization can be reduced by the addition of a material that will react with the aluminum to form finely dispersed second-phase materials that act as sinks for migrating defects and coalescing voids. Copper is the common material added to aluminum metallization to reduce stress-induced voiding and electromigration (Ref 77). The copper forms the theta Al-Cu phase Al_2Cu.

Residual Stress. A high internal concentration of defects along with high intrinsic stress can lead to time-dependent changes of stress ("stress relaxation") in films.

Electrical Properties. Changes of the electrical resistivity of a film can be due to oxidation of the columnar surfaces. The combination of metallic conduction in the columns and the tunneling conduction through oxide layers on the column surfaces, allows the formation of films that have a low-temperature coefficient of resistivity.

References cited in this section

21. P.H. Holloway, Gold/Chromium Metallization for Electronic Devices, *Solid State Technol.,* Vol 23 (No. 2), 1980, p 109, and references therein
26. D.M. Mattox, Thin Film Adhesion and Adhesive Failure--A Perspective, *ASTM Proc. Conf. Adhesion Measurement of Thin Films, Thick Films and Bulk Coatings,* STP 640, ASTM, 1978, p 54
28. E. Philofsky, Intermetallic Formation in Gold Aluminum Systems, *Solid State Electronics,* Vol 13 (No. 10), 1970, p 1391
31. G.G. Fuller and K.L. Mittal, Ed., *Opportunities and Research Needs in Adhesion Science and Technology,* National Science Foundation Workshop on Adhesion, 14-16 Oct 1987 (Lake Tahoe, CA), Hitex Publication, 1988
39. R.E. Cuthrell, D.M. Mattox, C.R. Peeples, P.L. Dreike, and K.P. Lamppa, Residual Stress, Stress Anisotropy, Stress Control and Resistivity in Post Cathode Magnetron Sputter-Deposited Molybdenum Films, *J. Vac. Sci. Technol. A,* Vol 6, 1988, p 2914
54. F.G. Yost, D.E. Amos, and A.D. Romig, Stress Driven Diffusion Voiding of Aluminum Conductor Lines, *Proc. IEEE/IRPS '89,* 1989, p 193
63. M. Ohring, *The Material Science of Thin Films,* Academic Press, 1991, and references therein
64. H. Windischmann, Intrinsic Stress in Sputter-Deposited Thin Films, *Crit. Rev. Solid State Mater. Sci.,* Vol 17 (No. 6), 1992, p 547
65. R. Pestrong, Nature's Angles, *Pacific Discovery--Calif. Academy of Sciences,* Vol 44 (No. 3), Summer 1991, p 28
66. S.M. Wiederhorn and L.H. Bolz, Stress Corrosion and Static Fatigue of Glass, *J. Am. Ceram. Soc.,* Vol 53, 1970, p 543
67. D.M. Mattox, Particle Bombardment Effects on Thin Film Deposition: A Review, *J. Vac. Sci. Technol. A,* Vol 7 (No. 3), 1989, p 1105, and references therein
68. M.D. Thouless, The Role of Fracture Mechanics in Adhesion, *Adhesion in Solids,* Symp. Proc., Vol 119, D.M. Mattox, J.E.E. Baglin, C. Batich, and R. Gottschall, Ed., Materials Research Society, p 51
69. T.S. Oh, R.M. Cannon, and R.O. Ritchie, Subcritical Crack Growth along Ceramic-Metal Interfaces, *J. Am. Ceram. Soc.,* Vol 70, 1987, p C352
70. R.E. Cuthrell, Influence of Hydrogen on the Deformation and Fracture of the Near Surface Region of Solids: Proposed Origin of the Rehbinder-Westwood Effect, *J. Mater. Sci.,* Vol 14, 1979, p 6123
71. V.D. Venables, Adhesion and Durability of Metal-Polymer Bonds: A Review, *J. Mater. Sci.,* Vol 19, 1984, p 2431
72. J.T. Prater and R.W. Moss, Effect of the Coating Structure on the Adherence of Sputter-Deposited Oxide Coatings, *Thin Solid Films,* Vol 107, 1983, p 455
73. A.H.F. Muggleton, Deposition Techniques for Preparation of Thin Film Nuclear Targets: Invited Review, *Vacuum,* Vol 37, 1987, p 785
74. M. Simpson, P. Smith, and G.A. Dederski, Atomic Layer Epitaxy: State of the Art Review, *Surf. Eng.,* Vol 3, 1987, p 343
75. D.W. Skelly and L.A. Grunke, Significant Improvement in Step Coverage using Bias Sputtered Aluminum, *J. Vac. Sci. Technol. A,* Vol 4 (No. 3), 1986, p 457
76. L. Berenbaum and R. Rosenberg, Electromigration Damage in Al-Cu Thin Films, *IEEE/IRPS,* 1971, p 136
77. J.G. Ryan, J.B. Riendeau, S.E. Shore, G.J. Slusser, D.C. Beyar, D.P. Bouldin, and T.D. Sullivan, The Effects of Alloying on Stress Induced Void Formation in Aluminum Based Metallizations, *J. Vac. Sci. Technol. A,* Vol 8 (No. 3), 1990, p 1474

Unique Materials Formed by Atomic Deposition Processes

Amorphous materials are those that have no detectable crystal structure. Materials can be naturally amorphous, such as the nonmetallic glasses. Some normally crystalline materials can be formed in the solid amorphous condition by rapidly cooling ("quenching") from the liquid phase (Ref 78).

Amorphous film materials can be formed by:

- Deposition of a natural "glassy" material such as a glass composition
- Deposition at low temperatures where the adatoms do not have enough mobility to form a crystalline structure
- Ion bombardment of high-modulus materials (Ref 79)
- Deposition of materials some of whose bonds are partially saturated by hydrogen (e.g., a-Si:H, a-C:H, and a-B:H, where "a" stands for *amorphous*)
- Deposition of complex metal alloys

Hydrogen seems to play a very unusual role in the growth of some materials. In the case of depositing silicon from the silane (SiH_4) precursor gas in CVD, the incomplete decomposition of the precursor results in the deposition of a-Si, which can contain 10 to 15 at.% H. The hydrogen prevents Si-Si bonding, thus causing the film material to be amorphous in much the same way as "glass formers" do in forming glasses by melting. The a-Si seems to deposit much like a polymer film, giving very good surface replication and low void density in the early stages of film growth.

The unique applications of amorphous materials arise because of:

- Absence of grain boundaries--no grain boundary diffusion
- Low void/pinhole content
- Considerable compositional latitude
- Unique optical properties
- Unique electronic properties
- Ease of fabrication

Some semiconductor materials grow with some of their bonds unsaturated ("dangling"). This can lead to unacceptable electron trapping. It has been demonstrated that the unsaturated bonds in a-Si can be passivated by hydrogen doping, thus raising the electron mobility in the material. Hydrogen ion bombardment is now used to treat polycrystalline silicon photovoltaic materials to improve photoconversion efficiency.

Metastable or labile phases are unstable phases of materials that are easily changed if energy is available for mass transport processes to occur. Deposition processes allow the development of metastable forms of the material. Metastable crystal structures can be formed by rapid quenching of high-temperature phases of the deposited material, or they can be stabilized by residual stresses or impurities in the film. For example, diamond is a metastable phase of carbon that is formed naturally in a high-pressure and high-temperature environment and changes to graphitic carbon on heating. However, diamond films can be deposited using the proper deposition techniques. Metastable film compositions can also be formed under deposition conditions that do not allow precipitation of material when it is above the solubility limit of the system. For example, concurrent low-energy ion bombardment using "dopant ions" allows doping of semiconductor films to a level greater than that obtainable by diffusion-doping techniques (Ref 80).

Diamond and Diamond-like Carbon (DLC) Films. Recently great progress has been made in the deposition of diamond and diamond-like carbon (DLC) coatings for industrial applications. Natural diamond, with its high hardness, low coefficient of friction, high thermal conductivity (1.5 times that of silver), high packing density, good visible and infrared transparency, and chemical inertness, has long provided a goal for the thin film deposition community.

Diamond is a carbon material with a specific crystallographic structure (diamond structure) and specific chemical bonding (sp^3 bonding). DLC is an amorphous carbon material with mostly sp^3 bonding that exhibits many of the desirable

properties of crystalline diamond. DLC material is sometimes called "amorphous diamond," but that term is an oxymoron and should be avoided.

The property of the carbon sp^3 bonding that allows the deposition of both diamond and DLC coatings is its relative chemical inertness to hydrogen reduction. The sp^3 bonds formed during deposition are stable against hydrogen etching. Any sp^2 (graphite) bond formed, however, is susceptible to hydrogen etching.

Polycrystalline diamond films can be formed if the deposition temperature is high enough (>600 °C, or 1100 °F) to allow atomic rearrangement during deposition. DLC films are formed at lower temperatures (room temperature and even below) where the atoms cannot arrange themselves into the diamond structure, giving an amorphous material. The DLC films have varying amounts of sp^2 bonding and included hydrogen that affect their properties. The sp^3-bonded material can be deposited by a number of techniques, all of which involve "activating" both a hydrocarbon species, to allow carbon deposition, and hydrogen, to provide the etchant species.

Polycrystalline diamond films are most often deposited by the hot filament CVD technique, the combustion flame technique, or PECVD using a microwave plasma. In all cases, the diamond film that is formed is polycrystalline and has a rough surface. This is due to the method of film nucleation on the substrate surface and the nature of the film growth. This rough surface gives a high coefficient of friction, and a great deal of work is being done to try to improve this surface morphology for wear and friction applications. Other properties can approach those of natural diamond.

DLC films are made primarily using PECVD or ion beam techniques with low substrate temperatures (Ref 81). The DLC films are smooth with properties approaching those of natural diamond, except that thermal conductivity is much lower. DLC films can also be deposited by ion bombardment processes that do not involve hydrogen. These films are sometimes called "i-C" films (Ref 79). DLC films are being used as coatings on optical products such as eyeglasses, sunglasses and IR optics, and as wear-resistant coatings on storage media and cutting surfaces.

References cited in this section

78. K.H.J. Buschow, Amorphous Alloys, *J. Less-Common Met.,* Vol 110, 1985, p 205
79. C. Weismantel, Preparation, Structure and Properties of Hard Coatings on the Basis of i-C and i-BN, Chapter 4, *Thin Films from Free Atoms and Particles,* K.J. Klabunge, Ed., Academic Press, 1985, p 153, and references therein
80. J.E. Greene, A Review of Recent Research on the Growth and Physical Properties of Single Crystal Metastable Elemental and Alloy Semiconductors, *J. Vac. Sci. Technol. B,* Vol 1 (No. 2), 1983, p 229
81. H.-C. Tsai and D.B. Bogy, Critical Review: Characterization of Diamond-Like Carbon Films and Their Applications as Overcoats on Thin Film Media for Magnetic Recording, *J. Vac. Sci. Technol. A,* Vol 5 1987, p 3287, and references therein

Vacuum Deposition, Reactive Evaporation, and Gas Evaporation

Donald M. Mattox, IP Industries

Introduction

VACUUM DEPOSITION, or vacuum evaporation, is a physical vapor deposition process in which the atoms or molecules from a vaporization source reach the substrate without colliding with residual gas molecules. Generally, the vaporization source is one that vaporizes materials by thermal means (that is, evaporation or sublimation), but other vapor sources can be used. The advantage of vacuum evaporation is that films of a variety of materials can be deposited at high rates over large areas in a very pure form. Limitations of vacuum evaporation are that often the films do not have optimum properties and that there are relatively few deposition parameters that can be modified to improve the film properties.

Vacuum deposition requires a vacuum of better than 13 mPa (0.1 mtorr). At this pressure, there is still a large amount of concurrent bombardment of the substrate by potentially undesirable residual gases that can contaminate the film. If film

contamination is a problem, a high (13 μPa, or 10^{-7} torr) or ultrahigh (0.13 μPa, or 10^{-9} torr) vacuum environment can be used to produce a film with the desired purity, depending on the deposition rate, reactivities of the residual gases and depositing species, and the tolerable impurity level in the deposit.

Vacuum deposition of a film was first reported by Faraday in 1857 using exploding wires. Nahrwold was the first to use thermal evaporation in a vacuum to produce a thin film, in 1887. Vacuum deposition was not routinely used until about 1929, when it was first used for optical coatings (Ref 1). Strong, for example, metallized the 100 in. mirror for the Mount Wilson Observatory in 1935. The subject of vacuum deposition was thoroughly investigated by Glang in 1970 (Ref 2), and most review articles and book chapters on the subject since that time have drawn heavily on his work.

In reactive evaporation, a partial pressure of reactive gas is used to deposit compounds of the vaporized material by the reaction of deposited atoms with ambient gases. Reactive evaporation was first reported by Auwarter in 1952 and Brinsmaid et al. in 1953. In 1971, Heitmann used reactive evaporation to deposit oxide films by evaporating the film material through a plasma of the reactive gas, and this technique is now generally called activated reactive evaporation. With this method, either a gas, such as oxygen or nitrogen, or a hydrocarbon is metered into the vacuum chamber, where it reacts with the vapor from a metallic evaporant to form a metal oxide, nitride, or carbide coating.

In gas evaporation, a high residual gas pressure causes the formation of ultrafine (100 nm, or 1000 Å) particles by gas phase collision and nucleation. Gas evaporation is a term given to the deposition of ultrafine particles ("smokes"), which are formed by gas phase nucleation due to collision of the evaporated atoms with residual gas molecules. This typically requires an ambient gas pressure greater than about 1.3 mPa (10 torr). The formation of useful films of ultrafine particles formed by gas evaporation was reported by Pfund, who produced "zinc black" infrared absorbing films in 1933.

References

1. W.P. Strickland, "Optical Thin Film Technology: Past, Present and Future," *Society of Vacuum Coaters 33rd Ann. Tech. Conf. Proc.,* 1990, p 221
2. R. Glang, Vacuum Evaporation, Chapter 1, *Handbook of Thin Film Technology,* L.I. Maissel and R. Glang, Ed., McGraw-Hill, 1970, p 1-26

Vacuum Deposition

In the vacuum deposition process, elements, alloys, or compounds are vaporized and deposited in a vacuum. The process is carried out at pressures of less than 0.1 Pa (1 mtorr) and usually in vacuum levels of 10 to 0.1 mPa (100 to 1 μtorr). The substrate temperature typically ranges from ambient to 500 °C (930 °F). Figure 1 shows a typical batch vacuum deposition system. Vacuum deposition is commonly used to deposit pure metals (for example, aluminum, silver, gold, nickel, chromium, titanium, molybdenum, and tungsten), some alloys (for example, stainless steel, nickel-chromium, lead-tin, and M-Cr-Al-Y), and selected compounds (for example, Al_2O_3, TiC, and TiB_2).

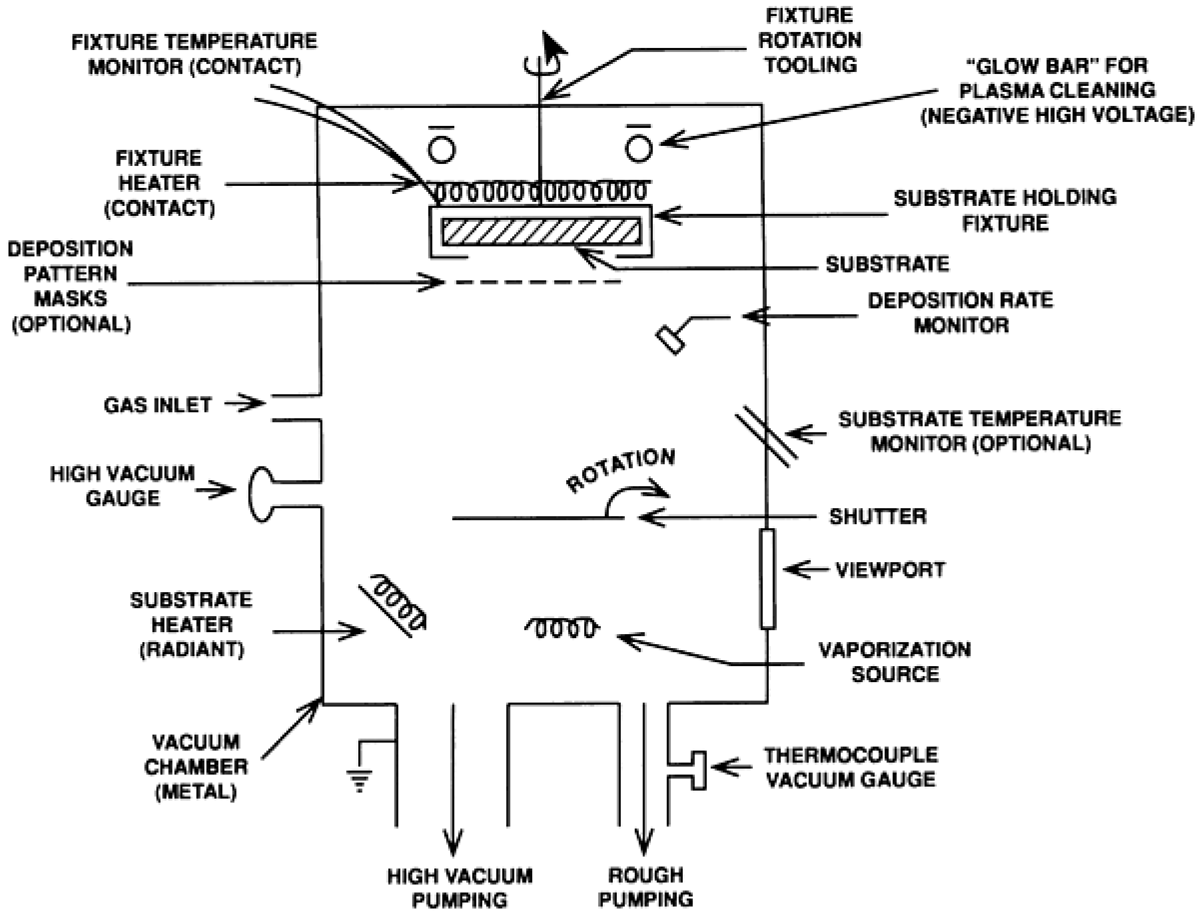


Fig. 1 Schematic diagram of a typical vacuum deposition chamber

Fundamentals of Thermal Vaporization

Equilibrium Vapor Pressure. The saturation or equilibrium vapor pressure of a material is defined as the vapor pressure of the material in equilibrium with the solid or liquid surface. At equilibrium, as many atoms return to the surface as leave the surface. The vapor pressure is measured by the use of a Knudsen cell, which consists of a closed volume with a small orifice of known conductance. When the container is held at a constant temperature the material that escapes through the hole depends on the pressure differential. In a vacuum environment and knowing the rate of material escaping, the equilibrium vapor pressure in the container can be calculated. The vapor pressures of the elements have been presented in tabular and graphical form (Ref 3). The Knudsen cell is often used as a source for molecular beam epitaxy, where the deposition rate can be carefully controlled by controlling the temperature of the source (Ref 4) or by mechanically interrupting the beam (Ref 5).

Figure 2(a) and 2(b) shows the vapor pressure of selected materials as a function of temperature. Note that the slopes of the vapor pressure curves are strongly temperature dependent (about 13 mPa/100 °C for cadmium and 13 mPa/250 °C for tungsten). The vapor pressures of different materials at a given temperature can differ by many orders of magnitude. For vacuum deposition, a reasonable deposition rate can be obtained only if the vaporization rate is fairly high. A vapor pressure of 1.3 Pa (10^{-2} torr) is typically considered the value necessary to give a useful deposition rate. Materials with that vapor pressure above the solid are described as subliming materials, and materials with that vapor pressure above the liquid are described as evaporating materials. Figure 3 shows the equilibrium vapor pressure curves of lithium and silver in detail and shows that at 800 K (527 °C) the vapor pressures differ by a factor of 10^7.

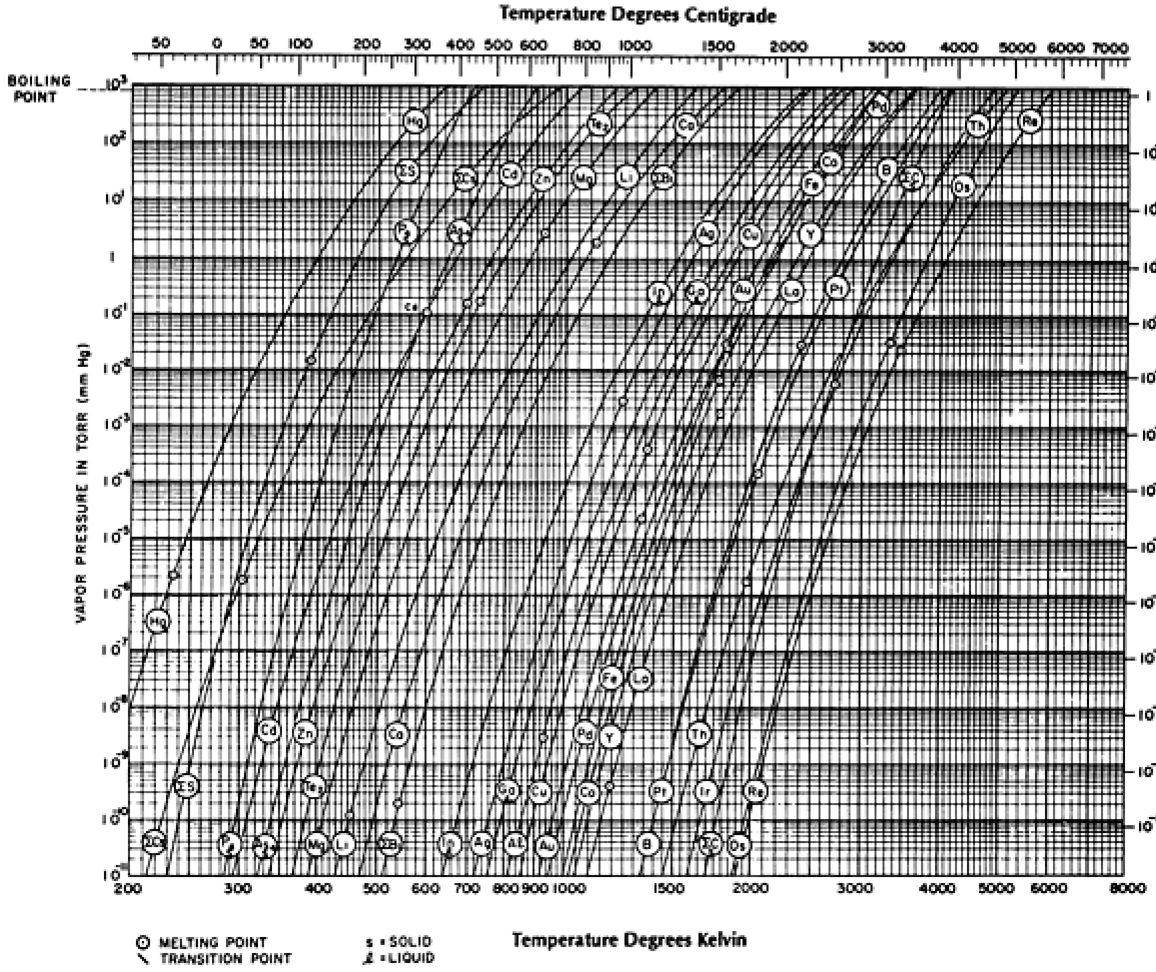


Fig. 2(a) Vapor pressure curves of the elements

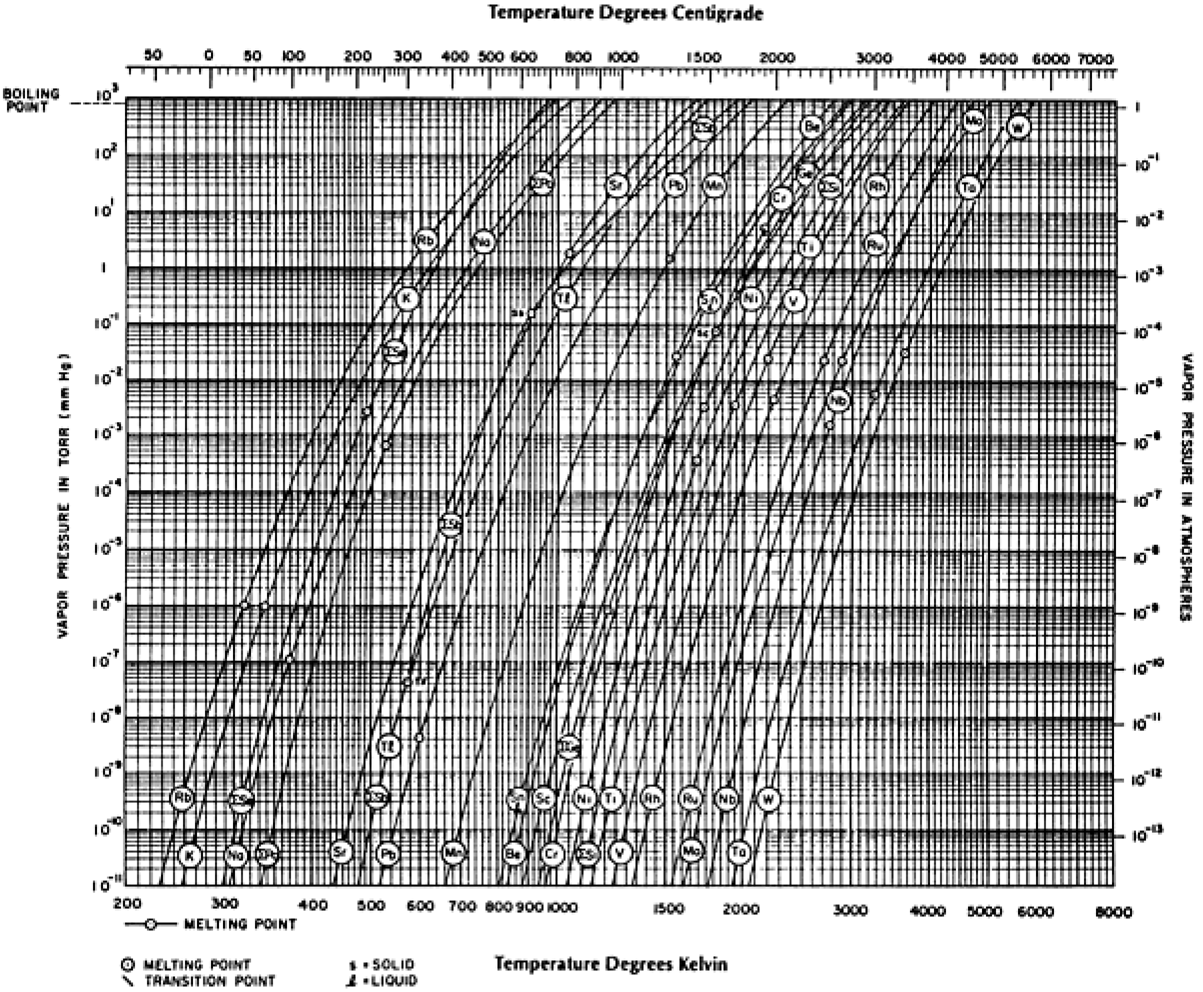


Fig. 2(b) Vapor pressure curves of the elements

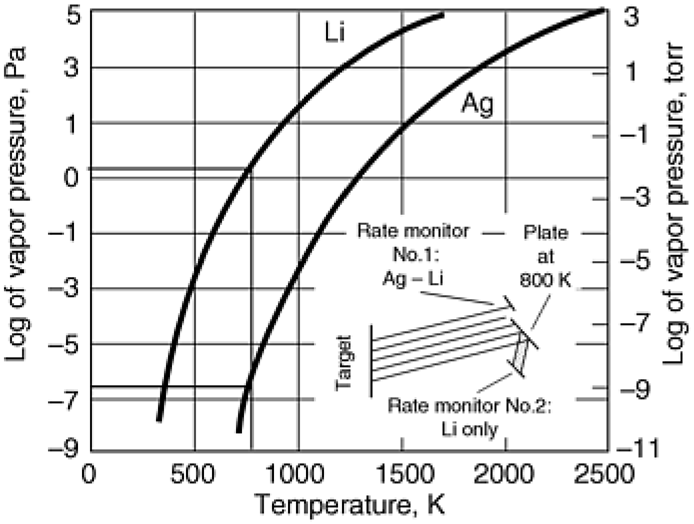


Fig. 3 Plot of equilibrium vapor pressure vs. temperature for lithium and silver

Vaporization Rate. A material vaporizes freely from a surface when the vaporized material leaves the surface with no collisions above the surface. The free surface vaporization rate, dN/dt (in s^{-1}) is proportional to the vapor pressure and is given by the Hertz-Knudsen vaporization equation (Ref 2, 6):

$$dN/dt = C\,(2\pi mkT)^{-1/2}\,(p^* - p) \qquad \textbf{(Eq 1)}$$

where dN/dt is the number of evaporating atoms per cm^2 of surface area per second, C is a constant that depends on the rotational degrees of freedom in the liquid and the vapor, p^* is the vapor pressure of the material at temperature T, p is the hydrostatic pressure of the vapor above the surface, k is Boltzmann's constant, T is the absolute temperature, and m is the mass of the vaporized species. The maximum vaporization rate is when $p = 0$ and $C = 1$. The actual vaporization rate will be one-third to one-tenth of this maximum rate because of collisions in the vapor above the surface (that is, $p > 0$ and $C \neq 1$), surface contamination, and other effects (Ref 7). Figure 4 shows some calculated maximum vaporization rates.

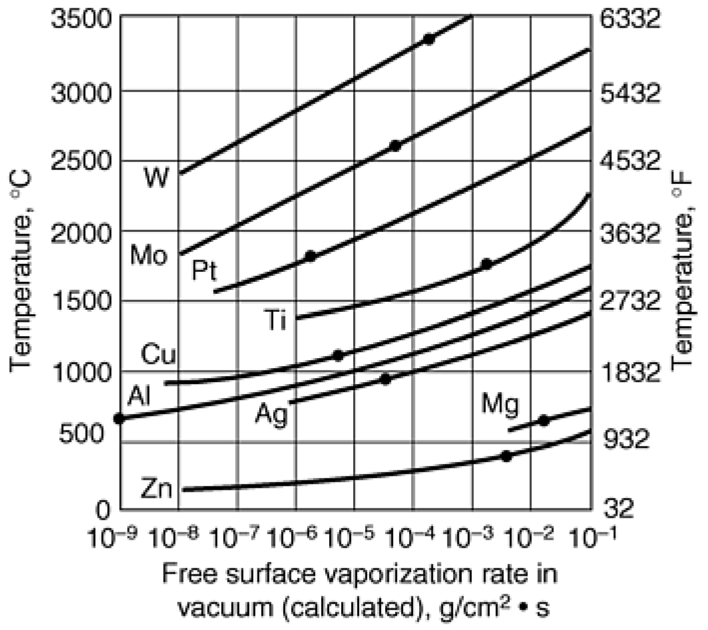


Fig. 4 Plot of temperature vs. free surface vaporization rate in a vacuum for selected elements. The symbol • indicates the melting point.

Vapor Flux Distribution on Vaporization. For low vaporization rates, the flux distribution can be described by a cosine distribution (Ref 2, 6). With no collisions in the gas phase, the material travels in a straight line between the source and the substrate (that is, line-of-sight deposition). The material from a point deposits on a surface with a distance and substrate orientation dependence given by the cosine deposition distribution equation:

$$dm/dA = (E/\pi r^2)\cos\theta\cos j \qquad \textbf{(Eq 2)}$$

where dm/dA is the mass per unit area, E is the total mass evaporated, r is the distance from the source to the substrate, θ is the angle from the normal to the vaporizing surface, and j is the angle from the source-substrate line.

Figure 5 shows the distribution of atoms vaporized from a point source and the thickness distribution of the film formed on a planar surface above the source based on Eq 2.

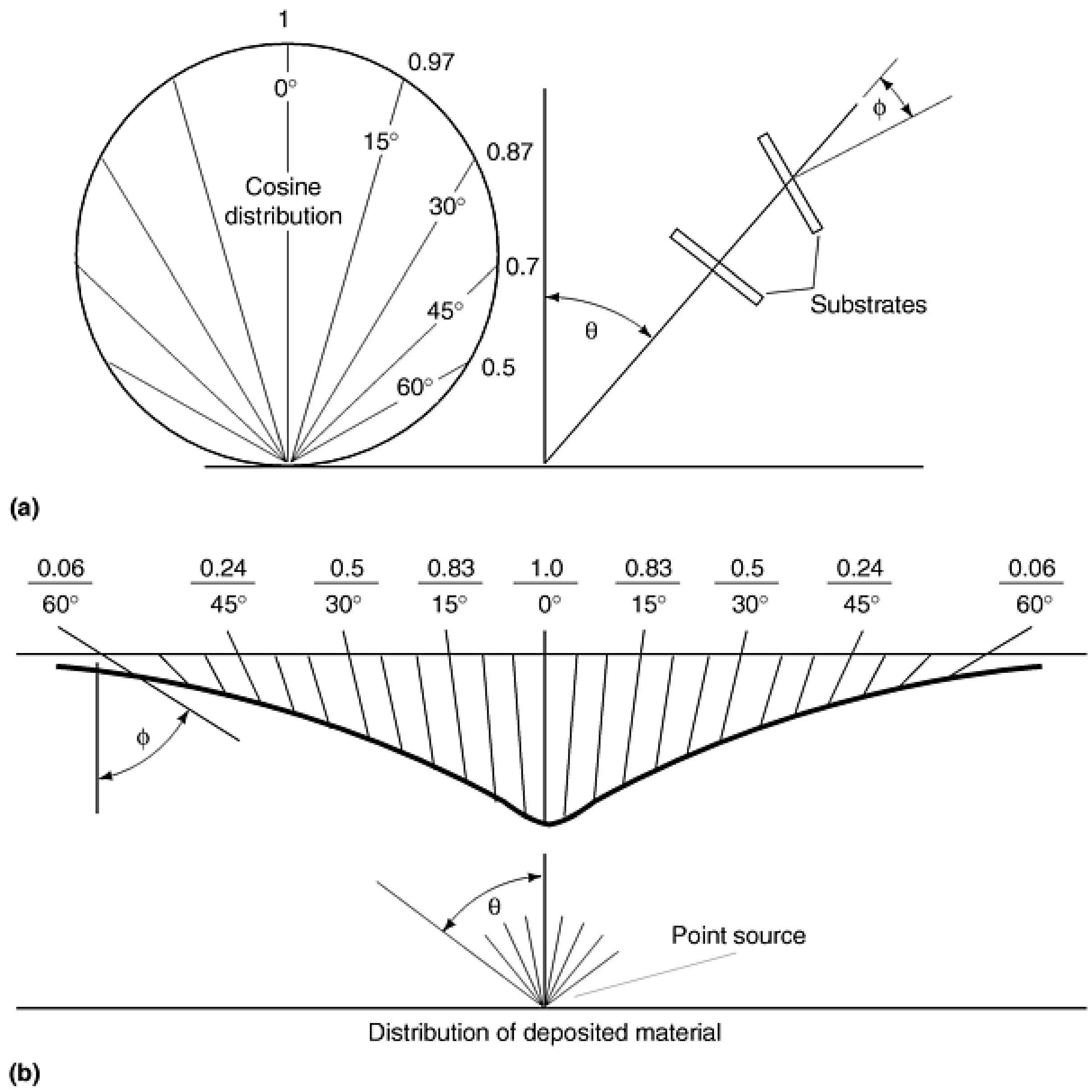


Fig. 5 Flux distribution above a point source, based on cosine deposition distribution equation. (a) Distribution of atoms vaporized from a point source. (b) Thickness distribution of film formed on planar surface above source

In actuality the flux distribution from a free surface may not be cosine but can be modified by source geometry, collisions associated with a high vaporization rate, level of evaporant in the source, and so on. In such cases, the flux distribution must be measured directly (Ref 8). A more complete model for the flux distribution from a Knudsen (orifice) source is given by the Knudsen effusion model proposed by Ruth and Hirth (Ref 9).

Particle Energies. Atoms leave a hot surface with thermal energies given by 3/2 kT, where k is Boltzmann's constant and T is the absolute temperature (Ref 2, 6). The atoms have a Maxwell-Boltzmann distribution in velocities. For example, for a 1500 °C evaporation temperature for copper, the mean energy of the vaporized copper atoms is 0.2 eV, and the mean atom velocity is about 1 km/s.

Shutters. Because the particles from a vaporizing source travel in straight lines in a vacuum, a shutter can be used to intercept vaporized material and prevent it from reaching the substrate. By opening and closing the shutter the deposition time can be precisely controlled.

Vaporization of Materials

Elements. Many elements evaporate, but many (for example, chromium, cadmium, magnesium, arsenic, and carbon) sublime, and many others (for example, antimony, selenium, and titanium) are on the borderline between evaporation and sublimation. Chromium has a vapor pressure of 1.3 Pa (10^{-2} torr) at 600 °C (1080 °F) below its melting point, and carbon cannot be melted except under high hydrostatic pressure. Materials such as aluminum, tin, gallium, and lead have very low vapor pressures above the just-molten material. Tin, for example, has a vapor pressure of 1.3 Pa (10^{-2} torr) at 1000 °C (1800 °F) above its melting point. Aluminum and lead have vapor pressures of about 1.3 Pa (10^{-2} torr) at 500 °C (900 °F) above their melting points.

Most elements vaporize as atoms, but some (for example, antimony, tin, carbon, and selenium) have a significant portion of the vaporized species as clusters of atoms. For materials that evaporate as clusters, special vaporization sources called *baffle sources* can be used to ensure that the depositing vapor is in the form of atoms. It should be noted that as a material is heated, the first materials that are volatilized are high-vapor-pressure surface contaminants, absorbed gases, and high-vapor-pressure impurities.

Alloys vaporize in a ratio that is the same as their vapor pressures (that is, the high vapor pressure constituent vaporizes more rapidly than the low vapor pressure material). This relationship is called Raoult's Law, and the effect can be used to purify materials by selective vaporization/condensation. When an alloy is evaporated from a molten pool, the higher-vapor-pressure material steadily decreases in proportion to the lower-vapor-pressure material in the melt. For example, when an Al:Mg (6.27 at.%) alloy is evaporated at 1919 K, the magnesium is totally vaporized in about 3% of the total vaporization time (Ref 10). Vaporization of alloys produces a gradation of film composition as the evaporant is selectively vaporized. This can be desirable or undesirable. For example, when copper-gold is deposited on polymers by evaporation of a copper-gold alloy, copper, which has a higher vapor pressure than gold, is deposited at a higher initial rate than the gold. This results in copper enrichment at the interface, which is conducive to better adhesion between the deposited film and the polymer.

In some cases, the nature of vaporization of an element can be changed by alloying it with another material. For example, chromium (melting point of 1863 °C, or 3385 °F), which normally sublimes, can be alloyed with zirconium (melting point of 1855 °C, or 3371 °F) to give a liquid melt from which the chromium evaporates. The eutectic alloy of zirconium-chromium (14 wt%) melts at 1332 °C (2430 °F), at which temperature chromium has a vapor pressure of approximately 1.3 Pa (10^{-2} torr) and zirconium has a vapor pressure of approximately 0.13 μPa (10^{-9} torr). Another eutectic alloy of zirconium-chromium (72 wt%) has a melting point of 1592 °C (2898 °F).

Compounds. Many compounds (for example, SiO, MgF_2, Si_3N_4, HfC, SnO_2, BN, PbS, and VO_2) sublime. Compounds often vaporize with a range of species, from clusters of molecules to dissociated or partially dissociated molecules (Ref 2). The degree of dissociation is strongly dependent on the temperature and composition of the compound (Ref 11). For example, in the thermal vaporization of SiO_2, a number of species are formed in addition to SiO_2, including $(SiO_2)_x$, SiO_{2-x}, SiO, Si, and O.

Evaporation from a very hot surface or by electron beams can give ionization of some of the molecular fragments. These charged species can be detrimental to the electrical properties of the deposited material. The ionized species can be deflected from the vapor flux using electrically charged plates above the source.

Fundamentals of Condensation

Thermally vaporized atoms may not condense when they impinge on a surface, but may rather be reflected or re-evaporate. Re-evaporation is a function of the surface temperature and the flux of depositing atoms. A hot surface can act as a mirror for atoms. For example, the deposition of cadmium on a steel surface having a temperature greater than 200 °C (390 °F) results in total re-evaporation of the cadmium. Figure 3 shows how this "hot mirror effect" can be used to monitor the deposition of the separate constituents of a depositing Ag-50Li alloy. The lithium is re-evaporated from the hot collector surface to deposit on the cold collector surface, while the silver remains on the hot surface. Hot surfaces can be used to reflect the evaporant flux of some materials, such as cadmium or zinc, into non-line-of-sight locations on a substrate to improve surface coverage and uniformity.

Nucleation and Nucleation Density. When adatoms (atoms adsorbed on a surface so that they migrate over the surface) move over a surface, they lose energy by making and breaking chemical bonds formed with the surface atoms, by colliding with other atoms, or by chemically reacting with an adsorbed species. If there is little chemical interaction between the surface atoms and the adatoms, the surface mobility will be high and the adatoms will nucleate on preferential nucleation sites such as steps, charge centers, impurities, grain boundaries, and so on. If the chemical reaction

is strong, the adatoms will have low surface mobility and the nucleation density will be high. The nucleation density plays an important role in determining film properties.

Condensation Energy. When a thermally vaporized atom condenses on a surface, it gives up energy, including:

- Heat of vaporization or sublimation (enthalpy change on vaporization): a few eV per atom, including the kinetic energy of the particle, which is typically 0.3 eV or less
- Energy to cool to ambient temperature: depends on heat capacity and temperature change
- Energy associated with chemical reaction (heat of reaction), which can be exothermic (when heat is released) or endothermic (when heat is adsorbed)
- Energy released on solution (alloying): heat of solution

The heat of vaporization for gold is about 3 eV/atom, and the mean kinetic energy of the vaporized gold atom is about 0.3 eV. This means that the kinetic energy is only a small part of the energy released at the substrate during deposition. However, it has been shown, using mechanical velocity filters, that the kinetic energy of the depositing gold atoms is important to the film structure, properties, and annealing behavior (Ref 12). At high deposition rates, the condensation energy can produce appreciable substrate heating (Ref 13).

Deposition rates for vacuum deposition processes vary greatly. They range from less than one monolayer per second (MLS) (<0.3 nm/s, or 3 Å/s) to more than 10^4 MLS (>3 μm/s, or 3×10^4 Å/s). The rate depends on the thermal power input to the source, the system geometry, and the material. Generally, the power input to the source is controlled by monitoring the deposition rate.

Deposition Uniformity. As shown in Fig. 5, the deposition thickness uniformity from a vaporizing point onto a plane is poor. A more uniform deposit over a planar surface can be obtained by using multiple sources with overlapping patterns. However, this produces source control and flux distribution problems (Ref 8). By moving the substrate farther away, the uniformity over a given area can be improved; however, the deposition rate is decreased. The most common technique to improve uniformity is to move the substrate in a random manner over the vapor source(s). Because the vaporization rate can change during the deposition process, the movement should sample each position a number of times during deposition. Often the substrates are rotated on a hemispherical fixture (calotte) with the evaporant source at the center of the sphere to give a constant r (see Eq 2). Specially designed movable masks can be used to provide specific thickness distributions over a surface (Ref 14, 15, 16), or the substrate movement can be controlled to give a specific film thickness distribution.

Surface Coverage. Because the deposition is line-of-sight, deposition on a rough or nonplanar surface can give geometrical shadowing effects resulting in nonuniform film thickness and variable film morphology. This is particularly a problem at sharp steps and at oblique angles of deposition. Figure 6 shows the effect of the angle of incidence in covering a surface having a particle on the surface. These geometrical problems can be alleviated by extended vaporization sources, multiple sources, or substrate movement.

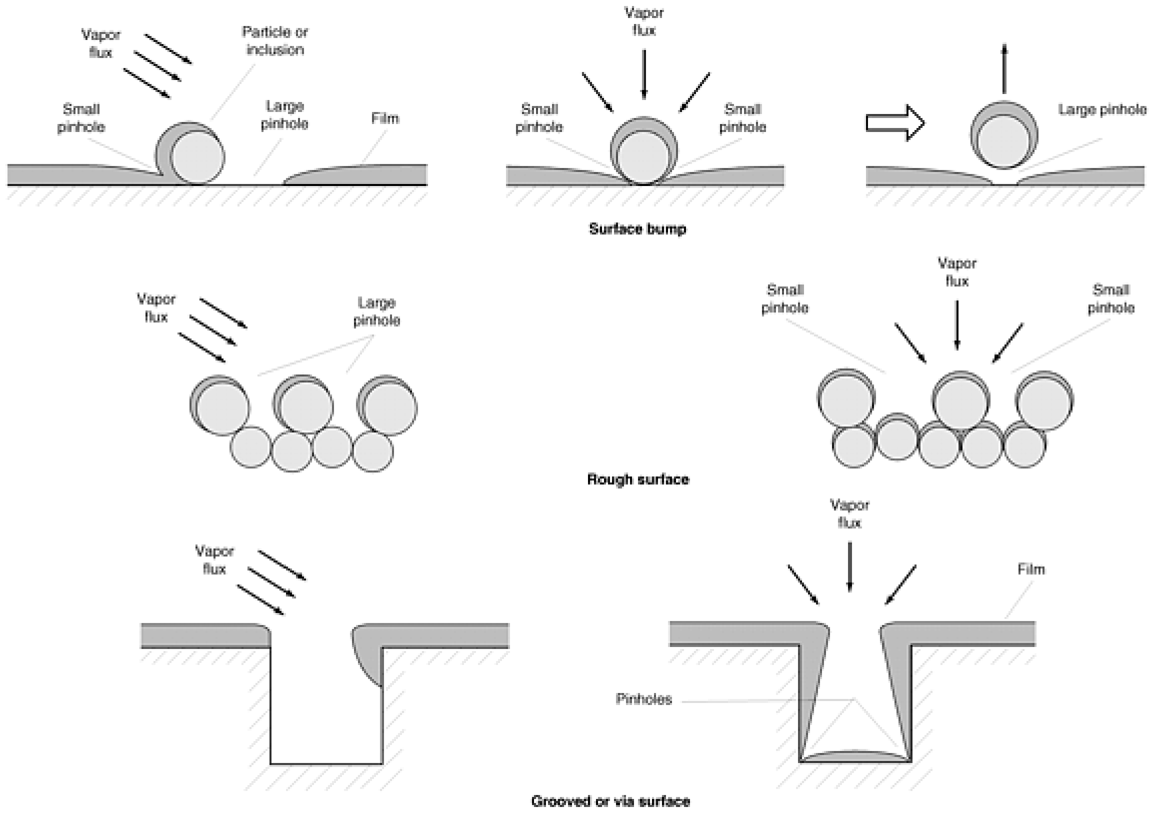


Fig. 6 Geometrical shadowing of the deposition flux by a particle on the surface relative to the angle of incidence and the surface morphology

Attempts to use gas scattering (that is, scatter plating, pressure plating, or gas plating) to randomize the flux distribution and improve the surface covering ability of evaporated films (Ref 17) have been singularly unsuccessful because of the poor density of the deposited material.

Additional information on condensation and growth is available in the article "Growth and Growth-Related Properties of Films Formed by Physical Vapor Deposition Processes" in this Volume.

Deposition of Materials

Deposition of Elements. Elements are typically deposited by vaporization of the elemental material directly. The purity of the deposited film depends on the purity of the starting material and contaminant gases in the ambient.

Deposition of Alloys. Alloys can be deposited directly by the vaporization of the alloy material if the vapor pressures of the constituent are comparable. However, if the vapor pressures differ, the composition of the film will change as the deposition proceeds and the composition of the melt changes.

Rod-Fed Source. One technique for depositing a constant composition alloy film is to use a rod-fed electron beam evaporation source and to keep the temperature and volume of the molten pool constant. After an equilibration time, the composition of the vapor flux is the same as the composition of the material being melted, even though the composition of the molten pool is not the same as that of the bulk material (Ref 18, 19). Using this technique, alloys whose constituents vary in vapor pressure by as much as 10^3 are being deposited on aircraft engine turbine blades.

Sequential Layers. Alloy films can be formed by depositing alternating layers of the different materials from different sources. The layers are then diffused to form the alloy film. The alloy composition then depends on the relative amounts of materials in the films.

Multiple Sources. Alloy films can be deposited using multiple separate vaporization sources with individual deposition rate controllers. In this case, the vapor flux distribution from each source must be taken into account. The multiple source technique can also be used to deposit layered composite films (Ref 2, 20). Sources with overlapping flux distributions can be used to form films having a range of compositions over the substrate surface.

Flash Evaporation. A constant-composition alloy film can be deposited using flash evaporation techniques, where a small amount of the alloy material is periodically completely vaporized (Ref 2, 21, 22, 23). Flash evaporation uses a very hot surface and requires dropping a pellet or periodically touching a wire tip to the surface, so that the molten pellet or tip is completely vaporized.

Deposition of Compounds. When compounds are vaporized, some of the lighter fragments, such as oxygen, may be lost by scattering in the gas phase and by not reacting with the deposited material when it reaches the substrate. In the vaporization of SiO_2, this results in an oxygen-deficient SiO_{2-x} film that is yellowish in color. The composition of the deposited material is determined by the degree of dissociation, the loss of materials in the mass transport process, and the reaction coefficient of the reactive species at the film surface. The lost oxygen can be replaced by reactive deposition in an oxygen environment (see the section "Reactive Evaporation" in this article), or postdeposition heat treatments in oxygen (Ref 24).

In some cases, the state of reaction can be increased by concurrent bombardment with a reactive species from a plasma (activated reactive ion plating) (Ref 25) or an ion source (reactive ion beam assisted deposition). For example, SiO, which is easily evaporated, can be bombarded with oxygen ions to give $SiO_{1.8}$, which is of interest as a transparent, insulating, permeation-barrier coating on polymers for the packaging industry.

Graded Interfaces. When layered structures are deposited, the interface between the layers can be graded from one composition to the other by beginning the second deposition before the first is completed. This forms a "pseudo-diffusion" interface between the two layers and prevents possible contamination/reaction of the first layer by the ambient environment before the second layer begins depositing. Grading the interface between deposited films often provides better adhesion than abruptly changing from one material to another.

Vaporization Sources

Common heating techniques for evaporation/sublimation include resistive heating, high-energy electron beams, low-energy electron beams, and inductive (radio frequency) heating. Figures 7, 8(a), and 8(b) show some vaporization source configurations. Resistive heating is the most common technique for vaporizing materialat temperatures below about 1800 °C (3270 °F), while focused electron beams are most commonly used above 1800 °C (3270 °F).

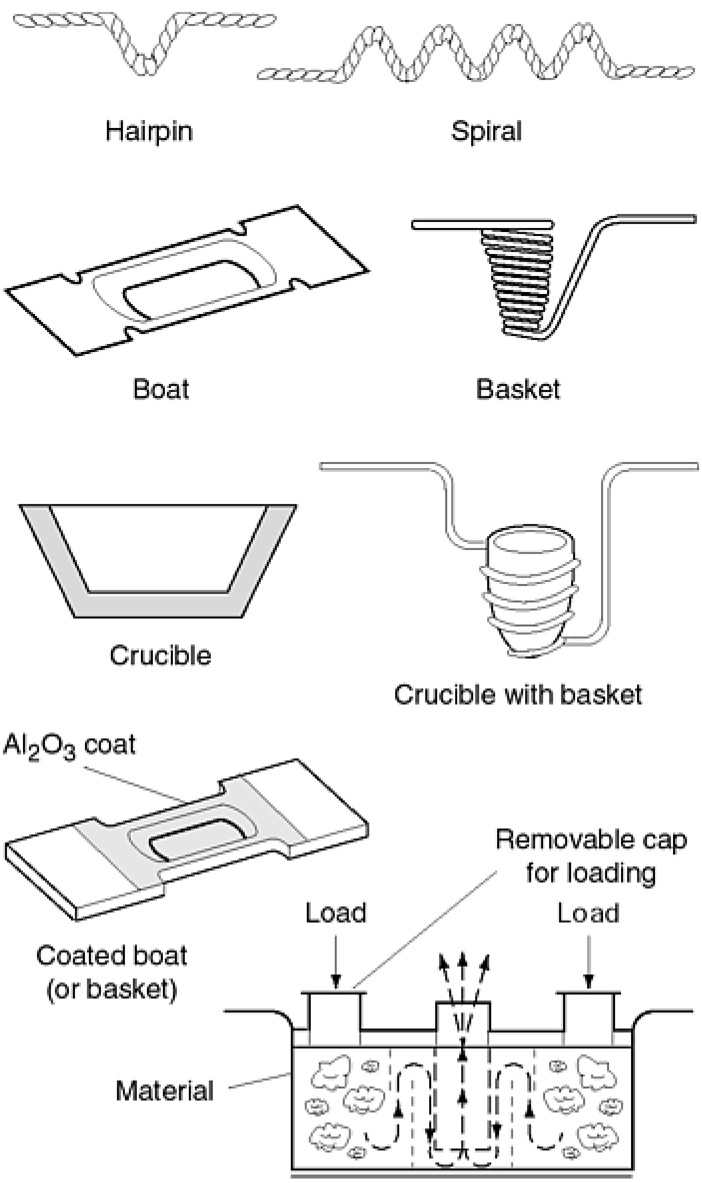


Fig. 7 Sources used for resistive heating of materials in evaporation processing

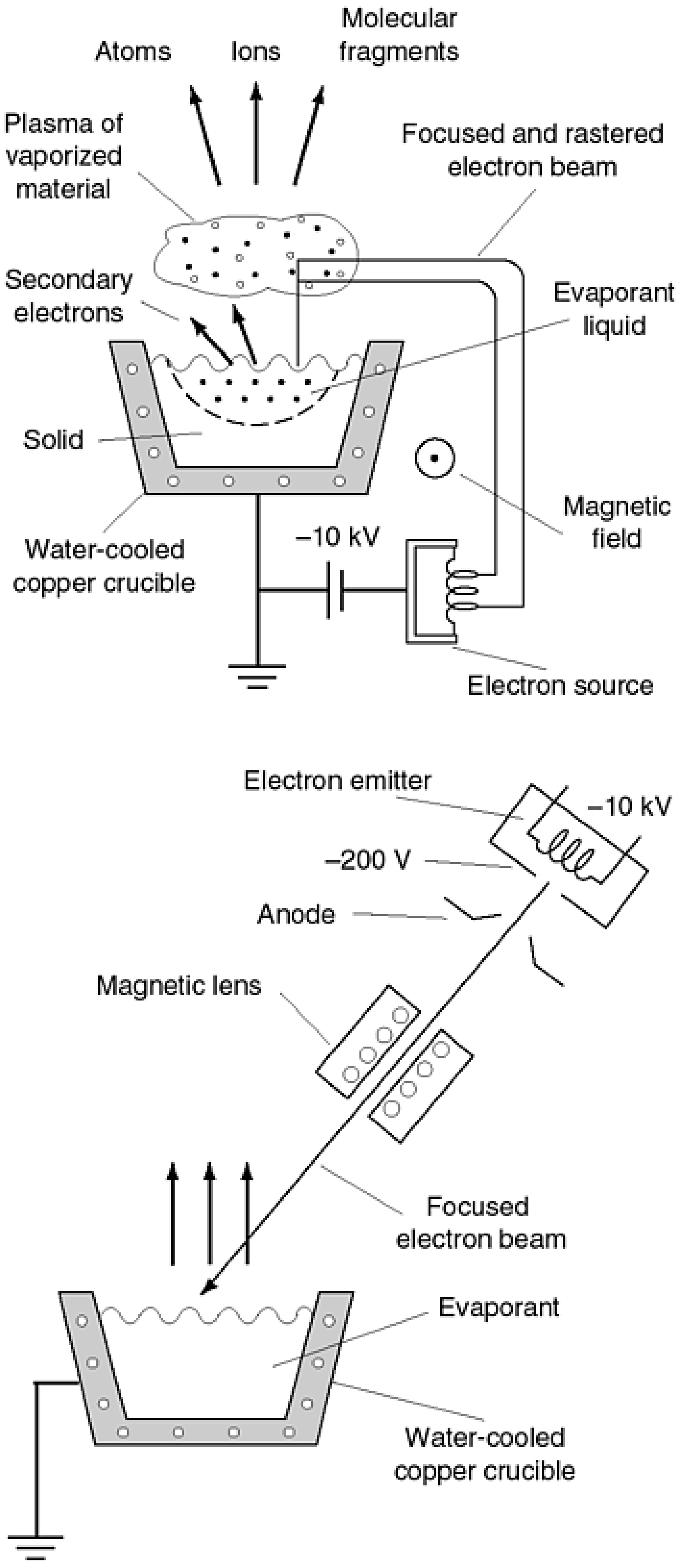
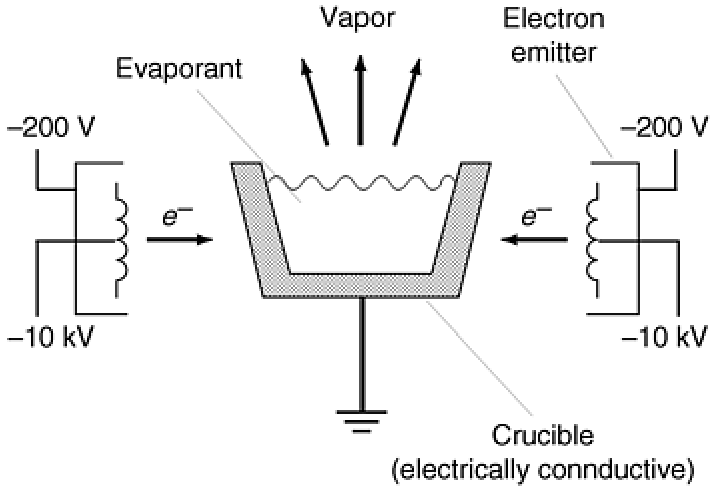


Fig. 8(a) Focused electron-beam sources used for evaporation processing. Bent-beam electron gun (top); long-focus gun (bottom)



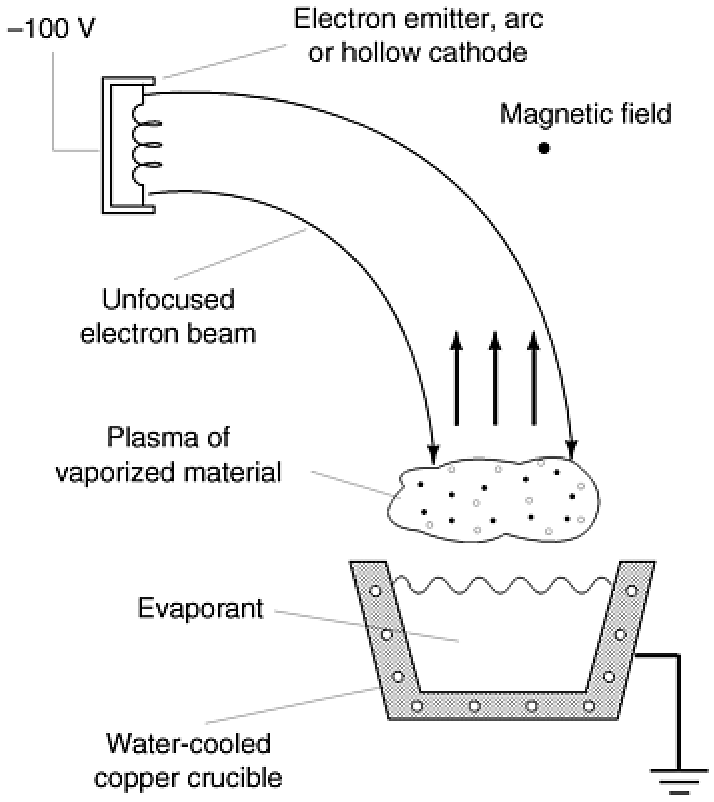


Fig. 8(b) Unfocused electron-beam sources used for evaporation processing. Work-accelerated gun (top); setup with magnetic confinement of electrons (bottom)

Resistive Heating. Resistively heated sources are the most widely used vaporization sources (Ref 26, 27). Typical conductive source materials are tungsten, tantalum, molybdenum, carbon, and BN/TiB_2 composite ceramics. Resistive heating of electrically conductive heater is typically by low voltage (<10 V), very high alternating current (several hundred amperes) transformer supplies. It is generally better to slowly increase the heater current than to suddenly turn on full heater power. Due to the low voltages used in resistive heating, contact resistance is an important factor in source design. As the temperature increases, thermal expansion causes the evaporator parts to move; this movement should be accounted for in the design of the heater fixturing. Because metals expand on heating, the contacting clamps between the fixture and the source may have to be water cooled to provide consistent clamping and contact resistance (Ref 27). Figure 7 shows some typical resistively heated source configurations. The resistively heated vaporization sources are typically operated near ground potential. If the sources are to be operated much above ground, filament isolation transformers must be used.

Electron-beam heating sources can be classified as being either focused or unfocused.

Focused, high-energy electron beams are necessary to provide local high temperatures when required for the evaporation of refractory materials, such as most ceramics, glasses, carbon, and refractory metals. This electron-beam heating is also useful for evaporating large quantities of materials. Graper has tabulated the electron-beam vaporization characteristics of a large number of materials (Ref 28). Figure 8(a) and 8(b) shows two sources that use focused electron-beam heating: the deflected electron gun and the long-focus gun (Fig. 8(a)).

With the deflected or bent-beam electron gun source, the high-energy electron beam is formed using a thermionic-emitting filament to generate the electrons, high voltages (typically 10 to 20 kV) to accelerate the electrons, and electric or magnetic fields to focus and deflect the beam (Ref 29, 30, 31). Electron-beam guns for evaporation typically require 10 to 50 kW of power. Using high power electron-beam sources, deposition rates as high as 50 μm/s (0.002 in./s) have been attained (Ref 32) from sources capable of vaporizing aluminum at rates of up to 10 to 15 kg/h (22 to 33 lb/h). Electron-beam evaporators can be made compatible with ultrahigh vacuum (UHV) processing (Ref 33). Electron-beam evaporators are typically built to deposit material in the vertical direction, but high-rate electron-beam source installations that deposit material in a horizontal direction are being used (Ref 34).

In many applications, the electron beam is magnetically deflected through greater than 180°, to avoid deposition of evaporated material on the filament insulators and to focus the beam onto the source material, which is contained in a water-cooled copper hearth "pocket". The electron beam can be rastered over the surface to produce heating over a large area. The electron bombardment produces secondary electrons that are magnetically deflected to ground. The high-energy electron bombardment also produces soft x-rays that can be detrimental to sensitive semiconductor devices (Ref 35, 36, 37). The electrons ionize a portion of the vaporized materials and these ionscan be used to monitor the evaporation rate. With the electron-beam evaporation of some materials (for example, beryllium), a significant number of ions are produced that can be accelerated to the substrate to modify the film microstructure (Ref 38).

Electron gun sources can have multiple pockets so that several materials can be evaporated. By moving the beam or the crucible, more than one material can be heated with the same electron source.

The long-focus gun uses electron optics to focus the electron beam on a surface that can be an appreciable distance from the electron emitter (Ref 32, 39). The optic axis is often a straight line from the emitter to the evaporant, and therefore the gun must be mounted off-axis from the source-substrate axis.

Unfocused, high-energy electron-beam heating can be accomplished with an electron source by applying a voltage between the electron emitter and the source material or source container, which is usually at ground potential (Fig. 8(b)). Such a source is referred to as a work-accelerated gun (Ref 40, 41). Magnetic confinement of the electrons along the emitter-source axis (Fig. 8(b)) can also be used to increase the electron path length and so increase the ionization probability (Ref 42, 43).

Unfocused, Low-Energy Electron-Beam Heating. High-current, low-energy electron beams can be produced by thermionic-emitting surfaces, plasma arcs (Ref 44), or hollow cathodes (Ref 45, 46, 47, 48, 49). They can be accelerated to several hundred volts and magnetically deflected onto the source, which is at ground potential. Low-energy electron beams are typically not very well focused, but they can have high current densities. The vaporization of a surface by the low-energy electron beam can provide appreciable ionization of the vaporized material because the vaporized atoms pass through a high-density, low-energy electron cloud as they leave the surface.

Electron-Beam Guns in a Plasma Environment. Electron-beam guns are not generally used in a plasma environment because of sputter erosion of the filament by positive ions. There are also problems with the reaction of the hot emitting filaments in reactive gases. In order to use an electron-beam evaporator in a plasma or reactive gas environment, the electron-emitter region can be differentially pumped by being isolated from the deposition environment. This is accomplished by having a septum between the differentially pumped electron-emitter chamber and the deposition chamber. This septum incorporates a small orifice for the electron beam to pass from one chamber to the other (Ref 50).

Inductive Heating. Inductive heating couples radio frequency (rf) energy directly into electrical conductors such as metals or carbon (Ref 51). The rf source can be used either to heat the source material directly or to heat the container ("susceptor") that holds the source material. This technique has been particularly useful in evaporating aluminum from boron nitride and BN/TiB_2 crucibles (Ref 52). When the source material is heated directly, the containing crucible can be cooled.

Evaporation sources must contain molten liquid without extensive reaction and prevent the molten liquid from falling from the heated surface. This is accomplished by having a wetted surface or by using a container (Ref 53). Commercial evaporation source manufacturers provide lists of recommended sources for various materials.

Wetted Sources. Wetting is desirable to obtain good thermal contact between the hot surface and the material being vaporized. Wetted sources are also useful for depositing downward, sideways, or from nonplanar surfaces. Metallic stranded wire, coils, and baskets are relatively cheap and can be used in many applications. Wires for evaporation are typically tungsten (Ref 2, 54, 55) but can be molybdenum or tantalum. Wire meshes and porous metals, through which the molten metals wet and wick by capillary action, can be used for large-area vaporization sources.

Wire and coil filaments have the often-frustrating property that the molten material runs to the low spots, where it can drop off. To help alleviate this problem, stranded wire is used to hold the molten material by capillary action. Bends or kinks can be put in the wire at selected points to collect the molten material, or coils of tantalum wire can be wrapped on the filament to hold the molten material at specific points.

Solid evaporants have poor thermal contact with the heater surface until they melt and wet the surface. To obtain wetting of the evaporant on the heater surface, it is often necessary to have a temperature in excess of that needed for a reasonable evaporation rate. When the material becomes molten and wets the surface, the vaporization rate is very high and can cause "spitting" as the molten evaporant spreads over the superheated surface. Refractory metals used for vaporization are covered with oxides, which volatilize at temperatures lower than the vaporization temperatures of many source materials. If film contamination by these oxides is to be avoided, the heater material should be cleaned before installation, shutters should be used, or the surface should be prewetted by the source material.

Premelting and wetting of the evaporant on the heater surface prior to the beginning of the deposition has several benefits:

- Good thermal contact can be established.
- There is volatilization of volatile impurities and contaminants from the evaporant and from the surface of the heater.
- Overheating of the heater surface is avoided, thereby minimizing spitting and radiant heating from the source.

Premelting can be done external to the deposition system if care is used in handling the source afterwards, to prevent surface contamination. Premelting can be done in the evaporator system by using shutters to prevent the deposition of undesirable material on the substrate before film deposition begins.

Crucible containers can hold large amounts of molten evaporant, but the vapor flux distribution changes as the level of the molten material changes. Electrically conductive crucibles can be heated resistively and are available in the form of boats, canoes, dimpled surfaces, crucibles, and so on (Ref 56). Typical refractory metals used for containers are tungsten, molybdenum, and tantalum, as well as refractory metal alloys such as TZM (titanium and zirconium added to molybdenum for improved high-temperature strength) and tungsten with 5 to 20% rhenium added for improved ductility. Metallic containers are often wetted by the molten material, and the material can spread to areas where it is not desired. This spreading can be prevented by having nonwetting areas on the surface. Such nonwetting areas can be formed by plasma spraying Al_2O_3 on the surface.

Commonly used crucible construction includes water-cooled copper, ceramics (both conductive and insulating), and glasses:

- *Water-cooled copper* is used as a crucible material when the evaporant materials are heated directly, as with electron-beam heating. The design of the coolant flow is important in high-rate evaporation from a copper crucible, because a great deal of heat must be dissipated (Ref 57). The water-cooled copper solidifies the molten material near the interface, forming a "skull" of the evaporant material so that the molten material is actually contained in a like material. This prevents reaction of the evaporant with the crucible material. On cooling, the evaporant "slug" shrinks and can be easily removed from the pocket of the electron-beam evaporator. In some cases, a liner can be used with a water-cooled crucible. Typical liner materials include pyrolytic graphite, pyrolytic boron nitride, BN/TiB_2, BeO, Al_2O_3, and

other such materials. In general, the liner materials have poor thermal conductivity. This property, along with the poor thermal contact that the liner makes with the copper, allows the liner to heat significantly. Liners can be fabricated in special shapes to obtain specific characteristics (Ref 58).

- *Electrically conductive ceramics* can be used as containers. Carbon and glassy carbon are commonly used container materials, and when a carbon-reactive material is evaporated from such a container, a carbide skull forms that limits the reaction with the container. For example, titanium in a carbon crucible forms a titanium carbide skull. An electrically conductive composite ceramic that is used for evaporating aluminum is BN-50TiB_2 composite ceramic (known by the tradename UCAR) (Ref 59). This composite ceramic is stable in contact with molten aluminum, whereas most metals react rapidly with the molten aluminum at vaporization temperature.
- *Glasses and electrically insulating ceramics* can be used as crucibles and are often desirable because of their chemical inertness with many molten materials. Typical crucible ceramics are ThO_2, BeO, stabilized ZrO_2 (additions of HfO_2 and CaO to ZrO_2), Al_2O_3, MgO, BN, and fused silica. Kohl has written an extensive review of the oxide and nitride materials that may be of interest as crucible materials (Ref 60). The ceramics can be heated by conduction or radiation from a hot surface though these are very inefficient methods of heating. For more efficient heating, the material contained in the electrically insulating crucible can be heated directly by electron bombardment of the surface or by rf inductive heating from a surrounding coil. Isotopic boron nitride is a good crucible material for containing molten aluminum for rf heating because most other ceramics are attacked by molten aluminum. Metal sources, such as boats, can be coated with a ceramic (for example, plasma-sprayed Al_2O_3) in order to form a ceramic surface in contact with the molten material.

Feeding sources are sources where additional evaporant material is added to the molten pool without opening the processing chamber. Feeding sources can use pellets (Ref 61), powder, wires, tapes, or rods of the evaporant material. Pellet and powder feeding is often done with vibratory feeders, while wires and tapes are fed by friction and gear drives. Multiple wire-fed electron-beam evaporators are often aligned to give a line source for deposition in a web coater (Ref 62, 63). Rod feeds are often used with electron-beam evaporators where the end of the rod, whose side is cooled by radiation to a cold surface, acts as the crucible to hold the molten material (Ref 18). Feeding sources are used to deposit large amounts of material.

Baffle Sources. Some elements vaporize as clusters of atoms, and some compounds vaporize as clusters of molecules. Baffle sources are designed so that the vaporized material must undergo several evaporations from heated surfaces before it leaves the source, to ensure that the clusters are decomposed. Baffle sources can also be used to allow deposition downward from a molten material. Baffle sources are desirable when evaporating silicon monoxide or magnesium fluoride for optical coatings, to ensure the vaporization of monomolecular SiO or MgF_2. Drumheller made one of the first baffle sources, called a "chimney source," for the vaporization of SiO (Ref 64).

Focused vaporization sources can be used to confine the vapor flux to a beam. Focusing can be done using wetted curved surfaces or by using defining apertures. A beam-type evaporation source that uses apertures has been developed to allow the efficient deposition of gold on a small area (Ref 65). This source forms a $2\frac{1}{2}°$ beam of gold and gives a deposition rate of 4 nm/s (40 Å/s) at 50 mm (2 in.).

Confined vapor sources confine the vapor in a heated cavity and pass the substrate through the vapor. The vapor that is not deposited stays in the cavity. Such a source uses material very efficiently and can produce very high rates of deposition. For example, a wire can be coated by having a heated cavity source such that the wire is passed through a hole in the bottom and out through a hole in the top. By having a raised stem in the bottom of the crucible, the molten material can be confined in a doughnut-shaped melt away from the moving wire. The wire can be heated by passing a current through the wire as it moves through the crucible.

Porous Evaporation Sources. Porous materials and meshes can be used to evaporate materials that wet and wick through the material. Examples of such materials are porous tungsten, tungsten meshes, and porous ceramics. These types of sources are sometimes called *dispenser sources* and are similar to the electron-emitted cathodes in electronic devices (Ref 60).

Radiation shields can be used to surround the hot vaporization source to reduce radiant heat loss (Ref 56). Generally radiation shields consist of several layers of refractory metal sheet separated from each other and from the heated surface. These radiation shields:

- Reduce the power requirements of the source
- Reduce radiant heating from the source
- Allow the source to reach a higher temperature
- Have a more uniform temperature over a larger volume

Source Degradation. Vaporization sources can degrade with time due to reaction of the evaporant material with the heated surface. When there is reaction between the molten source material and the heater material, the vaporization should be done rapidly. For example, palladium, platinum, aluminum, iron, and titanium should be evaporated rapidly from tungsten heaters. When tungsten is used as the heater material, crystallization at high temperatures makes the tungsten brittle and causes microcracks, which create local hot spots that result in burnout. On burnout, the tungsten is vaporized and can contaminate the film. In general, it is better to replace tungsten wire heaters after each deposition if such contamination poses a problem. When large masses of material that have wet the surface are allowed to cool in brittle containers (crucibles or boats), the stresses can crack the container material.

Sublimation Sources. Vaporization from solid sources has the advantage that the vaporizing material does not melt and flow. Vaporization from a solid can be sublimation from a chunk or pellet, or sublimation from a solid composed of a subliming phase and a nonvaporizing phase (for example, Ag-50Li and Ta-25Ti alloy wire, known by the tradename KEMET). Heating can be by resistive heating, direct contact with a hot surface, radiant heating from a hot surface, or bombardment by electrons.

A problem with sublimation of a solid material from a heated surface is the poor thermal contact with the surface. This is particularly true if the evaporant can "jump around" due to system vibration during heating. Changing the source setup can often alleviate the problem (for example, changing from a boat to a basket source, eliminating mechanical vibration, using mesh "caps" on open-top sources, etc.). Direct electron-beam heating of the material is generally more desirable than contact heating for heating a subliming material.

Better thermal contact between the subliming material and the heater can be obtained when forming the material in contact with the heater by pressing powders around the heater or by electroplating the material onto the heater surface. Powder pressing generally produces a porous material that has appreciable outgassing. Chromium is often electrodeposited on a tungsten heater. Electroplated chromium has an appreciable amount of trapped hydrogen, and such a source should be heated slowly to allow outgassing of the material before deposition commences.

Exploding Wires. Flash evaporation can be accomplished by "exploding wire" techniques, where very high currents are pulsed through a small wire by the discharge of a capacitor (Ref 66). The majority of the vaporized material is in the form of molten globules. This technique has the interesting feature that the wire can be placed through a small hole and the vaporized material can be used to coat the inside of the hole.

Radiant Heating from the Source. The radiant energy, E, from a hot surface is given by:

$$E = \varepsilon T^4 A \quad \textbf{(Eq 3)}$$

where ε is the emittance of the surface, T is the absolute temperature, and A is the area of emitting surface. Radiant energy heats all of the surfaces in the deposition chamber, leading to a rise in the substrate temperature, desorption of gases from surfaces, and surface creep of contaminants. Radiant heating of the substrate and interior surfaces can be minimized by:

- Using small heated areas (A)
- Using prewetted evaporant surfaces
- Using radiation shields
- Using shutters over the source until the vaporization rate is established
- Rapid vaporization of the source material onto the substrate

Some materials, such as gold, are good heat reflectors; as soon as a gold film is formed, a high percentage of the incident radiant heat is reflected from the coated surface. Some materials, such as silicon dioxide, do not adsorb infrared radiation very well and are not easily heated by radiation.

Spits and Comets. In the evaporation of materials from heated surfaces, "spits" and "comets" are often encountered. Spits are solidified globules of the source material found on the deposited film. When these poorly bonded globules are disturbed, they fall out, leaving large pinholes in the film. Comets are seen in the system during vaporization as the hot molten globules are ejected from the source.

Molten globules can originate from the molten material by any one of several processes. During heating, particularly rapid heating, gases and vapors in the molten source material agglomerate into bubbles and explode through the surface, giving spits. For example, silver can have a high content of dissolved oxygen and give spitting problems. The source of spits can be continual if new material is continually being added to the melt. Spits can be reduced by using pure vacuum-melted source material, handled and stored in an appropriate way, and by degassing the evaporant charge by premelting with slow heating to melting.

If the molten evaporant is held in a heated crucible, vapor bubbles can form on the crucible surfaces, where they grow and break loose. As the bubbles rise through the molten material, the hydrostatic pressure decreases and the bubbles grow in size. When the bubbles reach the surface they "explode," giving rise to globules of ejected molten material. Materials that have high vapor pressures at their melting points are more likely to give spits than materials that have low vapor pressures at their melting points. Spitting is common in boiling water; in high school chemistry, students are taught to add boiling beads to the water to reduce the violence and splashing. The same approach can be used to prevent spitting from molten material. For example, chunks of tantalum are placed in molten gold to prevent gold spits. The tantalum does not react with the gold and does not vaporize at the gold evaporation temperatures.

Spits from crucibles can be minimized by:

- Using source materials that are free of gases and high-vapor-pressure impurities
- Polishing the crucible surfaces so that bubbles do not stick well and break loose when they are small
- Using "boiling beads" in the molten material to prevent large bubbles from forming
- Using baffle-type sources so that the source material must be vaporized several times before the vapor leaves the source
- Using specially designed crucibles (Ref 58)
- Using electron-beam evaporation where the surface of the evaporant is heated
- Reducing source power if spitting occurs

Spits can also occur during melting and flowing of a material on a hot surface. A solid material placed on a surface has poor thermal contact with the surface, so the tendency is to heat the surface to a very high temperature. When the evaporant melts and spreads over the surface, the very hot surface creates vapor that "explodes" through the spreading molten material. This source of spits can be eliminated by premelting the charge on the surface, to give good thermal contact, and by using shutters in the system, to prevent the substrate from "seeing" the source until the molten charge has wetted the surface and is vaporizing uniformly.

Additional Vaporization Methods

Vaporization can also be produced by vacuum arc, laser, electric field, and polymer evaporation methods.

Vacuum Arc Vaporization. Arc vaporization was first reported by Robert Hare in 1839 and has been used to deposit carbon (Ref 67) and metal (Ref 68) films. Arc vaporization in vacuum occurs when a high-current, low-voltage arc passes between slightly separated electrodes in a vacuum, vaporizing the electrode surfaces and forming a plasma of the vaporized material (Ref 69, 70, 71, 72). In order to initiate the arc, a high voltage "trigger" arc is used. A high percentage of the vaporized material is ionized in the arc, and the ions are often multiply charged. A negative space charge is generated in the plasma, and the ions are accelerated away from the plasma to energies that are much higher than thermal energies. This means that the deposition is accompanied by concurrent bombardment from the high-energy film ions. This concurrent bombardment can have beneficial effects on the film density, as is found in ion plating.

If the arc anode is cooled or has a large area, vaporization primarily occurs from the solid cathode surface by arc erosion. At the present time,the principal arc vapor source in thin-film technology is the solid cathode. Problems with this deposition technique include stabilization and movement of the arc on the solid surface and the formation of globules of the ejected material. Arc confinement and controlled arc movement using magnetic fields have given rise to the "steered arc" source. The globules can be filtered from the arc using various means (for example, the "plasma duct") (Ref 73), all of which reduce the deposition rate. Carbon ions (500 eV) from a vacuum arc source have been used to deposit hydrogen-free, diamond-like carbon films (Ref 74).

If the anode is allowed to melt, material evaporates from the molten (consumable) anode surface. This vaporization technique is essentially the same as the vacuum-arc-remelting (VAR) process (Ref 75, 76). Some studies have been done using the vapor from the molten anode of a vacuum arc. This has the advantage that globules are formed to a lesser degree than in cathodic erosion (Ref 77, 78). A commercial source of metal ions from a vacuum arc is the metal vapor vacuum arc (MVVA) source (Ref 79).

Additional information is available in the article "Arc Deposition" in this Volume.

Globules. The number of globules produced from the cathode surface depends on the melting point of the cathode material and the arc movement. The distribution of globule emission is nonisotropic, with the maximum number being found at angles greater than 60° from the normal to the surface. The neutral atoms found in the arc vapor are thought to be produced by thermal evaporation from the ejected globules. This effect causes the composition of the deposited film to vary with thickness and position when an alloy material is deposited (Ref 80).

Laser Vaporization. Flash evaporation can also be done with pulsed laser heating of surfaces (Ref 81, 82). This technique is sometimes called laser ablation deposition (LAD) (Ref 83). Typically an excimer laser (yttrium-aluminum-garnet, or YAG, or argon-fluorine) is used to deposit energy in pulses. The YAG lasers typically deliver pulses (5 ns pulse length, 5 Hz frequency) with an energy of about 1 J/pulse (9×10^{-4} Btu/pulse), and the argon-fluorine lasers typically deliver pulses (20 ns, 50 Hz) with about 300 nJ/pulse (2.7×10^{-10} Btu/pulse). The vaporized material forms a plume above the surface, where some of the laser energy is adsorbed and ionization and excitation occur. In laser vaporization the ejected material is highly directed; this creates a problem with forming a uniform thickness over large areas. During vaporization molten globules are ejected, and these can be eliminated by using a velocity filter. Laser vaporization, combined with the passage of a high electrical current along the laser-ionization path to give heating and ionization, has been used to deposit hydrogen-free, diamond-like carbon films at an ablation energy density greater than 5×10^{14} W/m^2 (1.6×10^{14} Btu/ft^2 · h) (Ref 83). Laser vaporization with concurrent ion bombardment has been used to deposit a number of materials (Ref 84, 85), including high-quality, high-temperature superconductor oxide films (Ref 86), at low substrate temperatures. Laser vaporization can be used to vaporize material from a film on a transparent material onto a substrate facing the film, by shining the laser through the "backside" of the transparent material, vaporizing a controlled film area, and thus depositing a pattern directly onto the substrate (Ref 87).

Field Evaporation. Surface atoms of metals can be vaporized by a high electric field. This technique is known as field evaporation and can be directly observed in the field ion microscope (Ref 88). This vaporization technique is used to clean emitter tips in field ion microscopy and to form metal ions from liquid-metal-coated tips. Field evaporation has been used to directly deposit nanometer-size gold structures (Ref 89). The very sharp tips necessary to obtain the high field can be formed in a variety of ways (Ref 90).

Polymer Evaporation. Many monomers and polymers can be evaporated to produce thin organic films on a substrate surface. Some organics can be cross-linked in the vapor phase inside a heated furnace before condensing on the substrate surface (paralyene process) (Ref 91). Condensed polymers can be cross-linked on the surface by exposing them to an electron beam (Ref 92) or ultraviolet radiation (Ref 93).

Materials for Vaporization

Material placed in the vaporization source is called a *charge* and can be in the form of powder, chunks, wire, slugs, and so on. The desired purity of the source material depends on the application and the effect of purity on film properties and process reproducibility. It is possible to obtain some material with extremely high purity (>99.999%), although the cost increases rapidly with the purity level. Often impurities such as oxygen, nitrogen, carbon, and hydrogen are not specified by the supplier. They can be present in significant quantities as oxidized surfaces of reactive metals, hydrogen incorporated into electrorefined chromium, carbon monoxide in nickel purified by the carbonyl process, and helium in natural quartz. Generally, it is better to specify vacuum-melted materials from the supplier when possible. Very reactive

metals should be nitrogen-packed in glass ampules to prevent oxidation, and the ampules should be opened and handled in an inert gas dry box where the reactive gas content is kept low by the use of getter materials such as liquid NaK [K:Na (20-50%)].

Careful specification of purity, allowable impurities, fabrication method, postfabrication treatments, and packaging of the source materials purchased is important to obtaining a reproducible process. Using inexpensive material or material of unknown origin often creates problems. Source material should be carefully cleaned and handled, because on heating, the impurities and surface contaminants are the first materials to be vaporized. The source and source material can be outgassed and premelted prior to film deposition.

Materials Utilization. Often material utilization in an evaporation process is poor unless proper fixturing and tooling is used to intercept the maximum amount of the flux. This can be accomplished by having the substrates as close as possible to the vaporization source, though this can result in excessive heating of the substrate during deposition. Deposition on large numbers of parts or over large areas can be done using large chambers with many (or large) vaporization sources.

Excess deposited material builds up on walls and fixtures and can flake off, producing particulate contamination in the processing chamber. The deposit buildup on surfaces also generates high surface areas that can absorb contaminants and are slow to desorb the contaminants. This results in changes in the pumping characteristics of the deposition system with use. It is desirable to have an easy way to collect and remove the excess evaporated material, and it can also be important to collect the excess material for reclamation. Excess evaporant can be collected by surrounding the source with a removable collector that defines the flux of evaporant to the substrate and collects excess evaporant. The chamber can have a removable liner to collect excess material, and the fixtures can be surrounded with panels or foil that can be easily removed.

References cited in this section

2. R. Glang, Vacuum Evaporation, Chapter 1, *Handbook of Thin Film Technology,* L.I. Maissel and R. Glang, Ed., McGraw-Hill, 1970, p 1-26
3. R.E. Honig and H.G. Cook, "RCA Review 23," 1962, p 567
4. K.-G. Wagner, A Brief Review of Knudsen Cells for Application in Experimental Research, *Vacuum,* Vol 34 (No. 8/9), 1984, p 743
5. A. Beck, H. Jurgen, B. Bullemer, and I. Eisele, A New Effusion Cell Arrangement for Fast and Accurate Control of Material Evaporation under Vacuum Conditions, *J. Vac. Sci. Technol. A,* Vol 2 (No. 1), 1984, p 5
6. H.K. Pulker, Chapter 6, *Coatings on Glass,* Elsevier, 1984
7. E. Rutner, Some Limitations on the Use of the Langmuir and Knudsen Techniques for Determining Kinetics of Evaporation, *Condensation and Evaporation of Solids,* E. Ruthner, P. Goldfinger, and J.P. Hirth, Ed., 1964, p 149
8. J.A. Dobrowolski, M. Ranger, and R.L. Wilkerson, Measure the Angular Evaporation Characteristics of Sources, *J. Vac. Sci. Technol. A,* Vol 1, 1983, p 1403
9. V. Ruth and J.P. Hirth, The Angular Distribution of Vapor from a Knudsen Cell, *Condensation and Evaporation of Solids,* E. Ruthner, P. Goldfinger, and J.P. Hirth, Ed., 1964, p 99
10. A.D. Romig, A Time Dependent Regular Solution Model for the Thermal Evaporation of an Al-Mg Alloy, *J. Appl. Phys.,* Vol 62, 1987, p 503
11. S. Otani, T. Tanaka, and Y. Ishizawa, Evaporation from Molten TiC_x, *J. Mater. Sci.,* Vol 21, 1986, p 176
12. H. Fuchs and H. Gleiter, The Significance of the Impact Velocity of Vacuum-Deposited Atoms for the Structure of Thin Films, *Thin Films: The Relationship of Structure to Properties Symposium,* C.R. Aita and K.S. Sreeharsha, Ed., MRS Symp. Proc., Vol 47, MRS Publications, 1985, p 41
13. A.N. Pergellis, Evaporation and Sputtering Substrate Heating Dependence on Deposition Rate, *J. Vac. Sci. Technol. A,* Vol 7 (No. 1), 1989, p 27
14. J. Strong, *Procedures in Experimental Physics,* Prentice-Hall, 1938, p 183
15. K.H. Behrndt, Films of Uniform Thickness from a Point Source, *Trans. 9th AVS Symposium,* Macmillan,

1962, p 111

16. I.J. Hodgkinson, Vacuum-Deposited Thin Films with Specific Thickness Profiles, *Vacuum,* Vol 28, 1978, p 179
17. K.D. Kennedy, G.R. Scheuermann, and H.R. Smith, Jr., Gas Scattering and Ion Plating Deposition Methods, *R&D Mag.,* Vol 22 (No. 11), 1971, p 40
18. R. Nimmagadda, A.C. Raghuram, and R.F. Bunshah, Preparation of Alloy Deposits by Electron Beam Evaporation from a Single Rod-Fed Source, *J. Vac. Sci. Technol.,* Vol 9, 1972, p 1406
19. D.H. Boone, S. Shen, and R.M. McKoon, Electron Beam Evaporation of Low Vapor Pressure Elements in the M-Cr-Al Coatings Compositions, *Thin Solid Films,* Vol 63, 1979, p 299
20. H.Q. Yang, H.K. Wong, J.Q. Zheng, and J.B. Ketterson, Dual Electron Beam Evaporator for the Preparation of Composition-Modulated Structures, *J. Vac. Sci. Technol. A,* Vol 2 (No. 1), 1984, p 1
21. T. Strahl, Flash Evaporation--An Alternative to Magnetron Sputtering in the Production of High-Quality Aluminum-Alloy Films, *Solid State Technol.,* Vol 21 (No. 12), Dec 1978, p 78
22. F. Jansen, The Flash Evaporation of Low Melting Point Materials, *J. Vac. Sci. Technol.,* Vol 21 (No. 1), 1982, p 106
23. G. Adachi, H. Sakaguchi, K. Niki, N. Naga, and J. Shimokawa, Preparation of $LaNi_5$ Films and Their Electrical Properties under a Hydrogen Atmosphere, *J. Less-Common Met.,* Vol 108, 1985, p 107
24. A. Gupta, P. Gupta, and V.K. Srivasteva, Annealing Effects in Indium Oxide Films Prepared by Reactive Evaporation, *Thin Solid Films,* Vol 123, 1985, p 325
25. E. Moll, R. Buhl, H.K. Pulker, and E. Bergmann, Activated Reactive Ion Plating (ARIP), *Surf. Coat. Technol.,* Vol 39/40 (No. 1-3), 1990, p 475
26. L. Watts, 20 Years of Resistant Source Development, *Society of Vacuum Coaters 34th Ann. Tech. Conf. Proc.,* 1991, p 118
27. B. Ruisinger and B. Mossner, Evaporation Boats--Properties, Requirements, Handling, and Future Development, *Society of Vacuum Coaters 34th Ann. Tech. Conf. Proc.,* 1991, p 335
28. E.B. Graper, Evaporation Characteristics of Materials from an Electron Beam Gun II, *J. Vac. Sci. Technol. A,* Vol 5 (No. 4), 1987, p 2718
29. R.A. Denton and A.D. Greene, in *Proc. 5th Electron Beam Symp.,* Alloyd Electronics Corp., 1963, p 180
30. J. Knall, J.-E. Sundgren, L.C. Market, A. Rockett, and J.E. Greene, Influence of the Si Evaporation Sources on the Incorporation of In During Si Molecular-Beam Epitaxy Growth: Comparative Study of Magnetically and Electrostatically Focused Electron-Gun Evaporators, *J. Vac. Sci. Technol. B,* Vol 7 (No. 2), 1989, p 204
31. S. Schiller, U. Heisig, and S. Panzer, *Electron Beam Technology,* Wiley, 1982
32. S. Schiller and J. Jusch, Deposition by Electron Beam Evaporation with Rates of up to 50 Microns s^{-1}, *Thin Solid Films,* Vol 54, 1978, p 9
33. M. Heilblum, J. Bloch, and J.J. O'Sullivan, Electron-Gun Evaporators of Refractory Metals Compatible with Molecular Beam Epitaxy, *J. Vac. Sci. Technol. A,* Vol 3, 1985, p 1885
34. H.R. Smith, Jr., High Rate Horizontally Emitting Electron Beam Vapor Source, *Society of Vacuum Coaters 21st Annual Technical Symposium Proceedings,* 1978, p 49
35. T.H. Ning, Electron Trapping in SiO_2 due to Electron-Beam Deposition of Aluminum, *J. Appl. Phys.,* Vol 49, 1978, p 4077
36. D.R. Collins and C.T. Sah, Effect of X-Ray Irradiation on the Characteristics of the Metal-Oxide Silicon Structure, *Appl. Phys. Lett.,* Vol 8, 1966, p 124
37. J.R. Davis, *Instabilities in MOS Devices,* Gordon and Breach, 1981, p 74
38. R.F. Bunshah and R.S. Juntz, The Influence of Ion Bombardment on the Microstructure of Thick Deposits Produced by High Rate Physical Vapor Deposition Processes, *J. Vac. Sci. Technol.,* Vol 9, 1972, p 1404
39. J.R. Pierce, *Theory and Design of Electron Beams,* D. Van Nostrand, 1954
40. K.L. Chopra and M.R. Randlett, Modular Electron Beam Sources for Thin Film Deposition, *Rev. Sci. Instr.,* Vol 37, 1966, p 1421

41. J.R. Waldrop and R.W. Grant, Simple Evaporator for Refractory Metal Thin Film Deposition in Ultrahigh Vacuum, *J. Vac. Sci. Technol. A,* Vol 1, 1983, p 1553
42. H. Kaufmann, "Method of Depositing Hard Wear-Resistant Coatings on Substrates," U.S. Patent 4,346,123, 24 Aug 1982
43. H.K. Pulker, "Methods of Producing Gold-Color Coatings," U.S. Patent 4,254,159, 3 Mar 1981
44. J.R. Morley and H.R. Smith, High Rate Ion Production for Vacuum Deposition, *J. Vac. Sci. Technol.,* Vol 9, 1972, p 1377
45. Y.S. Kuo, R.F. Bunshah, and D. Okrent, Hot Hollow Cathode and Its Application in Vacuum Coating: A Concise Review, *J. Vac. Sci. Technol. A,* Vol 4 (No. 3), 1983, p 397
46. C. Schalansky, Z.A. Munir, and D.L. Walmsley, An Investigation on the Bonding of Hot-Hollow Cathode Deposited Silver Layers on Type 304 Stainless Steel, *J. Mater. Sci.,* Vol 22, 1987, p 745
47. H.R. Kaufman and R.S. Robinson, Broad-Beam Electron Source, *J. Vac. Sci. Technol. A,* Vol 3 (No. 4), 1985, p 1774
48. C.M. Horwitz, Hollow Cathode Etching and Deposition, Chapter 12, *Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Noyes Publications, 1989
49. J.J. Rocca, J.D. Meyer, M.R. Farrell, and G.J. Collins, Glow-Discharge-Created Electron Beams: Cathode Materials, Electron Gun Designs and Technological Applications, *J. Appl. Phys.,* Vol 56 (No. 3), 1984, p 790
50. D.L. Chambers and D.C. Carmichael, Development of Processing Parameters and Electron-Beam Techniques for Ion Plating, *Society of Vacuum Coaters 14th Ann. Tech. Conf. Proc.,* 1971, p 13
51. F.W. Curtis, *High Frequency Induction Heating,* Lindsay Publications reprint, 1990
52. I. Ames, L.H. Kaplan, and P.A. Roland, Crucible Type Evaporation Source for Aluminum, *Rev. Sci. Instr.,* Vol 37, 1966, p 1737
53. K.H. Behrndt, in *Techniques of Materials Research,* Vol I, Pt. 3, R.F. Bunshah, Ed., Interscience, 1968, p 1225
54. P. Dixit and R.W. Vook, A Highly Efficient Source for Vapor Deposition of Platinum, *Thin Solid Films,* Vol 110, 1983, p L133
55. J.L. Walter and C.L. Briant, Tungsten Wire for Incandescent Lamps, *J. Mater. Res.,* Vol 5 (No. 9), 1990, p 2004
56. J.A. Dobrowolski, A. Waldorf, and R.A. Wilkinson, A Practical High Capacity, High Evaporation Rate Resistance-Heated Source, *J. Vac. Sci. Technol.,* Vol 21, 1982, p 881
57. G. Crumley, Improved Cooling for an Electron Beam Crucible, *Society of Vacuum Coaters 33rd Ann. Tech. Conf. Proc.,* 1990, p 29
58. M.L. Rappaport and B. Berkovitz, A Graphite Crucible for Splitting-Free High Rate e-gun Evaporation of Ge, *J. Vac. Sci. Technol.,* Vol 21, 1982, p 102
59. H.J. Wilder, Application of Intermetallic Evaporation Sources, *Society of Vacuum Coaters 25th Ann. Tech. Symp. Proc.,* 1982, p 103
60. W.H. Kohl, Ceramics, Chapter 2, *Handbook of Materials and Techniques for Vacuum Devices,* Reinhold, 1967
61. N.B. Brennan, T. Pilkington, N.M. Samin, and A. Matthews, A Pellet Feeder for Pulsed Evaporation, *Vacuum,* Vol 34, 1984, p 805
62. K.A. Taylor and E.G. Ferrari, Design of Metallization Equipment for Web Coating, *Thin Solid Films,* Vol 109, 1983, p 295
63. F. Casey, Recent Advances in Source Design in Resistive Evaporation Web Coaters, in *Society of Vacuum Coaters 34th Ann. Tech. Conf. Proc.,* 1991, p 124
64. C.E. Drumheller, Silicon Monoxide Evaporation Techniques, *Trans. 7th AVS Symp.,* Pergamon Press, 1960, p 306
65. R.J. Ney, Nozzle Beam Evaporant Source, *J. Vac. Sci. Technol. A,* Vol 1 (No. 1), 1983, p 55

66. D.M. Mattox, A.W. Mullendore, and F.N. Rebarchik, Film Deposition by Exploding Wires, *J. Vac. Sci. Technol.,* Vol 4, 1967, p 123
67. B.J. Massey, Production of Self-Supporting Carbon Films, *Trans. 8th AVS Nat. Symp.,* 1962, p 922
68. M.S.P. Lucas, C.R. Vail, W.C. Stewart, and H.A. Owen, A New Deposition Technique for Refractory Metal Films, *Trans. 8th AVS Nat. Symp.,* 1962, p 988
69. D. Sanders, Vacuum Arc-Based Processing, Chapter 18, *Handbook of Plasma Processing Technology,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes Publications, 1990
70. D.M. Sanders, A Review of Ion-Based Coating Processes Derived from Cathodic Arc, *J. Vac. Sci. Technol. A,* Vol 7 (No. 3), 1989, p 2339
71. R.L. Boxman and S. Goldsmith, Cathode-Spot Arc Coating: Physics, Deposition and Heating Rates and Some Examples, *Surf. Coat. Technol.,* Vol 33, 1987, p 153
72. R.L. Boxman and S. Goldsmith, Characterization of a 1 kA Vacuum Arc Plasma Gun for Use as a Metal Vapor Deposition Source, *Surf. Coat. Technol.,* Vol 44, 1990, p 1024
73. P.J. Martin, R.P. Netterfield, and T.J. Kinder, Ion-Beam-Deposited Films Produced by Filtered Arc Evaporation, *Thin Solid Films,* Vol 193/194, 1990, p 77
74. J.-P. Hirvonen, R. Lappalainen, J. Koskinen, A. Anttila, T.R. Jervis, and M. Trkula, Tribological Properties of Diamond-Like Films Deposited with an Arc-Discharge Method, *J. Mater. Res.,* Vol 5 (No. 11), 1990, p 2524 (This journal issue is largely devoted to diamond films.)
75. F.J. Zanner and L.A. Bertam, Vacuum Arc Remelting--An Overview, in *Proc. 8th Int. Conf. Vacuum Metallurgy,* Vol I, 1985, p 512
76. F.J. Zanner, Metal Transfer during Consumable Arc Remelting, *Metall. Trans. B,* Vol 10, 1979, p 133
77. H. Ehrich, B. Hasse, M. Mausbach, and K.G. Muller, The Anodic Vacuum Arc and Its Application to Coating, *J. Vac. Sci. Technol. A,* Vol 8 (No. 3), 1990, p 2160
78. H. Ehrich, B. Hasse, M. Mausbach, and K.G. Muller, Plasma Deposition of Thin Films Utilizing the Anodic Vacuum Arc, *IEEE Trans. Plas. Sci.,* Vol 18 (No. 6), 1990, p 895
79. B.L. Gehman, G.D. Magnuson, J.F. Tooker, J.R. Treglio, and J.P. Williams, High Throughput Metal-Ion Implantation System, *Surf. Coat. Technol.,* Vol 41 (No. 3), 1990, p 389
80. D.M. Poirier and P.A. Lindfors, Non-Isotropic Deposition from a 304 Stainless Steel Cathodic Arc Source, *J. Vac. Sci. Technol. A,* Vol 9 (No. 2), 1991, p 278
81. H.M. Smith and A.F. Turner, Vacuum Deposited Thin Films Using a Ruby Laser, *Appl. Optics,* Vol 4, 1965, p 147
82. J. Cheung and J. Horwitz, Pulsed Laser Deposition History and Laser-Target Interactions, *MRS Bull.,* Vol 17 (No. 2), 1992, p 30 (This issue is devoted to laser deposition.)
83. D.C. Paine and J.C. Bravman, Ed., *Laser Ablation for Material Synthesis,* MRS Proc., Vol 191, MRS Publications, 1990
84. *Laser Assisted Deposition, Etching and Doping,* SPIE, Vol 459, 1984
85. J.T. Cheung and H. Sankur, Growth of Thin Films by Laser-Induced Evaporation, *Crit. Rev. Solid State/Material Sci.,* Vol 15, 1988, p 63
86. A. Kumar, L. Ganapath, P. Chow, and J. Narayan, In-Situ Processing of Textured Superconducting Thin Films of Bi(-Pb)-Ca-Sr-Cu-O by Excimer Laser Ablation, *Appl. Phys. Lett.,* Vol 56 (No. 20), 1990, p 2034
87. T. Bohandy, B.F. Kim, and F.J. Adrian, Metal Deposition from a Supported Metal Film Using an Excimer Laser, *J. Appl. Phys.,* Vol 60, 1986, p 1538
88. M. Wada, On the Thermally Activated Field Evaporation of Surface Atoms, *Surf. Sci.,* Vol 145, 1984, p 451
89. H.J. Mamin, S. Chiang, H. Birk, P.H. Guenther, and D. Rugar, Gold Deposition from a Scanning Tunneling Microscope Tip, *J. Vac. Sci. Technol. B,* Vol 9 (No. 2), 1991, p 1398
90. A.J. Melmed, The Art and Science and Other Aspects of Making Sharp Tips, *J. Vac. Sci. Technol. B,* Vol 9 (No. 2), 1991, p 601
91. R.A. Olsen, The Application of Thin, Vacuum-Deposited Poly Parxylyene to Provide Corrosion Protection for Thin Porous Inorganic Films, *Society of Vacuum Coaters 34th Ann. Tech. Conf. Proc.,* 1991, p 317

92. D.G. Shaw, A New High Speed Vapor Deposition Process, *Society of Vacuum Coaters 34th Ann. Tech. Conf. Proc.*, 1991, p 180

93. R.T. Lake, Ultraviolet Curing of Organic Coatings, *Society of Vacuum Coaters 25th Ann. Tech. Symp.*, 1982, p 87

Reactive Evaporation

Films of compounds can be deposited by reactive deposition, in which the elemental constituents of the compound are vaporized and codeposited, or in which the deposited material reacts with a reactive gaseous ambient on the surface of the depositing film. Most reactive deposition involves a condensible species (that is, titanium, zirconium, or aluminum) and a gaseous species (O_2, N_2), although some compounds of two or more condensible species can be deposited (for example, titanium and carbon). When codepositing two reactive species, obtaining the correct composition is often difficult, because the relative fluxes must be carefully controlled and generally the substrate temperature must be high to ensure reaction (for example, TiC from titanium plus carbon).

In reactive evaporation the reactive gas is in its natural (that is, molecular) state (Ref 94, 95, 96). This technique generally requires that there be many more reactive gas molecules striking the depositing film than are needed for forming the compound, because the reaction coefficient is generally much less than one.

Activated Reactive Evaporation. If the reactive gas is "activated" by forming new molecular species (that is, ions, radicals, and excited species), the reactive deposition process is termed activated reactive evaporation (ARE) (Ref 97, 98, 99, 100). Because the reactive gas is activated, the gas density needed for reaction is less than that needed for reactive evaporation. The reactive gas can be activated by a plasma (Fig. 9), thermal decomposition, photoadsorption, or some other means. The use of atomic or radical beams of the reactive gas, directed toward the depositing material during deposition, allows reactive deposition to take place at a relatively low chamber pressure. An example of activated reactive evaporation that does not use a plasma is the deposition of a thin layer of titanium nitride to reduce secondary electron emission, by evaporating titanium in ammonia where the ammonia is decomposed by the hot evaporating filament to provide reactive nitrogen radicals (Ref 101).

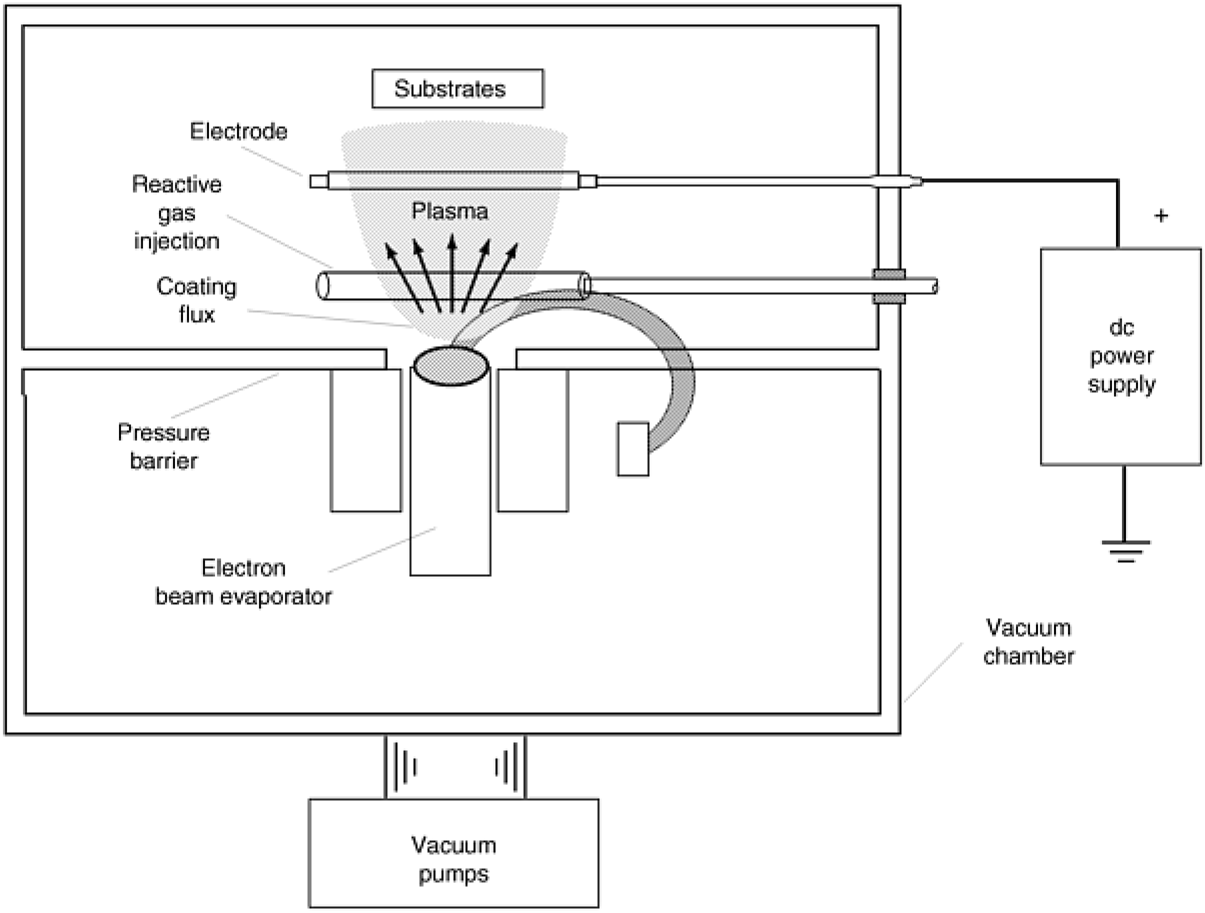


Fig. 9 Schematic of the activated reactive evaporation process using an electron-beam gun as an evaporation source. Source: Ref 99

In reactive evaporation, the interface can be graded by controlling the availability of the reactive gas. For example, in depositing titanium nitride the material can be graded from titanium to titanium nitride by controlling the availability of the nitrogen. Reactive evaporation can be used to form compounds when the evaporant is another compound. For example, cubic boron nitride (CBN) has been formed by the evaporation of H_3BO_3 in a plasma of NH_3 (Ref 102).

References cited in this section

94. E. Ritter, Deposition of Oxide Films by Reactive Evaporation, *J. Vac. Sci. Technol.,* Vol 3, 1966, p 225
95. L. Holland, Substrate Treatment and Film Deposition in Ionized and Reactive Gases (Invited review), *Thin Solid Films,* Vol 27, 1975, p 185
96. Martin, R.P. Netterfield, and W.G. Sainty, Optical Properties of TiN_x Produced by Reactive Evaporation and Reactive Ion Beam Sputtering, *Vacuum,* Vol 32, 1982, p 359
97. W. Heitmann, Reactive Evaporation in Ionized Gases, *Appl. Opt.,* Vol 10, 1971, p 2414
98. R.F. Bunshah and A.C. Raghurm, Activated Reactive Evaporation Process for High Rate Deposition of Compounds, *J. Vac. Sci. Technol.,* Vol 9, 1972, p 1385
99. C.V. Deshpandey and R.F. Bunshah, The Activated Reactive Evaporation (ARE) Process, Chapter 15, *Handbook of Plasma Processing Technology Fundamentals, Etching, Deposition and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes Publications, 1990
100. R.F. Bunshah and C. Deshpandey, The Activated Reactive Evaporation Process, *Physics of Thin Films,* Vol 13, 1987, p 59
101. R.J. Greiggs and W.D. Cornelius, Titanium Nitridation of Metallic Surfaces, *J. Vac. Sci. Technol. A,* Vol 7 (No. 3), 1989, p 2515
102. K.L. Chopra, V. Agarwal, V.D. Vankar, C.V. Deshpandey, and R.F. Bunshah, Synthesis of Cubic Boron Films by Reactive Evaporation of H_3BO_3, *Thin Solid Films,* Vol 126, 1985, p 307

Additional Evaporative Vacuum Deposition Techniques

Other deposition processes that use the vacuum environment to control contamination and provide a long mean free path for vaporized material can be defined as *vacuum deposition* processes:

- Molecular beam epitaxy
- Ionized cluster beam deposition
- Ion beam sputter deposition
- Jet vapor deposition

Molecular Beam Epitaxy. Probably the most sophisticated vacuum deposition system/process is that used for molecular beam epitaxy (MBE), or vapor phase epitaxy (VPE) (Ref 103). Molecular beam epitaxy is used to form epitaxial films of semiconductor materials. A vacuum environment of better than 0.13 μPa (10^{-9} torr) is used to deposit atoms from carefully rate-controlled vapor sources (Knudsen-type sources) (Ref 9). The MBE deposition chamber can also contain a wide range of analytical instruments for in situ analysis of the growing film. These analytical techniques include methods for measuring crystal parameters, such as reflection high energy electron diffraction (RHEED) and low energy electron diffraction (LEED).

Gaseous or vaporized metal-organic compounds can also be used as the source of film material in MBE. The molecular species are decomposed on the hot substrate surface to provide the film material. The use of metal-organic precursor

chemicals is called metal-organic molecular beam epitaxy (MOMBE) (Ref 104). MOMBE is used in low-temperature formation of compound semiconductors with low defect concentrations.

Ionized Cluster Beam Deposition. Clusters of atoms (approximately 1000) can be charged and accelerated to such high velocities that the average kinetic energy of the depositing atom is greater than that associated with thermal vaporization. This is the basis of the ionized cluster beam (ICB) deposition process (Ref 105, 106). There is some controversy about how and if clusters are formed and what actually happens at the surface in this deposition process (Ref 107, 108, 109). There are numerous technical papers detailing the advantages of the ICB deposition process in forming epitaxial films at low temperatures that are defect free, have good adhesion, and have good surface coverage.

Ion-Beam Sputter Deposition. Ion guns can be used to sputter deposit films in a vacuum environment (Ref 110). This technique has limited applications because high-energy neutrals reflected from the sputtering target can bombard the growing film during deposition, giving rise to uncontrolled film property variations.

Jet Vapor Deposition. In the "jet vapor deposition" process, evaporated atoms/molecules are "seeded" in a supersonic jet flow of inert carrier gas into a rapidly pumped vacuum chamber (Ref 111, 112). The jet transports the atoms/molecules to the substrate surface, where they are deposited. The vapor source can be in the form of thermal evaporation or sputtering and is located in the jet nozzle. The deposition chamber pressure is about 130 Pa (1 torr) and is pumped using high-capacity mechanical pumps.

References cited in this section

9. V. Ruth and J.P. Hirth, The Angular Distribution of Vapor from a Knudsen Cell, *Condensation and Evaporation of Solids,* E. Ruthner, P. Goldfinger, and J.P. Hirth, Ed., 1964, p 99
103. P. Chow, Molecular Beam Epitaxy, Chapter II-3, *Thin Films Processes II,* J.L. Vossen and W. Kern, Ed., Academic Press
104. L.M. Fraas, P.S. McLeod, L.D. Partain, and J.A. Cape, Epitaxial Growth from Organometallic Sources in High Vacuum, *J. Vac. Sci. Technol. B,* Vol 4, 1986, p 22
105. T. Takagi, *Ionized-Cluster Beam Deposition and Epitaxy,* Noyes Publications, 1988
106. I. Yamada, Ionized Cluster Beam (ICB) Deposition Techniques, Chapter 14, *Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes Publications, 1990, p 356
107. F.K. Urban and A. Bernstein, Formation of Gold Clusters in Ionized Cluster Beam Deposition Technique, *Thin Solid Films,* Vol 193/194, 1990, p 92
108. F.K. Urban, Effects of Space Charge on Ion Energy in Ionized Cluster Beam Film Deposition Technique, Paper TF-WeP11 in 38th National AVS Symp., to be published in *J. Vac. Sci. Technol.*
109. W. Knauer, Formation of Large Metal Clusters by Surface Nucleation, *J. Appl. Phys.,* Vol 62, 1987, p 841
110. J.M.E. Harper, Ion Beam Deposition, Chapter II-4, *Thin Film Processes,* J.L. Vossen and W. Kern, Academic Press, 1978
111. J.J. Schmitt, "Method and Apparatus for the Deposition of Solid Films of Material from a Jet Stream Entraining the Gaseous Phase of Said Material," U.S. Patent No. 4,788,082, 29 Nov 1988
112. B.L. Halpern, J.J. Schnidtt, J.W. Golz, Y. Di, and D.L. Johnson, Gas Jet Deposition of Thin Films, *Appl. Surf. Sci.,* Vol 48/49, 1991, p 19

Advantages and Limitations of Vacuum Deposition Processes

Vacuum deposition has advantages and limitations relative to other physical vapor deposition (PVD) techniques.

Advantages of vacuum deposition include:

- Line-of-sight deposition allows the use of masks to define the area of deposition.
- Large-area sources can be used for some materials (for example, "hog trough" boat crucibles for aluminum and zinc).

- High deposition rates can be obtained.
- Deposition rate monitoring is relatively easy.
- Vaporization source material can be in many forms (for example, chunks, powder, wire, chips, and so on).
- Vaporization source material of high purity is relatively inexpensive.
- High-purity films are easily deposited from high-purity source material, because the deposition ambient can be made as noncontaminating as required.
- The technique is relatively inexpensive compared to other PVD techniques.

Limitations of vacuum deposition include:

- Line-of-sight deposition gives poor surface coverage, thus requiring elaborate tooling and fixturing.
- Line-of-sight deposition prevents uniform deposits over a large surface area unless complex fixturing and tooling are available.
- Deposition of many alloys and compounds is difficult.
- Capital equipment costs are high relative to those of other deposition techniques (for example, electroplating).
- High radiant heat loads are required during processing.
- Vaporized material is used inefficiently.
- Film properties are suboptimal (typical defects include pinholes, less than bulk density, columnar morphology, high residual film stress, and so on).
- Few processing parameters are available to control film properties.

Vacuum Deposition Applications

Applications of evaporation processes include:

- Electrically conductive coatings for ceramic metallization (for example, Ti-Au, Ti-Pd-Au, Al, Al-Cu-Si, Cr-Au, Ti-Ag), semiconductor metallization (for example, Al-2Cu on silicon), and metallization of capacitor foils (for example, zinc and aluminum)
- Optical coatings for reflective, antireflective, and abrasion-resistant topcoat (for example, SiO, MgF_2) applications
- Decorative coatings (for example, aluminum and gold)
- Moisture and oxygen permeation barriers for packaging materials (for example, aluminum and $SiO_{1.8}$ on polymer webs)
- Corrosion resistance (for example, aluminum on steel)
- Insulating layers for microelectronics (Ref 113)
- Coating of engine turbine blades (M-CrAl alloys) (Ref 19, 114, 115)
- Avoiding the pollution problems associated with electroplating (that is, "dry processing")
- Vacuum plating of high-strength steels to avoid the hydrogen embrittlement associated with electroplating (for example, cadmium on steel, or "vacuum cad plating")

Freestanding Structures. Evaporation processes can be used to form freestanding structures by depositing the film on an appropriately shaped mandrel. On the mandrel, either there is a "parting layer" (for example, evaporated NaCl) or the surfaces may be nonadhering (for example, copper on the oxide on stainless steel). In some cases, the mandrel must be dissolved to release the deposited form. This technique is used to fabricate thin-wall structures and windows (Ref 116).

Multilayer Structures. Many applications of evaporation processes require deposition of layered structures. These applications range from simple two- to three-layer metallization systems to x-ray diffraction gratings that consist of alternating low-mass material (carbon) and high-mass material (tungsten) and form a stack of thousands of layers with each layer only 3 to 4 nm (30 to 40 Å) thick.

References cited in this section

19. D.H. Boone, S. Shen, and R.M. McKoon, Electron Beam Evaporation of Low Vapor Pressure Elements in the M-Cr-Al Coatings Compositions, *Thin Solid Films,* Vol 63, 1979, p 299
113. H. Oetzmann, N.-J. Krokoszinski, H. Gernoth, and C. Schmidt, Evaporated Insulating Layers for Thin Film Circuits, *Thin Solid Films,* Vol 140, 1986, p 209
114. D.H. Boone, T.E. Strangman, and L.W. Wilson, Some Effects of Structure and Composition on the Properties of Electron Beam Vapor Deposited Coatings for Gas Turbine Superalloys, *J. Vac. Sci. Technol.,* Vol 11, 1974, p 641
115. H. Lämmermann and G. Kienel, PVD Coatings for Aircraft Turbine Blades, *Adv. Mater. Proc.,* Dec 1991, p 18-23
116. A.H.F. Muggleton, Deposition Techniques for Preparation of Thin Film Nuclear Targets: Invited Review, *Vacuum,* Vol 37, 1987, p 785

Gas Evaporation and Ultrafine Particles

Vapor phase nucleation can occur in a dense vapor cloud by multibody collisions. The nucleation can be encouraged by passing the atoms to be nucleated through a gas to provide the necessary collisions and cooling for nucleation. These particles have a size range of 1 to 100 nm (10 to 1000 Å) and are called *ultrafine particles* or *ultrafine clusters*. The process of forming the particles is called *gas evaporation* (Ref 117, 118, 119). The size and size distribution of the particles depend on the gas density, the gas species, the evaporation rate, and the geometry of the system. When these particles deposit on a surface the resulting film is very porous and can be used as an optical radiation trap; for example, "black gold" infrared radiation bolometer films, germanium film solar absorber coatings (Ref 120) and low secondary electron emission surfaces (Ref 121). The particles themselves are used for various powder metallurgical processes, such as low-pressure, low-temperature sintering (Ref 122). Ultrafine particles of reactive materials are very pyrophoric because of their high surface area.

Evaporation into a plasma causes the ultrafine particles to have a negative charge and to be suspended in the plasma near walls where they can grow to appreciable size (Ref 123, 124, 125). Ultrafine particles of alloys can be formed by evaporation from a single source, or they can be evaporated from separate sources and nucleated in the gas. Ultrafine particles of compounds can be formed by having a reactive gas present during nucleation or by decomposing and reacting precursor gases in an arc or plasma.

Buckminster Fullerenes. Recent gas evaporation techniques have allowed the formation of the Buckminster fullerenes (C^{60} and C^{70} "Buckeyballs"), a newly discovered form of the carbon molecule that resembles the shape of a soccer ball (Ref 126, 127). The synthesis involves arcing two pure graphite electrodes in a partial vacuum containing helium. The carbon "soot" that forms contains from 3 to 40% fullerenes, depending on the experimental conditions. The fullerenes are extracted from the soot by dissolving them in boiling benzene or toluene, and then this extract is vacuum dried.

References cited in this section

117. A.H. Pfund, The Optical Properties of Metallic and Crystalline Powders, *J. Opt. Soc. Am.,* Vol 23, 1933, p 375
118. R. Uyeda, The Morphology of Fine Metal Crystallites, *J. Cryst. Growth,* Vol 24/25, 1974, p 69
119. J.K.G. Panitz, D.M. Mattox, and M.J. Carr, Salt Smoke: The Formation of Submicron Sized RbCl Particles by Thermal Evaporation in 0.5-100 Torr of Argon and Helium, *J. Vac. Sci. Technol. A,* Vol 6 (No. 6), 1988, p 3105
120. D.M. Mattox and G.J. Kominiak, Deposition of Semiconductor Films with High Solar Absorptivity, *J. Vac. Sci. Technol.,* Vol 12 (No. 1), 1975, p 182
121. S. Thomas and E.B. Pattinson, The Controlled Preparation of Low SEE Surfaces by Evaporation of Metal Films under High Residual Gas Pressure, *J. Phys. D, Appl. Phys.,* Vol 3, 1970, p 1469

122. C. Hayashi, Ultrafine Particles, *Physics Today,* Vol 40, 1987, p 44
123. W.J. Yoo and Ch. Steinbruchel, Kinetics of Growth of Silicon Particles in Sputtering and Reactive Ion Etching Plasmas, *J. Vac. Sci. Technol. A,* Vol 10 (No. 4), 1992, p 1041
124. G.S. Selwyn and E.F. Patterson, Plasma Particle Generation Control II. Self-Cleaning Tool, *J. Vac. Sci. Technol. A,* Vol 10 (No. 4), 1992, p 1053
125. D.M. Mattox, Fundamentals of Ion Plating, *J. Vac. Sci. Technol.,* Vol 10, 1973, p 47
126. W. Krätschmer, L.D. Lamb, L.B. Fostiropoulos, and D.R. Huffman, Solid C^{60}: A New Form of Carbon, *Nature,* Vol 347 (No. 6291), 1990, p 354-358
127. P.E. Ross, Buckeyballs, *Sci. Am.,* Vol 263 (No. 7), 1991, p 114-116

Evaporation Process Equipment

The primary function of the vacuum system associated with evaporation processing is to reduce contaminating residual gases and vapors to an acceptable level. Potential sources of the gases and vapors in the processing chamber and related systems include:

- Residual atmospheric gases and vapors
- Desorption from surfaces in the vacuum (for example, water vapor and oils)
- Outgassing from materials in the vacuum (for example, water vapor and oxygen)
- Vaporization of construction materials (especially at high temperatures)
- Leakage from real and virtual leaks
- Permeation through materials such as rubber O-rings
- Desorption, outgassing, and vaporization from fixtures, tooling, substrates, and deposition source materials introduced into the system

In all cases, specifications for system performance, deposition procedures, and vacuum conditions should be established when the system and procedures produce a reproducible workpiece with the desired properties. Figure 10 shows a vacuum deposition system that can use a plasma discharge for plasma cleaning or the ARE process. Usually there are tradeoffs between the optimum design for achieving a good vacuum and the practicality of design for processing. For example, processing may require a large access door so that fixturing and substrates can be assembled externally and installed in the chamber.

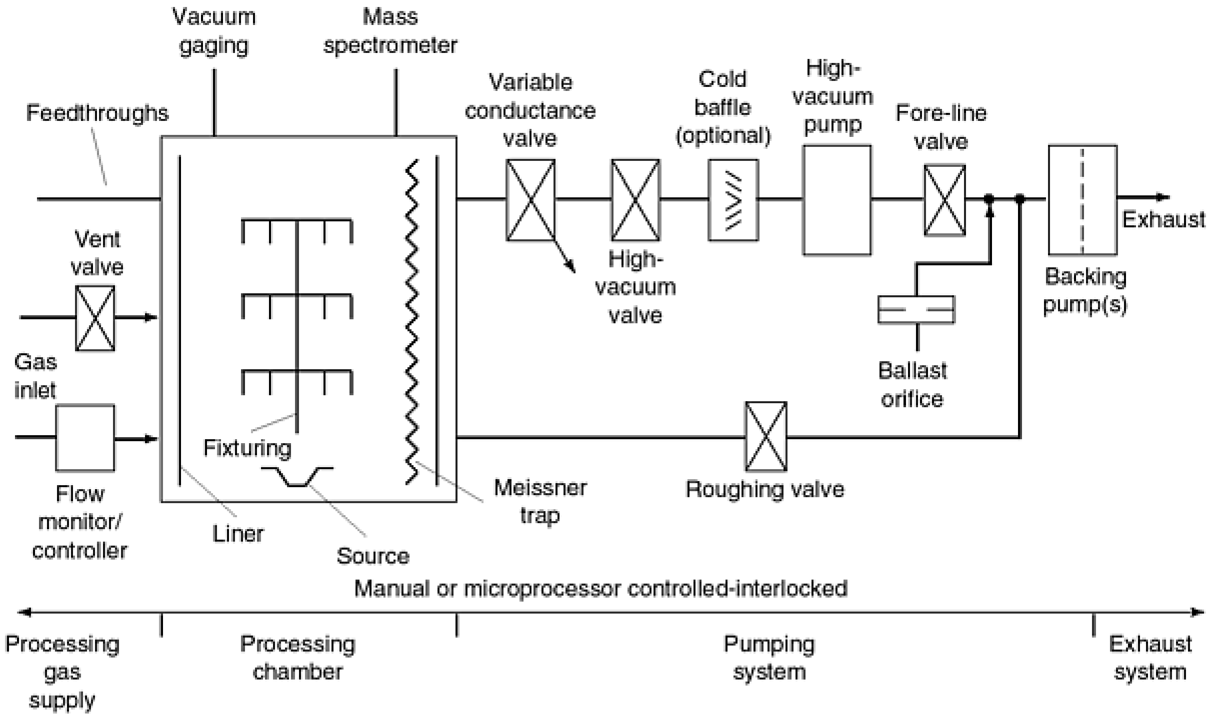


Fig. 10 Primary components of a batch-type vacuum deposition system that can be used for plasma processing

Processing Chamber. There are several chamber configurations for vacuum deposition systems (Fig. 11). The batch-type system is the most common but exposes the system to the ambient air with each deposition, which can introduce uncontrolled process variables. Load-lock systems allow the deposition chamber to be kept under a more controlled environment.

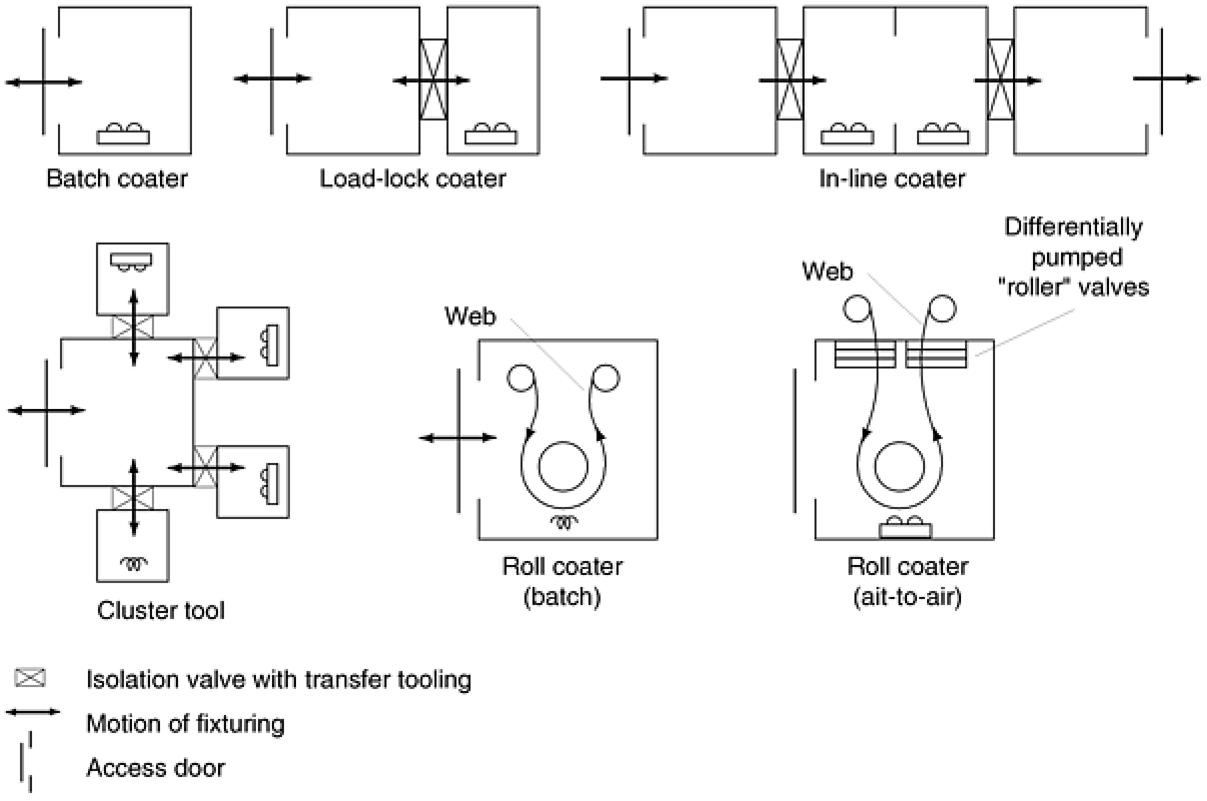


Fig. 11 Chamber configurations employed in vacuum deposition systems

Vacuum deposition systems need to be kept clean in order to operate efficiently. Deposit buildup results in increased pumpdown time because of slower desorption of adsorbed contaminants (for example, water). Deposit buildup also results in flaking from walls and fixtures, which can cause pinholes in coatings. Good vacuum practices should be used in all aspects of the use of deposition equipment. The design of the system should allow good access for cleaning and mounting of appropriate fixturing, sources, shutters, and so on.

Heating from the vaporization source can raise the system temperature to unacceptable levels, leading to desorption, outgassing, and the failure of organic seals. Heat is generally removed by water cooling the chamber walls or by using an internal heat sink, such as a water-cooled surface (Ref 128). The cooling channels in the chamber walls can be used to heat the surface using hot water when the system is opened to the ambient air. This heating minimizes water adsorption on the surface when the system is open to the ambient air.

Pumping System. Pumping in the vacuum deposition system is generally relatively simple because there are typically no high-gas loads. However, in some cases, the gas and vapor loads can be high from outgassing and desorption, and the system should be designed accordingly. An example is web (roll) coating, where trapped gases are released during unrolling of the plastic web in the deposition chamber. Where water vapor release is a problem, it is often desirable to have an in-chamber cryocondensation surface. These surfaces are cooled by refrigeration and "freeze out" the water vapor in the chamber at low temperatures (<-130 °C, or -202 °F).

In reactive deposition processes and gas evaporation, where the gas pressures are high, the vacuum pumping system can generate pressure differentials in the chamber. This can have a significant effect if the system has a great deal of fixturing in the processing volume. This problem has been noted at processing pressures as low as 0.13 Pa (10 mtorr).

Fixturing and Tooling. The definitions of *fixturing* and *tooling* are not universally accepted, but in general, *fixturing* is used to hold the substrates while *tooling* is used to move the fixtures. Fixturing and tooling should be constructed to minimize virtual leaks, particle generation by flaking, and shadowing effects on the deposition process. Fixtures and tooling should be easily removable for cleaning or rearrangement. Fixture surfaces often represent a major portion of the surface in the processing chamber and should be cleaned, handled, and stored with care.

Tooling is used to randomize the substrate position and angle with respect to the direction of the depositing flux. A common tooling in evaporation processing is a spherical dome-shaped (calotte) holder that maintains a constant line-of-sight distance between the source and substrates. Often this holder is rotated to randomize the position of the substrates. This results in improved surface coverage, a more uniform thickness distribution, and more consistent film properties (Ref 6, 129, 130). However, it should be realized that no amount of movement can completely overcome the angle-of-incidence and thickness variations on a complex surface. Angle-of-incidence differences can lead to significant film property variations.

Mounting of Substrates. Substrates should be mounted so that particles in the deposition ambient do not settle on the substrate surface. This requires mounting the substrates so that they face downward or to the side. Mechanical clamping is often used to secure the substrates, but this entails having a region that is uncoated. Mechanical clamping provides poor and variable thermal contact to the fixture surface and can result in variable substrate temperatures during the vaporization/deposition process.

Substrate Heating and Cooling. Substrates can be heated from a number of sources:

- Condensation of the depositing atoms
- Radiant heating from the vaporization source
- Separate radiant heaters (for example, quartz radiation lamps) in the system to heat the substrate directly
- Embedded heaters to heat the fixturing
- Accelerated electrons from a heated filament, used to heat conductive substrates or fixtures
- Laser radiation, used to provide local heating during the deposition process

Substrates can be cooled by being in contact with a cooled substrate fixture. Circulating chilled water or oil, a cooled water/ethylene glycol mixture (at -25 °C, or -13 °F), dry ice/acetone (at -78 °C, or -109 °F), or liquid nitrogen (at -196 °C, or -321 °F) can be used as coolants.

Masks. Because in vacuum deposition the vapor flux travels in a straight line to the substrate surface, physical masks can be used to intercept the flux to produce defined patterns of deposition on a surface. The effectiveness of masks depends on the mask-surface contact, mask thickness, edge effects, and mask alignment on the surface. Masks can be made by numerous methods (for example, etching or machining) (Ref 131) and can allow pattern resolutions as small as several microns. Masking allows the patterning of hard-to-etch materials and in situ patterning during deposition. Deposited masks are used in the lift-off patterning process (Ref 131). Programmed moving masks can also be used to control the film thickness distribution on a surface (Ref 14, 15, 132)

Shutters. The shutter is an important part of the vacuum deposition system. Shutters can be used to isolate the substrate from the source and to allow outgassing and wetting of the source without contaminating the substrate. Shutter design is limited only by the ingenuity of the designer. The shutter can be the moving part, or the substrate can be moved. Shutters can be in the form of fans, leaves, flaps, or sections of geometrical shapes (for example, cones, cylinders, and so on). In designing a shutter, care must be taken to keep the complexity to a minimum. Shutter design should provide for easy removal when cleaning is necessary. In some cases, it may be desirable to cool the shutter as an aid in pumping condensables.

Source fixturing involves making good electrical contact with the resistively heated vaporization source (for example, wire or sheet). Thermal expansion requires that the fixture be slightly flexible. If the fixture is too rigid, the vaporization source can be stressed and subsequently broken. If the source is flexible (for example, a wire or coil), the source can

distort and thus produce changes in the flux distribution pattern on heating and in actual use. In some cases, the source and its electrical connections are moved during deposition to increase coverage uniformity over a large stationary substrate.

High current connections to the source should be of a high-conductivity material such as copper. Physical contact to boats and crucibles can be improved by using spring contacts of a material such as tungsten, along with graphite paper shimming materials, such as that known by the tradename Grafoil. In some cases, cooled clamps can be used to hold the source. Multiple evaporation sources can be arranged to produce large-area or linear vaporization patterns.

In Situ Cleaning. Many vacuum deposition systems, particularly optical coating systems, are equipped with the capability to establish a plasma discharge for cleaning substrate surfaces prior to film deposition (Ref 1). Pure air is often used as the cleaning plasma for oxide surfaces. Often a plasma ring is used as the cathode in the processing chamber. The plasma ring should be shielded to prevent sputtered material deposits on the substrate. The cathode can be cooled if the power to the cathode is high.

The effectiveness of plasma cleaning depends on the packing of surfaces in the volume. If there is a large volume of fixturing and close spacing of surfaces in the chamber, the effectiveness of plasma cleaning will vary throughout the volume of the system.

Getter Pumping. When reactive materials are deposited, the fixturing and shields in the deposition system can be arranged to provide getter pumping by the excess deposited film material. This gettering lowers the contamination level in the system and at the substrate.

References cited in this section

1. W.P. Strickland, "Optical Thin Film Technology: Past, Present and Future," *Society of Vacuum Coaters 33rd Ann. Tech. Conf. Proc.,* 1990, p 221

6. H.K. Pulker, Chapter 6, *Coatings on Glass,* Elsevier, 1984

14. J. Strong, *Procedures in Experimental Physics,* Prentice-Hall, 1938, p 183

15. K.H. Behrndt, Films of Uniform Thickness from a Point Source, *Trans. 9th AVS Symposium,* Macmillan, 1962, p 111

128. D.J. Missimer, Removal of Excess Heat in a Vacuum Deposition Operation--An Overview, *Society of Vacuum Coaters 33rd Ann. Tech. Conf.,* 1990, p 269

129. P. Chang, The Relation Between Position and Degree of Step Coverage for a Wafer on a High Speed Planetary Dome, *Society of Vacuum Coaters 34th Ann. Tech. Conf.,* 1991, p 321

130. S. Bosch, Computer-Aided Techniques for Optimization of Layer Thickness Uniformity in Thermal Evaporation Physical Vapor Deposition Chambers for Lense Coating: Enhanced Procedures, *J. Vac. Sci. Technol. A,* Vol 10 (No. 1), 1992, p 98

131. R. Glang and L.V. Gregor, Generation of Patterns in Thin Films, Chapter 7, *Handbook of Thin Film Technology,* L.I. Maissel and R. Glang, Ed., McGraw-Hill, 1970

132. I.J. Hodgkinson, Vacuum-Deposited Thin Films with Specific Thickness Profiles, *Vacuum,* Vol 28, 1978, p 179

Process Monitoring and Control

To provide a reproducible vacuum deposition process, the principal deposition parameters that need to be monitored and controlled are:

- Residual gas pressure and composition prior to and during deposition
- Substrate temperature and temperature variations over the substrate surface
- Deposition rate
- Angle of incidence of depositing flux
- Purity of source material

- Preprocessing, such as surface preparation and substrate heating

In the case of reactive evaporation, the following parameters also need to be monitored and controlled:

- Availability of reactive gases over the substrate surfaces
- Activation of reactive gases
- Gas density distribution in the processing chamber

Substrate Temperature Monitoring. The substrate loses heat by conduction and radiation, thus often making it difficult to monitor substrate temperature. Thermocouples embedded in the substrate fixture often give a poor indication of the substrate temperature, because the substrate often has poor thermal contact with the fixture. In some cases, thermocouples can be embedded in or attached directly to the substrate material. Optical (infrared) pyrometers can be used to determine the temperature if the surface emissivity and adsorption in the optics are constant and known.

Passive temperature monitors can record the maximum temperature a substrate has approached during processing. Passive temperature monitors register color changes, phase changes (for example, melting of indium), or crystallization of amorphous materials (Ref 133).

Source Temperature Monitoring. Generally, source temperatures are very difficult to monitor or control with precision. In molecular beam epitaxy, the deposition rate is controlled by carefully controlling the temperature of a well-shielded Knudsen cell source using embedded thermocouples (Ref 7).

Deposition Rate and Deposited Mass Monitors. Quartz crystal monitors measure the frequency of the oscillations as a function of the mass added to the crystal face. By calibrating the frequency change with the mass deposited, the quartz crystal output can measure deposition rate and total mass deposited (Ref 134). Ionization rate monitors compare the ionization currents in a reference chamber and a chamber through which the evaporant flux is passing. By calibration, the differential in gage outputs can be used as a deposition rate monitor (Ref 135). A vacuum microbalance can be used to measure the deposition rate and the total amount of material deposited. In electron-beam evaporation, the ions that are formed above the molten pool can be used to monitor the vaporization rate and the mass deposited.

The total amount of deposited material is sometimes controlled by evaporating to completion a specific amount of source material. This avoids the need for a deposition controller and is used where many repetitious depositions are to be made.

Film Thickness Monitoring. There is no easy way to measure the geometrical thickness of a film during deposition because the thickness depends on the density for a given mass deposited. In general, thickness is determined from the mass deposited, assuming a density so that the mass monitor is calibrated to give thickness.

Optical Property Monitoring. In optical coating systems, in situ monitoring of the optical properties of the films is used to monitor film deposition and provide feedback that controls the evaporators (Ref 136, 137). Generally, the optical transmittance, interference (constructive and destructive), or reflectance at a specific wavelength is used to monitor the optical properties. Ellipsometric measurements can be used to monitor the growth of oxides on semiconductor materials.

Electrical Property Monitoring. An electrically conducting path between electrodes can be deposited using a mask, and the electrical resistivity of the path can be used as a deposition monitor (Ref 138).

Film Stress Monitoring. There are several techniques for measuring the film stress during the deposition process. These techniques typically measure the movement of surfaces, as monitored by changes in capacitance between two plates, or they measure the deflection of a beam by optical interferometry (Ref 139) or an optical lever arm. X-ray diffraction measurements of the lattice spacing can be used to measure film stress due to lattice deformation (Ref 140).

References cited in this section

7. E. Rutner, Some Limitations on the Use of the Langmuir and Knudsen Techniques for Determining

Kinetics of Evaporation, *Condensation and Evaporation of Solids,* E. Ruthner, P. Goldfinger, and J.P. Hirth, Ed., 1964, p 149

133. K. Miyoshi, T. Spalvins, and D.H. Buckley, Metallic Glass as a Temperature Sensor During Ion Plating, *Thin Solid Films,* Vol 127, 1975, p 115
134. A.R. Knoll, L.J. Matienzo, and K.J. Blackwell, Calibration of a Quartz Crystal Microbalance Deposition Rate Monitor by Spectroscopic Techniques, *Society of Vacuum Coaters 34th Ann. Tech. Conf. Proc.,* 1991, p 247
135. H. Schwartz, Method of Measuring and Controlling Evaporation Rates During the Production of Thin Films in Vacuum, *Trans. 7th Ann. AVS Symp.,* 1961, p 326
136. W.P. Thoeni, Deposition of Optical Coatings: Process Control and Automation, *Thin Solid Films,* Vol 88, 1982, p 385
137. F. Meyer, In Situ Deposition Monitoring, *J. Vac. Sci. Technol. A,* Vol 7 (No. 3), 1989, p 1432
138. J.L. Provo, Film-Thickness Resistance Monitor for Dynamic Control of Vacuum-Deposited Films, *J. Vac. Sci. Technol.,* Vol 12 (No. 4), 1975, p 946
139. P.H. Wojciechowski, Stress Modification of Ni-Fe Films by Ion Bombardment Concurrent with Film Growth by Alloy Evaporation, *J. Vac. Sci. Technol. A,* Vol 6 (No. 3), 1988, p 1924
140. B.M. Clemens and J.A. Bain, Stress Determination in Textured Thin Films Using X-ray Diffraction, *MRS Bull.,* Vol 17 (No. 7), 1992, p 46

Sputter Deposition

S.L. Rohde, University of Nebraska-Lincoln

Introduction

SPUTTERING is a nonthermal vaporization process in which surface atoms are physically ejected from a surface by momentum transfer from an energetic bombarding species of atomic/molecular size. Typically, sputtering uses a glow discharge or an ion beam (Ref 1) to generate a flux of ions incident on the target surface. These ions cause atoms, and occasionally clusters of atoms, to be knocked free from the target surface by impact transfer, or sputtering. Sputtering is used in two principal applications: sputter etching, in which the primary objective is removal of material from the target surface (Ref 2); and sputter deposition, in which redeposition of these sputtered atoms onto another surface, or substrate, is the primary goal. The latter application is discussed in this article. The fundamentals of plasma formation and the interactions on the target surface are discussed first, followed by the differences between reactive and nonreactive sputtering, and several methods of process control. In the third section, the basic principles and relative advantages and disadvantages of the most common sputtering techniques are examined, specifically direct-current (dc) diode, radio-frequency (rf) diode, triode, magnetron sputtering, and a relatively new technique known as "unbalanced" magnetron sputtering.

Compared to other thin-film deposition methods, sputter deposition techniques have several distinct advantages:

- Use of an unlimited range of source and film materials (i.e., metals, semiconductors, insulators, alloys, and compounds)
- Small sputtering-yield variations from one material to another as compared to the relative variation in the evaporation rates at a given temperature
- Ease of low-temperature deposition of refractory materials
- Elimination of droplet emission from the source that can occur in thermal evaporation
- Absence of droplets, which are common in arc-deposited films
- Ease of forming multicomponent films
- Uniformity of film thickness over large areas
- High degree of film adhesion
- Environmentally friendly processing

Sputter deposition processes have several limitations as well:

- Target (source) materials must ordinarily be in sheet or tube form.
- Deposition rates are typically less than 300 nm/min (3000 Å/min).
- Setup costs are high because of the required vacuum environment.
- Line-of-sight process may not be suitable for three-dimensional components.
- Energy efficiency is low (70% or more of the input energy is expended in target heating).

References

1. J.E. Harper, Ion Beam Sputtering, *Thin Film Processes,* J.L. Vossen and W. Kern, Ed., Academic Press, 1978, p 175-206
2. R.E. Lee, Microfabrication by Ion Beam Etching, *J. Vac. Sci. Technol.,* Vol 16 (No. 2), 1979, p 164-170

Glow Discharge Sputtering

Glow Discharge Formation. The simplest case of a glow discharge, the dc diode discharge, is illustrated in Fig. 1. At the far left of Fig. 1(a) is the cathode and adjacent to it the cathode glow region, which is luminous because of positive and negative ion neutralization at the cathode surface. Next to the cathode glow region is the cathode dark space, or sheath, across which most of the voltage is dropped (Fig. 1b), providing the accelerating force driving the ions into the target. The net space charge (Fig. 1c) also changes dramatically across the cathode dark space. To the right of the cathode dark space are the negative glow, the Faraday dark space, the positive column, and the anode, as shown in Fig. 1(a).

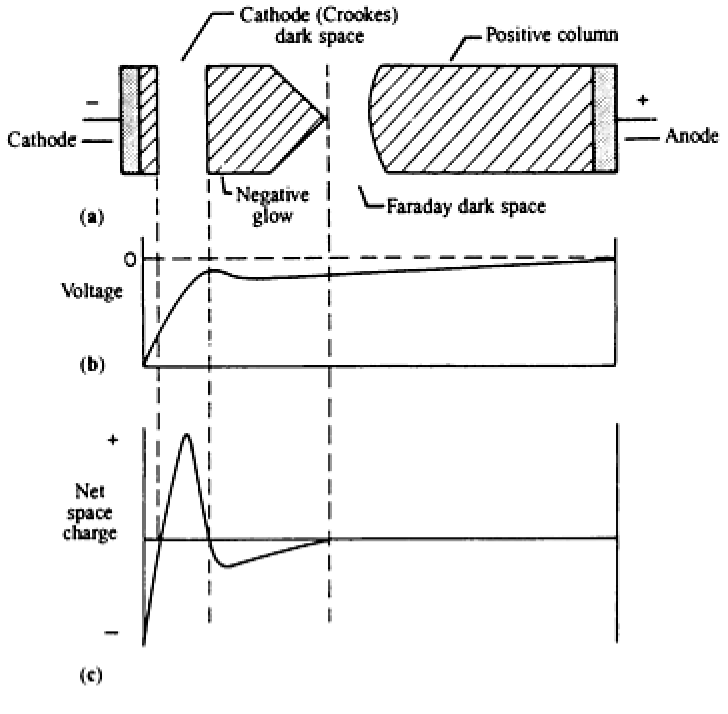


Fig. 1 Schematic illustration of the (a) primary regions, (b) voltage characteristics, and (c) net space charges for a dc glow discharge. Source: Ref 32

When an ion strikes the cathode, in addition to the generation of heat and the removal of neutral atoms and ions, there is about a 5 to 10% probability of secondary electron emission. These secondary electrons are then accelerated back across the dark space into the negative glow region where they expend most of their energy creating additional ions, approximately 10 to 20 ions/electron. It is these secondary electrons that are primarily responsible for sustaining the discharge, in this case, a cold cathode discharge. In the case of self-sustaining plasmas, the regions beyond the negative glow are less important, and in many cases the anode can be moved closer to the cathode, eliminating the positive column

and shrinking the size of the negative glow region, without greatly affecting the discharge characteristics. Thus in sputter deposition, the substrates are often immersed in the negative glow region. In this case, an additional dark space will form surrounding the substrates, and the thickness of this dark space, as well as the type and energy of the charged carriers reaching the substrate surface, will depend on whether the substrates are at the anode potential or are externally biased relative to the plasma.

Target Considerations. A great variety of interactions can occur on the target surface because of the impinging positive ions, as illustrated in Fig. 2. These interactions include liberation of neutral atoms, ionized atoms, backscattering, x-ray emission, photon generation, secondary electron emission, and desorption of gas atoms from the target surface. In the target itself, several other processes can occur, including the generation of collisional cascades, the creation of point defects, local heating, amorphization, implantation, and compound formation. Within the plasma, the secondary electrons cause additional ionization, supporting the discharge. The color of the optical emission of the plasma is characteristic of the target material, gas species, pressure, excitation, and so on. Thus, it is often possible to detect the presence of certain components in the discharge simply by monitoring the characteristic spectral wavelengths, and, hence, this feature of glow discharges is often used in process control.

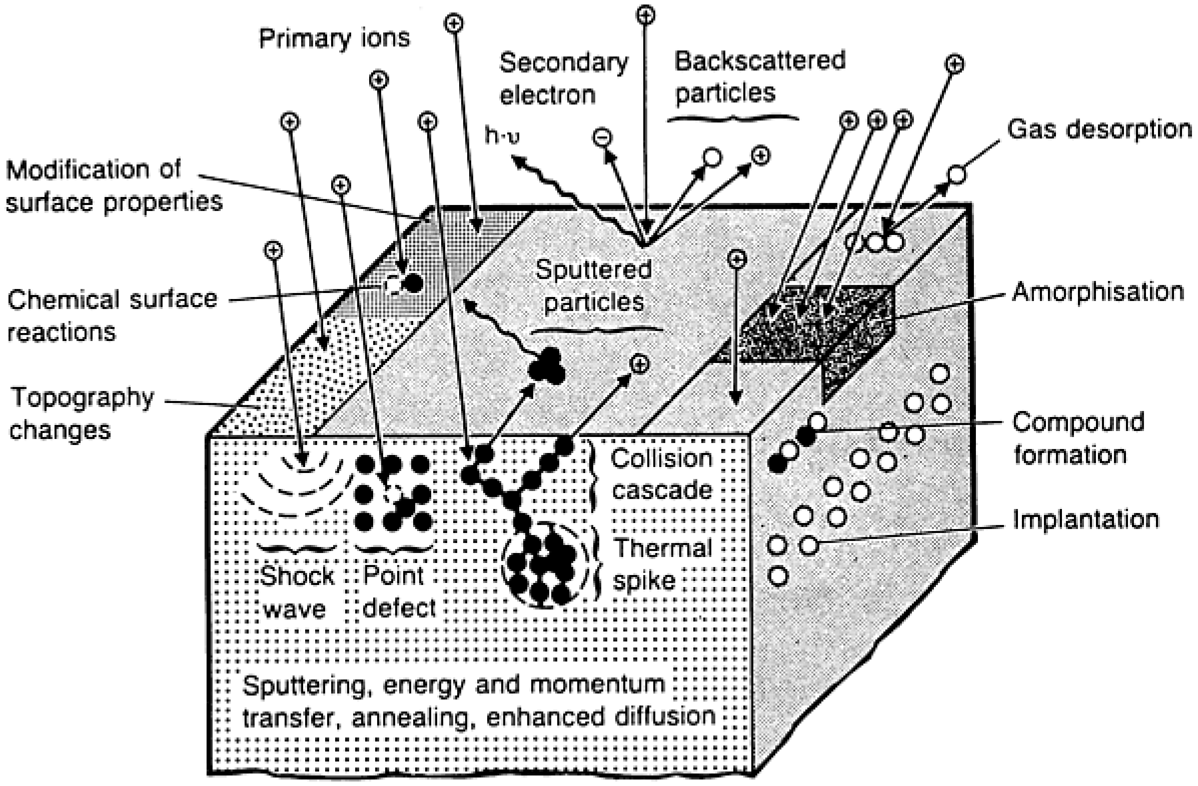


Fig. 2 Synopsis of the interaction events occurring at and near the target surface during the sputtering process. Source: Ref 5

One of the most important sputtering parameters is the sputtering yield, which is defined as the number of atoms ejected from the target surface per incident ion. The sputtering yield is dependent on the characteristics of the target material, incident ion energy, ion mass, and angle of incidence, as shown in Table 1. Detailed studies of sputtering yields for a large variety of materials can be found in the literature; see, for instance, Maissel (Ref 3) and Wehner (Ref 4). Although the variation in sputtering yields is as high as one order of magnitude, it is considerably lower than the rate variations that occur for evaporation from liquid sources at a specific temperature, which are often several orders of magnitude.

Table 1 Elemental sputtering yields for 500 eV ions

Element	Ion

	He	**Ne**	**Ar**	**Kr**	**Xe**
Be	0.24	0.42	0.51	0.48	0.53
C	0.07	. . .	0.12	0.13	0.17
Al	0.16	0.73	1.05	0.96	0.82
Si	0.13	0.48	0.50	0.50	0.42
Ti	0.07	0.43	0.51	0.48	0.43
V	0.06	0.48	0.65	0.62	0.63
Cr	0.17	0.99	1.18	1.39	1.55
Mn	. . .	. . .	. . .	1.39	1.43
Fe	0.15	0.88	1.10	1.07	1.00
Co	0.13	0.90	1.22	1.08	1.08
Ni	0.16	1.10	1.45	1.30	1.22
Cu	0.24	1.80	2.35	2.35	2.05
Ge	0.08	0.68	1.10	1.12	1.04
Y	0.05	0.46	0.68	0.66	0.48
Zr	0.02	0.38	0.65	0.51	0.58
Nb	0.03	0.33	0.60	0.55	0.53
Mo	0.03	0.48	0.80	0.87	0.87
Ru	. . .	0.57	1.15	1.27	1.20
Rh	0.06	0.07	1.30	1.43	1.38
Pb	0.13	1.15	2.08	2.22	2.23

Ag	0.02	1.77	3.12	3.27	3.32
Sm	0.05	0.69	0.80	1.09	1.28
Gd	0.03	0.48	0.83	1.12	1.20
Dy	0.03	0.55	0.88	1.15	1.29
Er	0.03	0.52	0.77	1.07	1.07
Hf	0.01	0.32	0.70	0.80	. . .
Ta	0.01	0.28	0.57	0.87	0.88
W	0.01	0.28	0.57	0.91	1.01
Re	0.01	0.37	0.87	1.25	. . .
Os	0.01	0.37	0.87	1.27	1.33
Ir	0.01	0.43	1.01	1.35	1.56
Pt	0.03	0.63	1.40	1.82	1.93
Au	0.07	1.08	2.40	3.06	3.01
Th	0.00	0.28	0.62	0.96	1.05
U	. . .	0.45	0.85	1.30	0.81

Source: Ref 32

Sputtering processes are governed primarily by energy transfer, momentum transfer, annealing effects, and enhanced diffusion, which often limits the performance of targets and creates a need for process control (Ref 5). For example, adsorbed gases tend to desorb under the influence of ion bombardment and heating. This is an important consideration when using powder metallurgically prepared targets that can liberate water vapor and cause surface chemical reactions if not properly degassed. Additionally, chemical surface reactions occur in the presence of reactive or residual gases such as nitrogen, oxygen, or hydrocarbons and can cause compound formation on the target surface. These reactions usually result in decreased sputtering rates, and compound formation is further intensified by a low target heat conductivity and cooling rate.

Additionally, topographical changes in the target surface may occur over time, particularly in multiphase polycrystalline targets in which the crystallites have different sputtering yields, leading to cone formation and arcing on the target. It is essential to consider these interactions in the selection and operation of various targets. More detailed information on these aspects of sputter processes is provided in the general literature (Ref 6, 7, 8, 9, 10, 11).

Process Parameter Effects on Film Microstructure. Scattering within the discharge significantly affects the energy with which atoms impact the film surface and, hence, the microstructure and properties of the sputtered film. Ejected atom energies range from a few tenths of an electron volt up to nearly that of the ions impinging on the target, but because of intense scattering within the discharge, the atoms usually arrive at the substrate with energies of only a few electron volts. Scattering also causes the deposition rate to decrease as the target-to-substrate separation increases. Additionally, the incidence of scattering increases with increasing gas pressure, because the mean-free-path between collisions decreases as the pressure rises. Thermalization of these ejected atoms occurs after the ejected atoms suffer a sufficient number of energy-loss events that their energy is reduced to the thermal energy of the discharge. The distance required for thermalization depends on the pressure, initial atom energy, atomic mass, and several plasma characteristics and is typically a centimeter or less (Ref 12). In low-pressure, high-voltage discharges, the mean free path between collisions is long, and it is therefore possible for a statistically significant number of atoms to reach the substrate with energies in excess of the thermal energy; these atoms are termed *energetic neutrals*. Energetic neutrals can cause additional bombardment of the growing film; however, their energy is difficult to determine and their effect on film properties is not easily understood.

In addition to neutral atom bombardment, auxiliary substrate heating and negative substrate bias voltages are often employed during deposition, and these parameters also influence the microstructure of the growing film. Thornton (Ref 13) and others have examined the influences of substrate temperature and discharge pressure on film microstructure. It has been shown that, in general, increasing substrate temperatures can be associated with a transition from an open columnar arrangement (zone I), to a dense columnar formation (T-zone), to a second dense columnar microstructure (zone II), and, finally, to dense equiaxed grain structure (zone III), as shown in Fig. 3. Thus, increasing the growth temperature causes the density of the films to increase, whereas increasing the pressure produces the opposite effect (Ref 13). Of course, changes in microstructure with pressure are closely related to changes in the thermalization distance and hence the ion/atom energy. Some caution should be exercised in applying such models, because these early models were developed using only scanning electron microscope investigations, and more recent studies using transmission electron microscopy have shown these models to be overly simplistic.

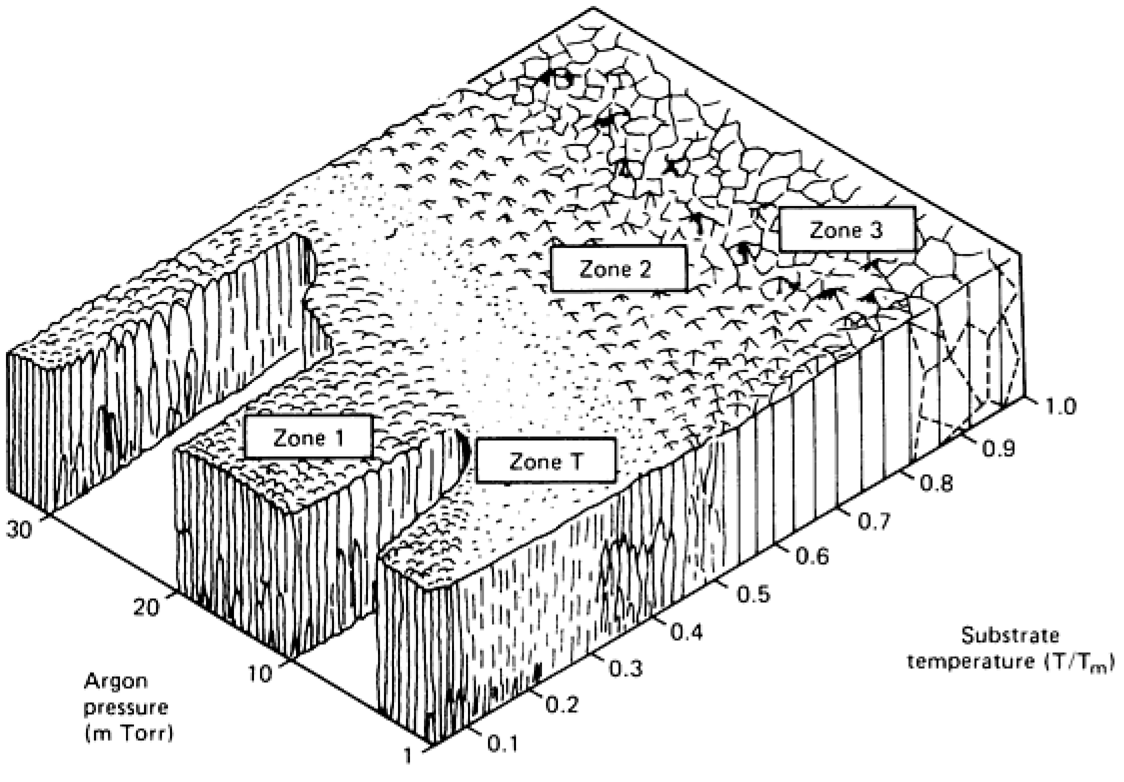


Fig. 3 Microstructural dependence of sputtered thin films on argon pressure and substrate temperature

Microstructural changes similar to those induced by temperature and pressure can be reproduced to some degree by applying a negative bias potential to the substrate during deposition. Under the influence of this negative potential, positively charged ions impact the substrate surface, resulting in increased adatom mobilities, substrate heating, point

defect generation, and so on. In this case, the dense T-zone moves toward lower temperatures with increasing negative bias (Ref 14). This effect has also been shown experimentally; for example, Mattox showed that ion bombardment during the condensation process resulted in increased film density of sputter-deposited refractory tantalum with increasing negative bias (Ref 15, 16). The evolution of film morphology is covered in detail in the article "Growth and Growth-Related Properties of Films Formed by Physical Vapor Deposition Processes" in this Volume.

References cited in this section

3. L.I. Maissel, The Deposition of Thin Films by Cathode Sputtering, *Physics of Thin Films,* G. Hass and R.E. Thun, Ed., Vol 3, Academic Press, 1966, p 61-127
4. G.K. Wehner, Sputtering by Ion Bombardment, *Advances in Electronics and Electron Physics,* Vol 7, Academic Press, 1955, p 239-298
5. C.R. Weissmantel, Deposition of Metastable Films by Ion Beam and Plasma Techniques, *Proc. 9th Int. Vacuum Congress and 5th Int. Conf. on Solid Surfaces* (Madrid), 26 Sept-1 Oct 1983, p 229-308
6. J.L. Vossen and W. Kern, Ed., *Thin Film Processes,* Academic Press, 1978
7. L.I. Maissel and R. Glang, Ed., *Handbook of Thin Film Technology,* McGraw-Hill, 1970
8. R.F. Bunshah, J.M. Blocher, T.D. Bonifield, J.G. Fish, P.B. Ghate, B.E. Jacobson, D.M. Mattox, G.E. McGuire, M. Schwartz, J.A. Thornton, and R.C. Tucker, *Deposition Technologies for Thin Films and Coatings,* Noyes Publications, 1982
9. R.W. Berry, P.M. Hall, and M.F. Harris, *Thin Film Technology,* Van Nostrand, 1968
10. J.J. Cuomo, S.M. Rossnagel, and H.R. Kaufman, Ed., *Handbook of Ion Beam Processes,* Noyes Publications, 1989
11. S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., *Handbook of Plasma Processing Technology,* Noyes Publications, 1990
12. W.D. Westwood, Calculation of Deposition Rates in Diode Sputtering Systems, *J. Vac. Sci. Technol.,* Vol 15 (No. 1), 1978, p 1-9
13. J.A. Thornton, Influence of Apparatus Geometry and Deposition Conditions on the Structure and Topography of Thick Sputtered Coatings, *J. Vac. Sci. Technol.,* Vol 11 (No. 4), 1974, p 666-670
14. R. Messier, A.P. Giri, and R.A. Roy, Revised Structure Zone Model for Thin Film Physical Structure, *J. Vac. Sci. Technol. A,* Vol 2 (No. 2), 1984, p 500-503
15. D.M. Mattox, Fundamentals of Ion Plating, *J. Vac. Sci. Technol.,* Vol 10 (No. 1), 1973, p 47-52
16. D.M. Mattox and G.J. Kominiak, Structure Modification by Ion Bombardment, *J. Vac. Sci. Technol.,* Vol 9 (No. 1), 1972, p 528-532
32. J.L. Vossen and J.J. Cuomo, Glow Discharge Sputter Deposition, *Thin Film Processes,* J.L. Vossen and W. Kern, Ed., Academic Press, 1978, p 12-73

Reactive Sputtering and Process Control

Reactive versus Nonreactive Processes. Both reactive and nonreactive processes may be used in the formation of sputter-deposited films. For nonreactive sputtering, an inert gas, which does not participate directly in the formation of compounds on either the target or the substrate, is used to generate a plasma and sputter material from the target. The inert gas is also sometimes termed the *working gas*. Argon is used in most cases because its mass is high enough to ensure adequate sputtering yields and it is less expensive than xenon or krypton. Although inert gas ions and atoms are not incorporated as primary constituents, incorporation even in very small concentrations can have deleterious effects on film properties. For example, argon incorporation can cause lattice expansions, increasing the internal stress of the films (Ref 17). Additionally, inert-gas ion bombardment of the substrate/film couple using an applied negative-substrate bias can increase inert gas incorporation as well as alter the growth mode, stoichiometry, and properties of deposited films. Nonreactive sputtering processes are common in the deposition of thin metallic overlayers for electron microscopy, industrial-scale deposition of metals and metallic alloys, industrial-scale deposition of some insulators, and research-scale deposition of insulators and compounds. The primary advantage of this type of thin-film deposition is its simplicity.

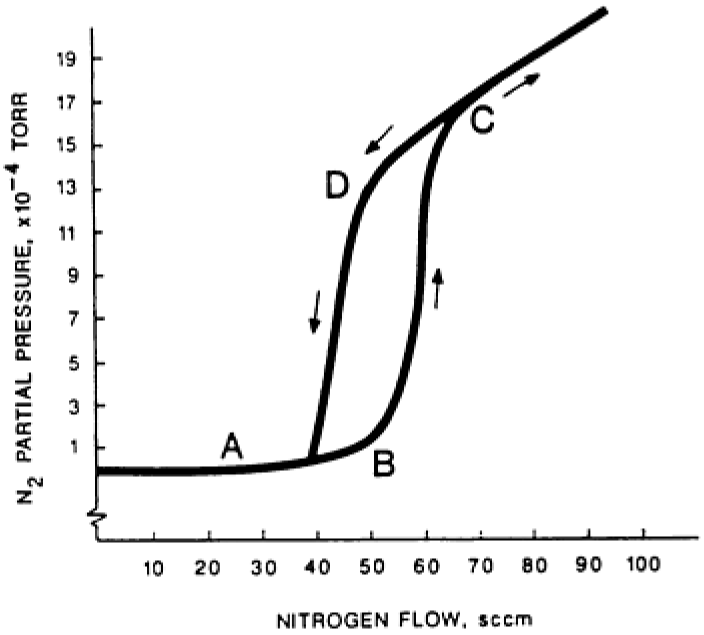
Nonreactive processes can be used to directly sputter compound targets such as TiN, which is used in many decorative and wear-resistant applications. However, this use presents several difficulties: (a) the rate at which The pure metal (titanium) can be sputtered is about an order of magnitude lower than the rate at which pure titanium can be sputtered; (b) off-stoichiometry of the films can occur during deposition; and (c) the thermal conductivity of the compound is often much lower than that of the pure metallic species, and thus the target power must be reduced accordingly due to the heating and fracture of the target. These difficulties often preclude the cost-effective use of nonreactive processes in many applications. In these cases, use of reactive sputtering becomes a necessity.

Reactively sputtered films can be deposited using a variety of methods including dc diode, rf diode, triode, magnetron, and modified rf magnetron sputtering. In any case, there are only two basic reactive sputtering modes: compound-coated cathode and metallic cathode. Sputtering in the compound-coated cathode mode is straightforward: sufficient reactive gas is bled into the chamber during sputtering to form the desired compound on the target surface; this compound is then sputtered off and redeposited on the substrate. In many ways, there is little difference between reactive sputtering in the compound-coated cathode mode and nonreactive sputtering from a compound target. The sputtering rates are usually much lower for compounds because of a reduction in the sputtering yield and an increase in the secondary electron emission that is observed with most compound targets. Additionally, depending on the sputtering technique, materials, and deposition conditions, the film may not possess the same chemical composition as the target material. For these reasons, sputtering in the metallic cathode mode is often preferable.

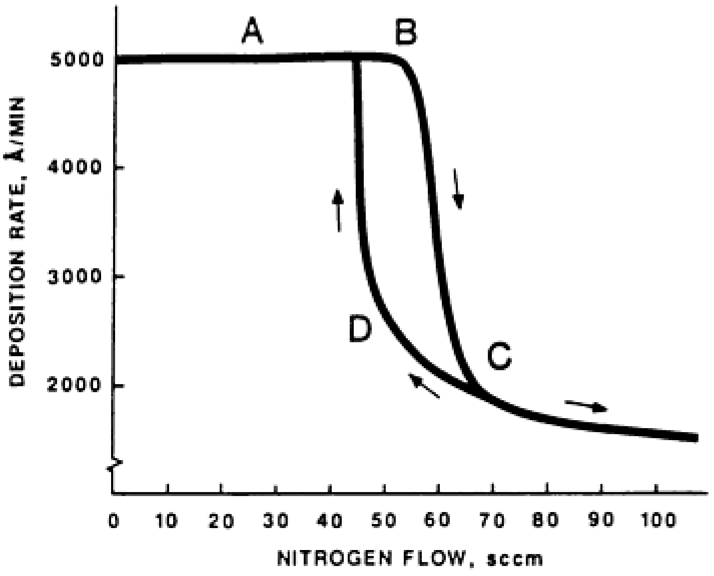
In the metallic cathode mode, the target is maintained as a clean metallic surface and compound formation is limited to the deposited material. Although simple in concept, careful process control is necessary to avoid contamination of the target or deposition of substoichiometric films. Control of the reactive gas species is often costly, requiring at a minimum an automated feedback control and a sensor system to measure partial pressure of the reactive species. However, this is often the only cost-effective means of depositing compound thin-film materials on an industrial scale.

Process Control. The process control necessary for successful reactive sputtering in the metallic cathode mode is often quite difficult to achieve. When flow control is used, the reactive gas is bled into the chamber until there is sufficient gas to form the desired compound at the substrate. However, in most cases this also means that there is sufficient reactive gas present to form the compound on the target surface as well. This phenomenon is known as *poisoning of the target* and generally results in a several-fold decrease in the sputtering rate and, hence, the deposition rate.

During the early 1980s a number of gas-control methods were proposed based on timed or pulsed gas flows. Although they provided significant improvements in the film deposition rates, truly homogenous films are unlikely to result from this type of pulsing technique (Ref 18). The problem is that simple gas flow control does not permit direct control of the partial pressure of the reactive gas species in the chamber. This is illustrated in the hysteresis behavior observed in measuring the reactive gas partial pressure as a function of gas flow, shown for the case of TiN deposition in Fig. 4(a). In this case, stoichiometric TiN is formed under the partial-pressure conditions of point "B." Clearly this exact condition is difficult to maintain by manually pulsing the gas flow, and in the case of slow pulsing, it is likely that the full hysteresis is traveled with each pulse, creating nonstoichiometric layered films.



(a)



(b)

Fig. 4 (a) Nitrogen partial pressure vs. reactive gas flow in a mixed Ar-N_2 discharge under mass flow control, at a target power of 10 kW. (b) Deposition rate vs. flow hysteresis behavior for TiN_x deposition, at a target power of 10 kW, in a mixed Ar-N_2 discharge. Source: Ref 18

As discussed, as the target surface becomes compound coated the deposition rate drops precipitously. This effect can be illustrated by plotting the deposition rate as a function of the reactive gas flow, as shown in Fig. 4(b); again the desired operating conditions are given by point "B." However, the problem of achieving stable operation at point "B," in both Fig. 4(a) and 4(b), is nontrivial because a relatively small increase in flow results in a large decrease in the deposition rate, which is then accompanied by a rapid increase in the partial pressure of the reactive species in front of the target.

This instability is influenced by several other factors. During film deposition at the optimum flow rate, the target can very quickly become completely poisoned if the partial pressure or flow increases slightly, as commonly occurs during slight arcing at the target surface. The consequent decrease in the sputtering rate in turn results in an excess partial pressure of

the reactive gas species in front of the target, creating a circular chain of events that amplifies the initial instability. Another factor fueling this instability is the target power, because the current-voltage requirements of the target change as the target becomes poisoned. In order to avoid driving the process up or down the hysteresis curve, the input current and/or voltage must be adjusted to maintain a constant target power constant.

Associated with this hysteresis effect is the problem of maintaining film stoichiometry. It has been shown that for Ti_xN_{1-x} film microhardness increases monotonically with increasing nitrogen flow rate until stoichiometric TiN is formed (i.e., point "B" in Fig. 4 a and b). Once this optimal nitrogen flow rate is exceeded, the microhardness drops precipitously and the target becomes poisoned (Ref 19). Before film growth can be resumed, intensive "presputtering" is required to return the target surface to a purely metallic state.

A significant advance in process control was the development of automated flow-control systems using a feedback control loop. Sproul and Tomashek introduced the first closed-loop feedback control system in 1984, which monitored the nitrogen peak height obtained from mass spectrometer analysis and generated a feedback signal for a gas flow controller (Ref 20). Because the peak height obtained from the mass spectrometer can be correlated to a certain gas partial pressure within the chamber, this type of automated flow control is, in effect, a partial pressure control system. Similarly, Affinito and Parsons developed a microprocessor-based system to monitor a number of discharge parameters and provide feedback control of the reactive gas. In this case, control of the reactive gas was possible for nitrogen, but not for oxygen (Ref 21). Both of these control systems work well, but in most cases it is necessary to differentially pump the mass spectrometer head, which adds to the cost and complexity of these systems and can also generate undesirable delays in the control process and signal distortions.

Schiller et al. developed a somewhat different control system, the plasma emission monitor (PEM), that uses the optical emission spectra from the target material to produce a feedback signal to control the reactive gas flow and more directly monitor the conditions at the target surface (Ref 22). The optical emission spectra from the plasma near the target is collected using a collimator connected to a quartz fiber. This signal is fed into a monochromator that is linked to a photomultiplier. The photomultiplier outputs an amplified electrical signal to a control unit where the incoming signal level is compared to a preset "optimum" signal level. A control signal is then sent from the control unit to a piezoelectric gas-control valve that is opened or closed in response to a change in the spectral signal. Typically, the optimum reactive gas level is set as some fraction of the spectral peak height of the metallic species. The spectral peak height of pure metal must be measured for each run just prior to the introduction of the reactive gas, and a thin metallic layer may be deposited before the reactive process attains stoichiometry. In some applications this thin metallic underlayer can create a problem; however, this difficulty can be overcome. The primary advantage of the PEM technique is that neither a mass spectrometer nor differential pumping of the sensor is required, so it is less expensive. This and several similar systems are now commercially available.

Another commercially available device for partial-pressure control is the optical gas controller (OGC), which uses the optical emission generated within the sensor from a gas sample drawn directly from the chamber to determine the partial pressure and drive the closed-loop control system at sputtering pressures (Ref 23, 24). Like the PEM system, no mass spectrometer or differential pumping is required. However, unlike the PEM system, the OGC is based on electron-impact ionization spectroscopy. This permits the process gases to be ionized under reproducible conditions within the sensor head, but it also adds the limitation that the sensor must be located very close to the target to provide accurate control (Ref 24, 25, 26, 27).

Alternatively, research by Penfold (Ref 28), Kadlec et al. (Ref 29), and others has shown that the hysteresis effect can be eliminated entirely by increasing the pumping speed of the system beyond a critical level. While successful, this technique is rather expensive in practice, resulting in reduced deposition rates, inefficient gas use, and very high pumping throughput requirements. Whatever the method, effective process control of sputtering is critical in the production of reproducible high-quality thin films at rates that allow them to be commercially competitive with other thin-film processes.

References cited in this section

17. L. Hultman, G. Håkansson, U. Wahlström, J.-E. Sundgren, I. Petrov, F. Adibi, and J.E. Greene, Transmission Electron Microscopy Studies of Microstructural Evolution, Defect Structure, and Phase Transitions in Polycrystalline and Epitaxial $Ti_{1-x}Al_xN$ and TiN Films Grown by Reactive Magnetron Sputter Deposition, *Thin Solid Films,* Vol 205, 1991, p 153-164

18. W.D. Sproul, High Rate Reactive Sputtering Process Control, *Surf. Coat. Technol.,* Vol 33, 1987, p 73-81
19. W.-D. Münz and D. Hofman, Production of Hard Decorative Gold-Colored Titanium Nitride Coatings by Means of High-Power Cathode Sputtering, *Metalloberfläche,* Vol 37 (No. 7), 1983, p 279-285
20. W.D. Sproul and J.A. Tomashek, U.S. Patent 4,428,811, 1984
21. J. Affinitio and R.R. Parsons, Mechanisms of Voltage Controlled, Reactive, Planar Magnetron Sputtering of Al in Ar/N_2 and Ar/O_2 Atmospheres, *J. Vac. Sci. Technol. A,* Vol 2 (No. 3), 1984, p 1275-1284
22. S. Schiller, U. Heisig, Chr. Korndörfer, G. Beister, J. Reschke, K. Steinfelder, and J. Strümpfel, Reactive D.C. High Rate Sputtering as Production Technology, *Surf. Coat. Technol.,* Vol 33, 1987, p 405-423
23. C.A. Gogol, U.S. Patent 4,692,630, 1987
24. C.A. Gogol and R. Mueller, A New Type of Transducer for Partial Pressure Control, *Surf. Coat. Technol.,* Vol 36, 1988, p 939-947
25. W.D. Sproul, P.J. Rudnik, and C.A. Gogol, The Effect of Target Power on the Nitrogen Partial Pressure Level and Hardness of Reactively Sputtered Titanium Nitride Coatings, *Thin Solid Films,* Vol 171, 1989, p 171-181
26. W.D. Sproul, P.J. Rudnik, C.A. Gogol, and R.A. Mueller, Advances in Partial-Pressure Control Applied to Reactive Sputtering, *Surf. Coat. Technol.,* Vol 39/40, 1989, p 499-506
27. W.D. Sproul, P.J. Rudnik, and M.E. Graham, The Effect of N_2 Partial Pressure, Deposition Rate and Substrate Bias Potential on the Hardness and Texture of Reactively Sputtered TiN Coatings, *Surf. Coat. Technol.,* Vol 39/40, 1989, p 355-363
28. A.S. Penfold, Influence of Pump Size on D.C. Reactive Sputtering Systems, *Proc. 29th Ann. Tech. Conf.* (New Orleans), 28 April-2 May, 1986, Society of Vacuum Coaters, 1984, p 381-403
29. S. Kadlec, J. Music, and J. Vysko[ccirc]il, Influence of the Pumping Speed on the Hysteresis Effect in Reactive Sputtering of Thin Films, *Vacuum,* Vol 37 (No. 10), 1987, p 729-738

Sputtering Techniques

Since the discovery of sputtering by W.R. Grove in the mid-1800s, a number of sputter deposition techniques have been developed to deposit thin films of various materials, and much has been written about these techniques (Ref 6, 7, 8, 9, 10, 11, 30, 31). The following section provides a brief overview of several common techniques, including dc diode, rf diode, triode, magnetron, and unbalanced magnetron sputtering.

Diode sputtering is the oldest sputtering technique. A dc diode plasma may be formed by applying a relatively large potential (approximately 300 to 5000 V) between the cathode and anode electrodes in the presence of a sufficient gas density (approximately 10 to 500 μbar). Under a sufficiently large electric potential, the gas atoms between the electrodes become ionized and diffuse through the plasma. However, only the ions in the near-cathode region will "feel" the effect of the potential drop and thus be accelerated across the cathode dark space, impacting the target or cathode surface (see Fig. 1). It is these ions that are responsible for the sputtering.

A common application of dc diode sputtering is the deposition of thin conductive films on samples for electron microscopy. This has two notable advantages:

- A large variety of single- and multi-component target materials can be used.
- It is a simple process, perhaps its greatest advantage.

However, dc diode sputtering also has definite limitations:

- The target must be electrically conductive.
- Deposition rates are generally low.
- Electron bombardment heating of the substrate may be significant because the discharge is not confined.
- Energy efficiency is low because since 75 to 95% of the power supplied to the targets is dissipated through target heating (Ref 32, 33, 34).

Radio-Frequency Sputtering. The use of an oscillating power source to generate a sputtering plasma offers several advantages over dc methods. Principally, when the frequency of oscillation is greater than about 50 kHz, it is no longer necessary for both electrodes to be conductive because the electrode can be coupled though an impedance (Ref 35). The coupled electrode must be much smaller than the direct electrode in order to effectively sputter only the insulating or coupled electrode; this is usually accomplished by connecting the rf generator directly to the grounded chamber walls or substrate fixtures. An impedance matching network is integrated into the circuit between the rf generator and the load to introduce the inductance necessary to form a resonant circuit. It is important in rf systems to provide adequate grounding, minimize the lead lengths, and eliminate any unneeded flange projections to reduce excessive inductive and capacitive losses.

An additional benefit of using rf frequencies above 50 kHz is that the electrons in the negative glow region have sufficient energy to directly ionize the gas atoms; hence, the number of electrons required to sustain the discharge is substantially reduced (Ref 32). This, in turn, means that lower sputtering pressures can be used, reducing the potential for film contamination.

At frequencies above the low megahertz range, the ions, because of their relatively large mass, are no longer able to follow the oscillations of the potential, and, hence, there is little ion accumulation at the cathode (Ref 30). Thus, any frequency above about 5 MHz can be efficiently used for sputtering; however, the most commonly used frequencies are 13.56 and 27 MHz, because these are the FCC-specified frequencies for medical and industrial use (Ref 35). The applications of rf sputtering are quite varied and include deposition of metals, metallic alloys, oxides, nitrides, and carbides (Ref 36, 37, 38).

A number of comprehensive reviews and discussions of rf discharges are available in the literature (Ref 34, 35, 39, 40, 41). In general, the primary advantages of rf sputtering are:

- Ability to sputter insulators as well as almost any other material
- Accessibility of lower operating pressures

Unfortunately, the deposition rates in rf sputtering are often limited by the low thermal conductivity of the insulating target materials. This low thermal conductivity of the materials, leads to the formation of "hot spots" on the target; the hot spots generate stresses that cause fracture of the brittle target materials. For this reason, it may be preferable to deposit insulating films reactively from a metal source. Although compound materials can be readily sputtered in an rf discharge, the resulting films may not be representative of the initial target composition.

Triode sputtering uses a cathode separate from the sputtering target to sustain the plasma. The target electrode then extracts ions from the plasma. This additional electron source, typically either a simple biased conductor or a thermionic electron emitter, provides a means of sustaining the discharge that is independent of the secondary electron generation at the cathode. Thus, the discharge may be maintained at pressures as low as 0.001 Pa (10^{-5} torr) or at discharge voltages as low as 40 V (Ref 42). By varying the emission of the electron source, the discharge current can be varied independently of the sputtering voltage, allowing high ion densities at the target and substrate while maintaining a low discharge potential.

Triode discharges, both dc and rf, have been used successfully to deposit films of a great variety of materials for semiconductor, wear-resistant, optical, and other coating applications (Ref 42, 43, 44, 45, 46, 47, 48, 49). The primary advantages of triode sputtering are:

- Lower discharge pressures
- Lower discharge voltages
- Higher deposition rates
- Independent control of the plasma density and the bombardment conditions of the sputtering target

The major weaknesses of triodes are that they:

- Are often more complicated to use

- Can increase film contamination from the electron source
- Are difficult to scale up for industrial processing
- May not be suitable in temperature-sensitive and reactive processes because of the electron source

Magnetron sputtering differs from other techniques in that most of the plasma is confined to the near-target region. This plasma confinement is achieved by establishing strong magnetic fields above the target surface that reshape the trajectories of the secondary electrons ejected from the target surface into convoluted spiral-like patterns skipping across the surface of the cathode (Fig. 4). In such a magnetic arrangement, the secondary electrons are trapped and most of their energy is expended in the near-target region, increasing ionization and, hence, greatly improving the sputtering and deposition rates. This method is quite successful in producing high-quality, low-impurity films at reasonable deposition rates, and it has seen widespread commercial use since its development in the mid-1970s.

In magnetron sputtering, as for all sputtering techniques, planar target geometries are the most commonly used sources, as illustrated in Fig. 5. Both circular and rectangular planar magnetrons are commercially available in sizes ranging from a 2.5 cm diameter magnetron gun configuration to rectangular cathodes as large as 2 m in length. However, all planar magnetrons tend to erode preferentially in the areas where the magnetic field is parallel to the target surface. This creates a racetrack-like erosion pattern that often leads to an annular distribution of sputtered atoms.

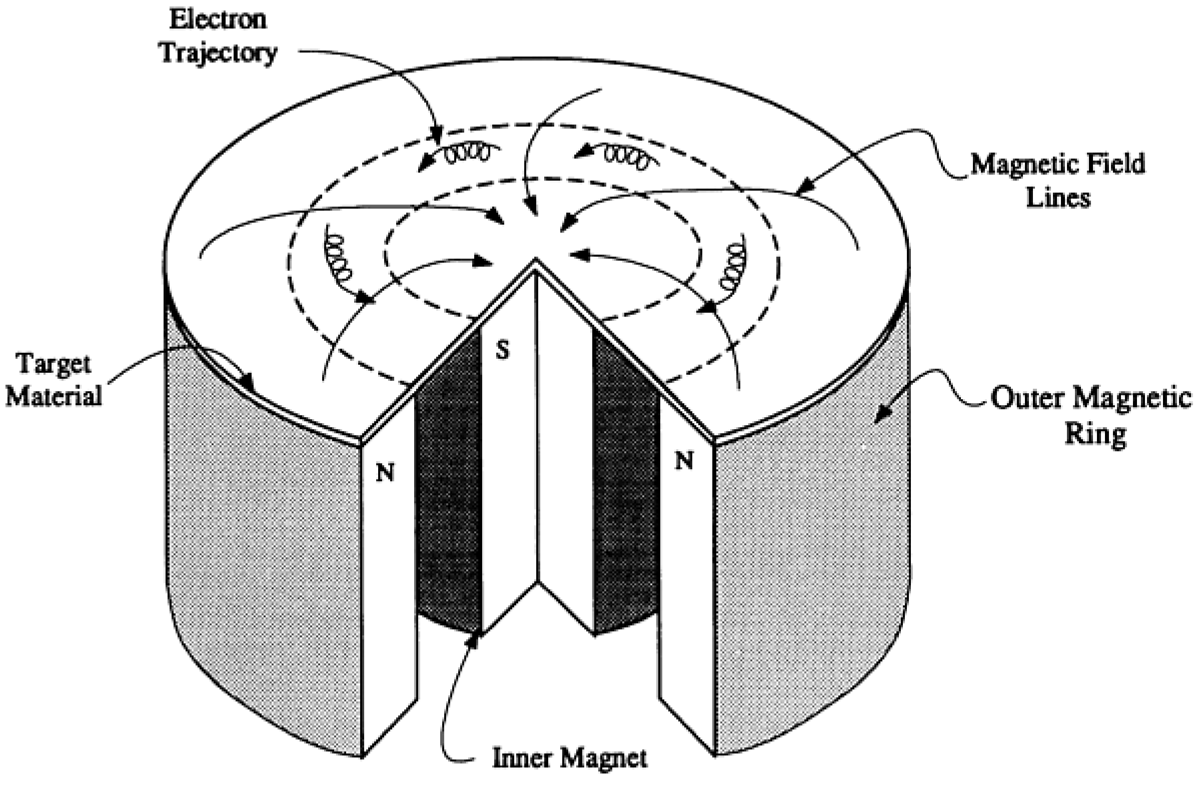


Fig. 5 Circular, planar magnetron cathode schematic, illustrating the magnetic confinement and the resulting electron trajectories

The issue of uneven target erosion has been studied in detail and a number of geometries have been developed to improve target use (Ref 50, 51, 52). For example, cylindrical magnetron geometries (Fig. 6) provide improved target use and typically yield higher sputtering rates, as do most other nonplanar geometries (Ref 53). However, the commercial applications of these magnetron systems has been hampered by the difficulties of producing nonplanar targets and the expense of creating large arrays of shaped magnets. Some of the most successful commercial nonplanar geometries are variations of the rotatable cylindrical cathode (Fig. 6 c, d).

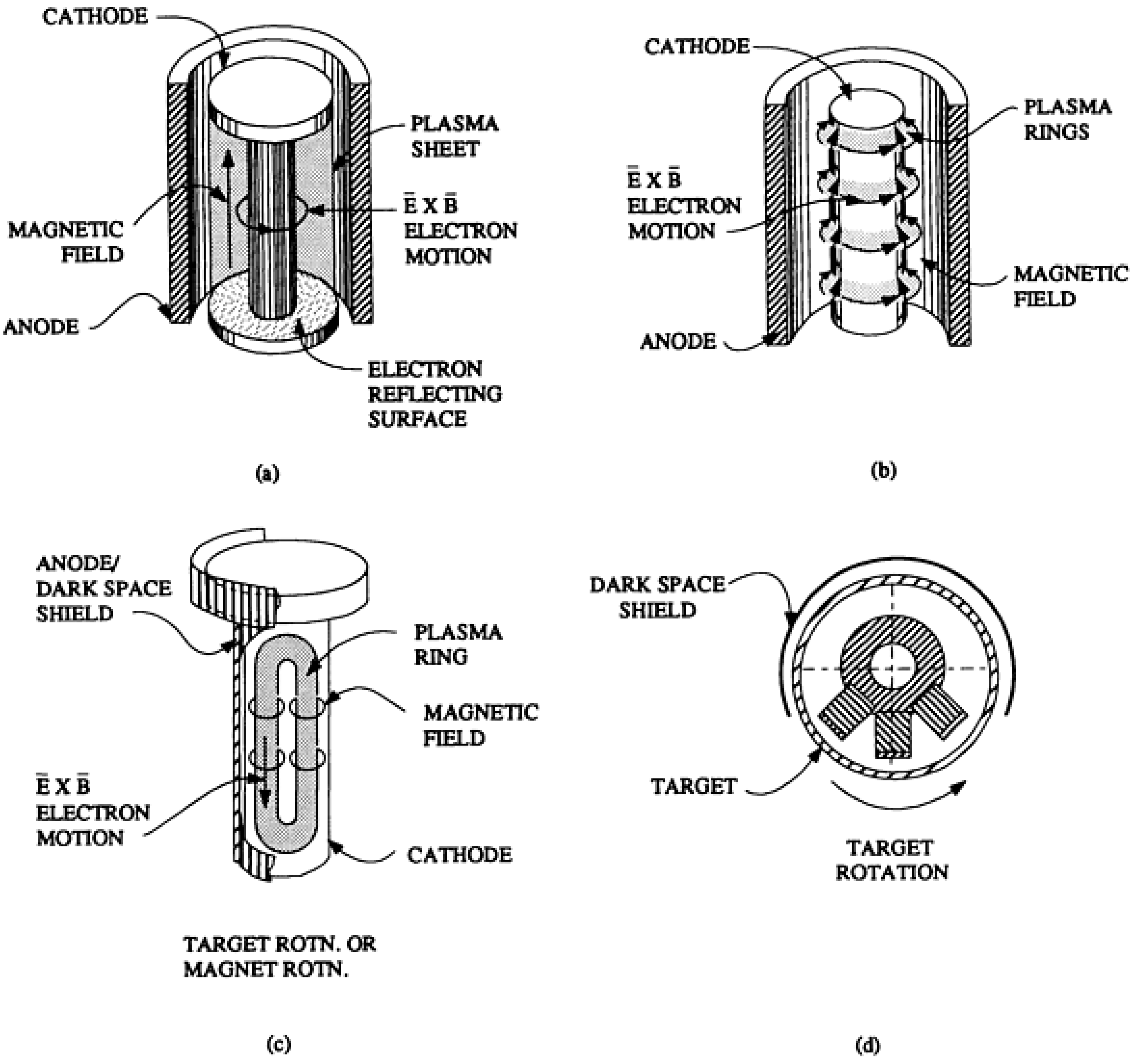


Fig. 6 Schematic illustration of several cylindrical magnetron sources. (a) A cylindrical post magnetron with a longitudinal magnetic field. (b) A cylindrical magnetron with a radial magnetic field. Source: Ref 53. (c) A rotating cylindrical magnetron and (d) its cross section. Source: Ref 54

Additionally, magnetron sources can be operated in triode mode or using an rf power source. For example, a hollow cathode discharge directly in front of the magnetron source can be used as the third electrode of a triode to increase ionization and enhance magnetron performance. However, this type of system suffers from many of the same scale-up difficulties as other triode systems (Ref 55). Additionally, when using an rf discharge voltage, it is important to realize that the magnetron source functions as a "true" magnetron only during a portion of the voltage oscillation. Because the electric field vector varies in amplitude and direction, the forces acting on the electrons in the plasma vary during the cycle, and thus the plasma is no longer confined to the vicinity of the target (Ref 56, 57, 58).

There are several advantages to magnetron sputtering:

- Increased deposition rates (i.e., higher sputtering rates)
- Reduced sputtering from the substrate and chamber walls
- Reduced substrate heating from electron bombardment during deposition
- Reduced "working" gas pressure requirements
- Ease of conversion to industrial-scale processing

Of course, there are also a number of limitations:

- Target use of planar geometries is usually less than 40%
- There may be annular distribution of sputtered atoms, particularly from planar magnetrons
- Porous films may result from large target-to-substrate separations because of reduced electron and ion bombardment at the substrate
- There is inherent nonuniformity in the plasma because of the magnetic fields of the cathode

To overcome some of the line-of-sight limitations that are typical of most sputter processes, a number of magnetron systems have been developed to coat three-dimensional components by sandwiching the components between a face-to-face pair of magnetrons. This technique is very successful as long as the target-to-substrate separation (d_{t-s}) is small; hence the components must also be fairly small. At large d_{t-s} separations, the ion bombardment of the films is frequently insufficient to produce dense film microstructures, and matte, void-containing coatings result.

In general, ion bombardment during deposition can be used to alter favorably the nucleation behavior, growth kinetics, morphology, composition, and mechanical properties of thin films. These effects can be observed as changes in the residual stress, lattice parameter, resistivity, stoichiometry, orientation, film density, and apparent hardness of the resulting films (Ref 59). The extent to which a deposited film is affected by the ion bombardment is dependent on both the kinetic energy and the flux density of the impinging ions, or more correctly the ion-to-deposited-atom ratio and the mass ratio of the ions relative to the surface atoms.

Typically in magnetron sputtering, ions are extracted from the discharge surrounding the substrate by applying a negative potential of 50 to 500 V to the substrate. However, the current density incident on the film-substrate surface is generally quite low, 0.05 to 0.10 ions per deposited atom in conventional dc magnetrons (Ref 60). If this ratio can be increased without increasing the energy of the bombarding ions, denser film microstructures can be produced, while inducing minimal damage within the crystalline lattice. This is desirable because increasing the bias voltage typically results in the generation of defects within the grains and increased film stresses, resulting in poor adhesion and inferior film quality. To circumvent these limitations it would be preferable to increase the ion current density (i.e., the ion-to-deposited-atom ratio) while maintaining a reduced bias voltage, thus keeping the energy of the impinging ions low (Ref 92). In an effort to increase low-energy ion bombardment during film growth a new class of magnetron sources, known as *unbalanced magnetrons*, has been developed.

Unbalanced Magnetron Sputtering. Window and Savvides (Ref 60) introduced the unbalanced magnetron in 1986 in an article that described seven different magnetic configurations and grouped them in three basic types (Fig. 7). The type I magnetron is characterized by a strong inner pole and weak outer pole, and the type II is the converse. The intermediate type is nearly balanced and is typical of most conventional magnetrons. With type I geometry, ion bombardment at the substrate is very limited, resulting in ion-to-deposited-atom ratios as low as 0.25:1. In comparison, the type II geometry gives strongly enhanced ion bombardment, resulting in ion-to-deposited-atom ratios of the order of 2:1 at low substrate bias potentials. Thus, in most applications, only type II unbalanced magnetrons are of commercial interest.

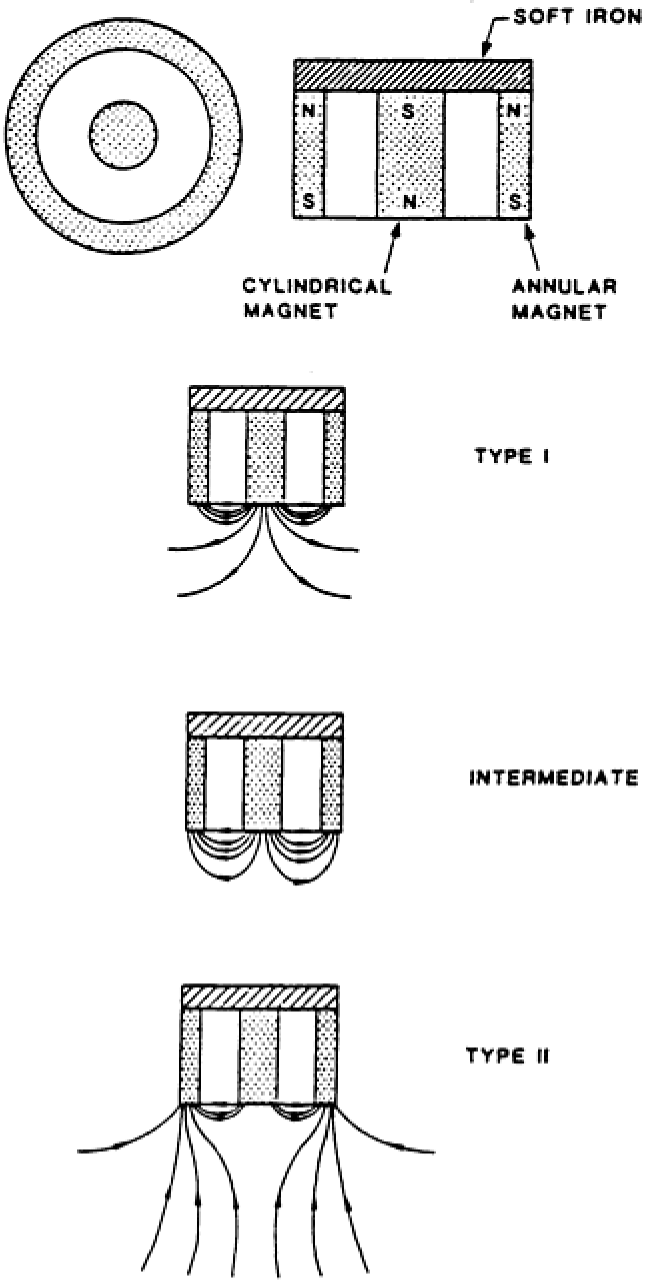


Fig. 7 Three types of magnetron configurations: type I, intermediate, and type II. Source: Ref 60

For unbalanced magnetrons, the ion current density has been shown to increase almost linearly with the discharge current and to be only weakly dependent on the gas pressure (Ref 61). In addition, the degree of "unbalance" and, hence, the ion current density, can be controlled independently of the discharge current by changing the magnetic field configuration (Ref 62, 93).

Several research groups have applied the unbalanced magnetron concept in a variety of sputtering applications, using both permanent magnets and electromagnets (Ref 33, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70). In contrast to the ion-to-deposited-atom ratios for conventional magnetrons, ratios as high as 10:1 have been reported for unbalanced magnetrons, a figure more akin to ion plating processes (Ref 63).

Using a single unbalanced planer magnetron with a pair of electromagnetic coils, Musil and Kadlec (Ref 69) were able to deposit TiN films with ion current densities as high as 6 mA/cm^2 and low substrate bias voltages ranging from -5 to -100 V at target-to-substrate distances of up to 200 mm. This work directly addressed the problem of decreasing substrate ion current density with increasing target-to-substrate distances. In many commercial applications, where it is more cost-

effective to coat large batches of components, the increased ion current density at the substrate provides unbalanced magnetrons with a distinct advantage over conventional magnetrons.

By allowing greater d_{t-s} separations, large multicathode unbalanced systems can be used to coat either large components or numerous smaller parts in a single run. Commercial multicathode systems as large as 1 m in diameter are currently available (Ref 71, 72). The primary restriction on these systems is that there must be an even number of cathodes so that the fields of each unbalanced magnetron cathode can be linked north pole to south pole with the adjacent cathodes. The interrelationship between cathodes is fairly complex because of the magnetic interactions and will differ according to the angle between cathodes (Ref 62). Hence, finite element modeling may be useful in modeling the magnetic interactions before building such systems.

References cited in this section

6. J.L. Vossen and W. Kern, Ed., *Thin Film Processes,* Academic Press, 1978
7. L.I. Maissel and R. Glang, Ed., *Handbook of Thin Film Technology,* McGraw-Hill, 1970
8. R.F. Bunshah, J.M. Blocher, T.D. Bonifield, J.G. Fish, P.B. Ghate, B.E. Jacobson, D.M. Mattox, G.E. McGuire, M. Schwartz, J.A. Thornton, and R.C. Tucker, *Deposition Technologies for Thin Films and Coatings,* Noyes Publications, 1982
9. R.W. Berry, P.M. Hall, and M.F. Harris, *Thin Film Technology,* Van Nostrand, 1968
10. J.J. Cuomo, S.M. Rossnagel, and H.R. Kaufman, Ed., *Handbook of Ion Beam Processes,* Noyes Publications, 1989
11. S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., *Handbook of Plasma Processing Technology,* Noyes Publications, 1990
30. J.A. Thornton, Coating Deposition by Sputtering, *Deposition Technologies for Thin Films and Coatings,* R.F. Bunshah, Ed., Noyes Publications, 1982, p 170-243
31. B. Chapman, Sputtering, *Glow Discharge Process,* Wiley, 1980, p 177-296
32. J.L. Vossen and J.J. Cuomo, Glow Discharge Sputter Deposition, *Thin Film Processes,* J.L. Vossen and W. Kern, Ed., Academic Press, 1978, p 12-73
33. R.P. Howson, H.A. J'afer, and A.G. Spencer, Substrate Effects from an Unbalanced Magnetron, *Thin Solid Films,* Vol 193/194, 1990, p 127-137
34. G.N. Jackson, R.F. Sputtering, *Thin Solid Films,* Vol 5, 1970, p 209-246
35. R.J. Hill, Ed., *Physical Vapor Deposition,* Temscal, 1986
36. J.-E. Sundgren, B.-O. Johansson, and S.-E. Karlsson, Mechanisms of Reactive Sputtering of Titanium Nitride and Titanium Carbide I: Influence of Process Parameters on Film Composition, *Thin Solid Films,* Vol 105, 1983, p 353-366
37. J.-E. Sundgren, B.-O. Johansson, S.-E. Karlsson, and H.T.G. Hentzell, Mechanisms of Reactive Sputtering of Titanium Nitride and Titanium Carbide II: Morphology and Structure, *Thin Solid Films,* Vol 105, 1983, p 367-384
38. J.-E. Sundgren, B.-O. Johansson, S.-E. Karlsson, and H.T.G. Hentzell, Mechanisms of Reactive Sputtering of Titanium Nitride and Titanium Carbide III: Influence of Substrate Bias on Composition and Structure, *Thin Solid Films,* Vol 105, 1983, p 385-393
39. J.L. Cecchi, Introduction to Plasma Concepts and Discharge Configurations, *Handbook of Plasma Processing Technology,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes Publications, 1990, p 14-69
40. J.S. Logan, RF Diode Sputter Etching and Deposition, *Handbook of Plasma Processing,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes Publications, 1990, p 140-159
41. B. Chapman, RF Discharges, *Glow Discharge Processes,* Wiley, 1980, p 139-175
42. S.L. Rohde, S.A. Barnett, and C.-H. Choi, An Ultrahigh Vacuum, Low-Energy Ion-Assisted Deposition System for III-V Semiconductor Film Growth, *J. Vac. Sci. Technol. A,* Vol 7 (No. 3), 1989, p 2273-2279
43. G. Mah, C.W. Nordin, and V.F. Fuller, Structure and Properties of Sputtered Titanium Carbide and

Titanium Nitride Coatings, *J. Vac. Sci. Technol.,* Vol 11 (No. 1), 1974, p 371-373

44. T.C. Tisone and J.B. Bindell, Low-Voltage Triode Sputtering with a Confined Plasma. Part I: Geometric Aspects of Deposition, *J. Vac. Sci. Technol.,* Vol 11 (No. 2), 1974, p 519-527
45. T.C. Tisone and P.D. Cruzan, Low-Voltage Triode Sputtering with a Confined Plasma. Part II: Plasma Characteristics and Energy Transport, *J. Vac. Sci. Technol.,* Vol 12 (No. 5), 1975, p 1058-1066
46. B.E. Nevis and T.C. Tisone, Low-Voltage Triode Sputtering and Backsputtering with a Confined Plasma. Part IV: Heat Transfer Characteristics, *J. Vac. Sci. Technol.,* Vol 11 (No. 6), 1974, p 1177-1185
47. T.C. Tisone and P.D. Cruzan, Low-Voltage Triode Sputtering with a Confined Plasma: Part V--Application to Backscatter Definition, *J. Vac. Sci. Technol.,* Vol. 12 (No. 3), 1975, p 677-688
48. A.G. Fitzgerald, M. Simpson, G.A. Dederski, P.A. Moir, A. Matthews, and D. Tither, Triode Technology in the Sputter Deposition of Carbon Films, *Carbon,* Vol 26 (No. 2), 1988, p 229-234
49. A. Matthews and D.G. Teer, Deposition of Ti-N Compounds by Thermionically Assisted Triode Reactive Ion Plating, *Thin Solid Films,* Vol 72, 1980, p 541-549
50. S. Swann, Spatial Distribution of Sputtered Atoms from a Magnetron Source, *J. Vac. Sci. Technol. A,* Vol 5 (No. 4), 1987, p 1750-1754
51. A.G. Spencer, C.A. Bishop, and R.P. Howson, The Design and Performance of Planar Magnetron Cathodes, *Vacuum,* Vol 37 (No. 3/4), 1987, p 363-366
52. Y. Yong-Kang, A Method of Increasing the Utilization Ratio of Planar Magnetron Sputtering Targets, *Surf. Coat. Technol.,* Vol 37 (No. 3), 1989, p 315-319
53. J.A. Thornton, Magnetron Sputtering: Basic Physics and Application to Cylindrical Magnetrons, *J. Vac. Sci. Technol.,* Vol 15 (No. 2), 1978, p 171-177
54. M. Wright and T. Beardow, Design Advances and Applications of the Rotatable Cylindrical Magnetron, *J. Vac. Sci. Technol. A,* Vol 4 (No. 3), 1986, p 388-392
55. J.J. Cuomo and S.M. Rossnagel, Hollow-Cathode-Enhanced Magnetron Sputtering, *J. Vac. Sci. Technol. A,* Vol 4 (No. 3), 1986, p 393-396
56. W.D. Westwood, Reactive Sputter Deposition, *Handbook of Plasma Processing Technology,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes Publications, 1990
57. R.K. Waits, Planar Magnetron Sputtering, *Thin Film Processes,* J.L. Vossen and W. Kern, Ed., Academic Press, 1978, p 131-173
58. R.K. Waits, Planar Magnetron Sputtering, *J. Vac. Sci. Technol.,* Vol 15 (No. 2), 1978, p 179-187
59. J.E. Greene, S.A. Barnett, J.-E. Sundgren, and A. Rockett, Low-Energy Ion/Surface Interactions during Film Growth from the Vapor Phase, *Beam Modification of Materials,* Vol 3, *Ion Beam Assisted Film Growth,* T. Itoh, Ed., Elsevier, 1989, p 101-152
60. B. Window and N. Savvides, Charged Particle Fluxes from Planar Magnetron Sputtering Sources, *J. Vac. Sci. Technol. A,* Vol 4 (No. 2), 1986, p 196-202
61. B. Window and N. Savvides, Unbalanced D.C. Magnetron as Sources of High Ion Fluxes, *J. Vac. Sci. Technol. A,* Vol 4 (No. 3), 1986, p 453-456
62. S. Rohde, "Metal-Nitride Thin Films Deposited by Unbalanced Magnetron Sputtering," Dissertation, Northwestern University, 1991
63. S. Kadlec, J. Musil, W.-D. Münz, and V. Valvoda, "TiN Films Deposited by the Unbalanced Magnetron," 7th Int. Conf. on Ion and Plasma Assisted Techniques (Geneva, Switzerland), 31 May-2 June 1989
64. N. Savvides and B. Window, Unbalanced Magnetron Ion-Assisted Deposition and Property Modification of Thin Films, *J. Vac. Sci. Technol. A,* Vol 4 (No. 3), 1986, p 504-507
65. B. Window and G.L. Harding, Ion-Assisting Magnetron Sources: Principles and Uses, *J. Vac. Sci. Technol. A,* Vol 8 (No. 3), 1990, p 1277-1282
66. A.G. Spencer, K. Oka, R.P. Howson, and R.W. Lewin, Activation of Reactive Sputtering by a Plasma Beam from an Unbalanced Magnetron, *Vacuum,* Vol 38 (No. 8-10), 1988, p 857-859
67. R.P. Howson, A.G. Spencer, K. Oka, and R.W. Lewin, The Formation and Control of Direct Current Magnetron Discharges for the High-Rate Reactive Processing of Thin Films, *J. Vac. Sci. Technol. A,* Vol 7

(No. 3), 1989, p 1230-1234
68. S. Kadlec, J. Musil, W.-D. Münz, G. Håkanson, and J.-E. Sundgren, Reactive Deposition of TiN Films Using Unbalanced Magnetron, *Surf. Coat. Technol.,* Vol 39/40, 1989, p 487-497
69. J. Musil and S. Kadlec, Reactive Sputtering of TiN Films at Large Substrate to Target Distances, *Vacuum,* Vol 40 (No. 5), 1990, p 435-444
70. R.D. Arnell and R.I. Bates, The Deposition of Highly Supersaturated Metastable Aluminium-Magnesium Alloys by Unbalanced Magnetron Sputtering from Composite Targets, *Vacuum,* Vol 43 (No. 1/2), 1992, p 105-109
71. W.D. Sproul, Multi-Cathode Unbalanced Magnetron Sputtering Systems, *Surf. Coat. Technol.,* Vol 49, 1991, p 284-289
72. W.-D. Münz, The Unbalanced Magnetron: Current Status of Development, *Surf. Coat. Technol.,* Vol 48, 1991, p 81-94
92. I. Petrov, F. Adibi, J.E. Green, L. Hultman, and J.-E. Sundgren, Average Energy per Deposited Atom: A Universal Parameter for Ion-Assisted Film Growth?, *Appl. Phys. Lett.,* Vol 63 (No. 1), 1993, p 36-38
93. I. Petrov, F. Adibi, J.E. Greene, W.D. Sproul, and W.-D. Munz, Use of an Externally Applied Axial Magnetic Field to Control Ion/Neutral Flux Ratios Incident at the Substrate Surface during Magnetron Sputter Deposition, *J. Vac. Sci. Technol. A,* Vol 10 (No. 5), 1992, p 3283-3287

Applications of Sputtered Films

In the fields of microelectronics and optoelectronics, sputtered thin films have been used extensively for:

- Metallization and diffusion barriers in microelectronic circuits (Ref 73, 74, 75)
- Insulating layers in microelectronic circuits
- Thin-film layers in compact disks
- Transparent conducting electrodes
- Thin-film resistors and capacitors
- Piezoelectric transducers
- Amorphous optical films in integrated circuits
- Thin-film lasers
- Memory devices
- High-temperature superconductors

A variety of sputtering techniques can be used in most applications, but rf and magnetron sputtering seem to be most prevalent. Magnetrons are fairly common because they allow very low substrate temperatures. Because most of the above applications are planar in nature, sufficient ion bombardment at the substrate is not an issue. Sputtered thin films are also used extensively in wear-resistant applications such as:

- Decorative coatings on eyeglass frames, watch cases, and other consumer goods (Ref 19, 76)
- Protective coatings on high-speed cutting tools (Ref 77, 78, 79)
- Tribological coatings on bearing surfaces (Ref 80, 81, 82)
- Heat-reflecting optical coatings on architectural glass panels (Ref 83)
- Multilayer dielectric coatings of laser mirrors and filters
- Chromium-base replacements for electrodeposited hard chrome (Ref 84, 85)

Transition metal nitrides, carbides, and oxides such as TiN, TiAlN, CrN, Ta_2O_3, and Al_2O_3 are frequently used in these applications because of their extreme hardness, corrosion resistance, attractive colors, and high spectral reflectance. In decorative applications, for instance, TiN-based films can be tailored to produce the color and brightness of gold but with superior scratch resistance at a reduced cost. With the previously described process control methods, various color values can be preselected and reproduced. In magnetron sputtering, substrate temperatures as low as 150 to 220 °C can be maintained throughout the deposition process, and, thus, temperature-sensitive materials such as electroplated brass, die-

cast zinc, and bronze can be used as substrate materials for decorative coatings. Sputtered decorative coatings are usually deposited in thicknesses ranging from 0.2 to 2 μm.

Although electronic and wear-resistant coatings are the two broadest categories of commercially produced sputtered thin films, there are many other applications. For example, sputter-deposited metallic thin films are widely used as moisture and gas-diffusion barrier coatings on polymer films in the packaging industry. The applications for sputter-deposited thin films continue to broaden in scope each year.

References cited in this section

19. W.-D. Münz and D. Hofman, Production of Hard Decorative Gold-Colored Titanium Nitride Coatings by Means of High-Power Cathode Sputtering, *Metalloberfläche,* Vol 37 (No. 7), 1983, p 279-285
73. M. Wittmer, B. Studer, and H. Melchior, Electrical Characteristics of TiN Contacts to *N* Silicon, *J. Appl. Phys.,* Vol 52 (No. 9), 1981, p 5722-5726
74. M. Wittmer and H. Melchior, Applications of TiN Thin Films in Silicon Device Technology, *Thin Solid Films,* Vol 93, 1982, p 397-405
75. K.Y. Ahn, M. Wittmer, and C.Y. Ting, Investigation of TiN Films Reactively Sputtered Using a Sputter Gun, *Thin Solid Films,* Vol 107, 1983, p 45-54
76. A.J. Aronson, D. Chen, and W.H. Class, Preparation of Titanium Nitride by a Pulsed D.C. Magnetron Reactive Deposition Technique Using the Moving Mode of Deposition, *Thin Solid Films,* Vol 72, 1980, p 535-540
77. W.D. Münz, D. Hofmann, and K. Hartig, A High Rate Sputtering Process for the Formation of Hard Friction-Reducing TiN Coatings on Tools, *Thin Solid Films,* Vol 96, 1982, p 79-86
78. B.M. Kramer, Requirements for Wear-Resistant Coatings, *Thin Solid Films,* Vol 108, 1983, p 117-125
79. H.A. Jehn, S. Hofmann, and W.-D. Münz, Surface and Interface Characterization of Heat-Treated (Ti,Al) N Coatings on High Speed Steel Substrates, *Thin Solid Films,* Vol 153, 1987, p 45-53
80. T.S. Chang, "Tribological Behavior of TiN Coated Rollers," Dissertation, Northwestern University, 1991
81. U. Engel, Development and Testing of New Multilayer Materials for Modern Engine Bearings: Part 1--Copper-Tin Bonding and Intermediate Layers, *Int. Congress and Exposition* (Detroit), 24-28 Feb 1986; Technical paper SP-657, No. 860354, Society of Automotive Engineers, 1986, p 65-74
82. U. Engel, Development and Testing of New Multilayer Materials for Modern Engine Bearings: Part 2--Copper-Lead- Three-Layer Bearings with Sputtered Overlay, *Int. Congress and Exposition* (Detroit), 24-28 Feb 1986; Technical paper SP-657, No. 860648, Society of Automotive Engineers, 1986, p 75-78
83. A.A. Karim, C. Deshpandey, H.J. Doerr, and R.F. Bunshah, Deposition of Tin-Doped Indium Oxide Films by a Modified Reactive Magnetron Sputtering Process, *Thin Solid Films,* Vol 172, 1989, p 111-121
84. A. Aubert, J. Danroc, A. Gaucher, and J.P. Terrat, Hard Chrome and Molybdenum Coatings Deposited by Physical Vapour Deposition, *Thin Solid Films,* Vol 126, 1985, p 61-67
85. W.-D. Münz and J. Göbel, Properties of CrN and (Ti,Al)N Coatings Produced by High Rate Sputter Deposition, *Surf. Eng.,* Vol 3 (No. 1), 1987, p 47-51

Future Trends

In the future, there are certain to be new applications for sputtering technology and new thin-film coatings tailored to special needs. Recently there has been a move away from simple binary alloy coatings into multicomponent coatings to provide increased film "tailorability." This trend can be observed both in microelectronics, with investigations into ternary and quaternary II-V and II-VI systems, and in the area of hard, wear-resistant coatings of TiAlN, TiZrN, and TiVN (Ref 86). For example, for enhanced corrosion resistance for turbine blades, (Ti,Al)N alloys appear very promising as a replacement for the current TiN coatings (Ref 85), especially because the high-temperature oxidation resistance of (Ti,Al)N coatings is also superior.

Multilayer coatings are another area in which there is likely to be continued development in the next decade. These materials are already beginning to see commercial use in optical and wear-resistant applications. Very recently, work

involving polycrystalline metal-nitride superlattice materials has produced films with hardness values in excess of 5000 HV.

It is foreseeable that sputtered chromium nitride coatings will also see increased use, because CrN has mechanical properties and color much like those of traditional electrodeposited hard chrome coatings and, in many applications, provides superior performance. In the past its cost has been prohibitively high, but with growing concern over process safety and environmentally hazardous wastes, sputter deposition processes are becoming increasingly attractive. Hence, the CrN sputter deposition process is an excellent candidate to replace traditional electroplating or chemical vapor deposition processes, at least in high-performance applications of hard chrome.

Improvements in the thermal stability of hard coatings for temperatures up to 800 °C and beyond seem possible in the near future. Development of more stable high-temperature coatings would open up a whole range of new applications.

In the area of decorative coating, there is a demand for distinctive new colors to supplement the well-known golden and black color tones that are currently available.

Although sputtered thin-film materials will continue to be developed, there will be some notable changes in the techniques used to deposit these films. One approach currently under investigation is to combine specific positive aspects from various deposition techniques. For instance, it has been shown that during the etching phase of the arc deposition process, titanium ions penetrate into regions below the substrate surface, forming intermetallic-like compounds and developing a gradually decreasing titanium atom density with depth into the steel substrate (Ref 87). This effect is thought to strengthen the adhesion performance of arc ion-plated coatings. On the other hand, unbalanced magnetron sputtering offers the possibility of depositing dense but rather low-stress coatings (Ref 88). A combination of arc etching and unbalanced magnetron sputter deposition may open new avenues (Ref 89, 90).

Another combined process, sputtering and plasma nitriding, can be used to increase the life of sputter-coated tools. $Ti_{0.5}Al_{0.5}N$ sputter coating of hobs has been shown to produce a sixfold improvement in tool life (Ref 91). After resharpening, however, the improvement decreased to a twofold increase in tool life when compared to the uncoated hobs. Instead of recoating the hobs by sputter deposition after each resharpening step, a simple plasma nitriding treatment was successful in restoring a fourfold increase in tool life. The $Ti_{0.5}Al_{0.5}N$ sputter-deposited coatings did not deteriorate appreciably under repeated plasma nitriding.

Examination of these trends suggests that sputtering processes should continue to hold a strong position among the competing deposition techniques. The environmentally friendly nature of sputtering processes should also make them increasingly attractive in the future.

References cited in this section

85. W.-D. Münz and J. Göbel, Properties of CrN and (Ti,Al)N Coatings Produced by High Rate Sputter Deposition, *Surf. Eng.,* Vol 3 (No. 1), 1987, p 47-51
86. W.-D. Münz, Oxidation Resistance of Hard Wear Resistant TiAlN Coatings Grown by Magnetron Sputter Deposition, *Werkstoffe und Korrosion (Materials and Corrosion),* Vol 41 (No. 12), 1990, p 753-754
87. W.-D. Münz, F.J.M. Hauzer, D. Schulze, and B. Buil, A New Concept for Physical Vapor Deposition Coating Combining the Methods of Arc Evaporation and Unbalanced-Magnetron Sputtering, *Surf. Coat. Technol.,* Vol 49, 1991, p 161-167
88. S. Kadlec, J. Musil, V. Valvoda, W.-D. Münz, H. Petersein, and J. Schroeder, TiN Films Grown by Reactive Magnetron Sputtering with Enhanced Ionization at Low Discharge Pressures, *Vacuum,* Vol 41 (No. 7-9), 1990, p 2233-2238
89. P. Robinson and A. Matthews, Characteristics of a Dual Purpose Cathodic Arc/ Magnetron Sputtering Source, *Surf. Coat. Technol.,* Vol 43/44, 1990, p 288-298
90. Hauzer Holding B.V., European Patent Application PCT/EP90,01032, June 1990
91. M. Zlatanovic and W.-D. Münz, Wear Resistance of Plasma-Nitrided and Sputter-Ion Plated Hobs, *Surf. Coat. Technol.,* Vol 41, 1990, p 17-30

Ion Plating

Donald M. Mattox, IP Industries

Introduction

ION PLATING is a generic term applied to film deposition processes in which the substrate surface and the growing film are subjected to a continuous or periodic flux of energetic massive bombarding particles (ions, radicals, atoms, or molecules--reactive or inert) sufficient to cause changes in the film formation process and the properties of the deposited film (Ref 1, 2, 3, 4). The bombarding species and the depositing species can be from a number of sources. Bombardment can take place in a plasma or vacuum environment. When a beam of energetic particles is used in vacuum, the process is often called ion-beam-assisted deposition (IBAD).

A vacuum can be defined as an environment where the gas density is low and the mean free path for collision is very long. In vacuum-barrel deposition processing, this means that the pressure is lower than about 1.3 mPa (1×10^{-5} torr). A plasma is a low-pressure gas that contains enough ions and electrons to have an appreciable electrical conductivity. This requires a gas pressure of greater than 13 mPa (1×10^{-4} torr). Plasmas can be low-pressure (less than about 0.4 Pa, or 3 mtorr) or higher-pressure (greater than about 0.4 Pa, or 3 mtorr), depending on whether or not collisions in the gas phase are sufficient to "thermalize" high-energy particles leaving a source (Ref 5, 6). This differentiation is important when using sputtering as a source for deposition because reflected high-energy neutrals from the target can have an important effect on the growing film. Figure 1 shows the distance traveled by particles of differing masses (12 and 400 atomic mass unit, or amu) and energies (5 eV, or 0.8 aJ, and 1 keV, or 160 aJ) in argon before becoming thermalized. It should be noted that the gas density in a plasma system can vary with position due to preferential gas motion and particle temperature distribution (Ref 7, 8, 9).

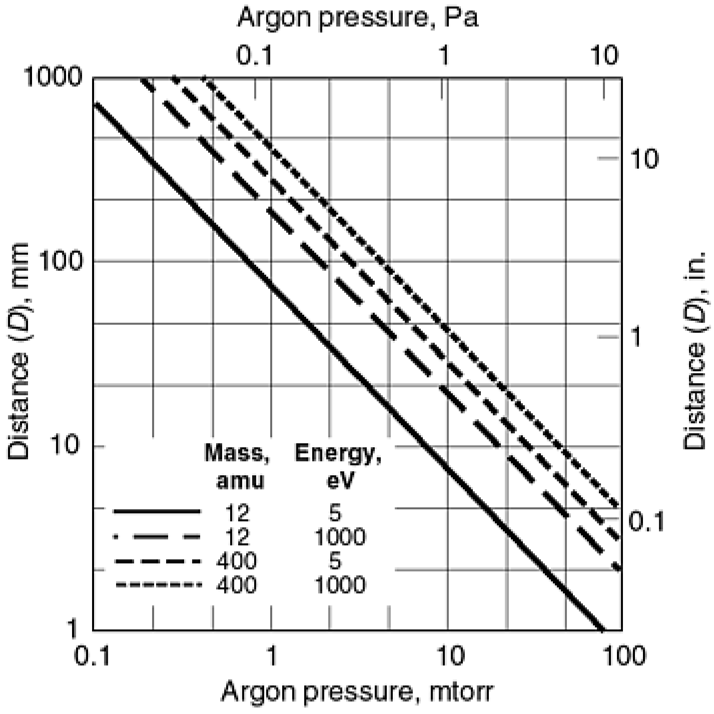


Fig. 1 Plot of distance traveled vs. argon gas pressure to show effect of variations in mass and energy of particles before thermalization. Results calculated from test data obtained at room temperature. Source: Ref 5

There are two basic versions of the ion plating process. In *plasma-based ion plating* the substrate is in contact with a plasma, and the ions are accelerated from the plasma and arrive at the surface with a spectrum of energies. In *vacuum-based ion plating* the film material is deposited in a vacuum and the bombardment is from an ion or plasma "gun." The plasma-based ion plating process was first described in the technical literature in 1963 (Ref 10, 11, 12), and the first reference to vacuum-based ion plating was in 1973 (Ref 13). In *reactive ion plating*, the plasma or ion/plasma gun can

form ions of a reactive species to both bombard and react with the depositing material to form a compound film material. In some cases, such as when using low-voltage, high-current electron-beam evaporation or arc vaporization, an appreciable portion of the vaporized source material can be ionized to allow bombardment by "film ions." Often the term *ion plating* is accompanied by modifying terms such as *sputter ion plating*, *reactive ion plating*, *chemical ion plating*, *alternating ion plating*, *arc ion plating*, and so on, which indicate the source of depositing material, the method used to bombard the film, or other particular conditions of the deposition.

Figure 2(a) shows a simple plasma-based ion plating configuration using a resistively heated vaporization source, and Figure 2(b) shows a simple vacuum-based system using an electron-beam evaporation source. In plasma-based ion plating, the substrate can be positioned in the plasma generation region or in a remote or downstream location outside the active plasma generation region.

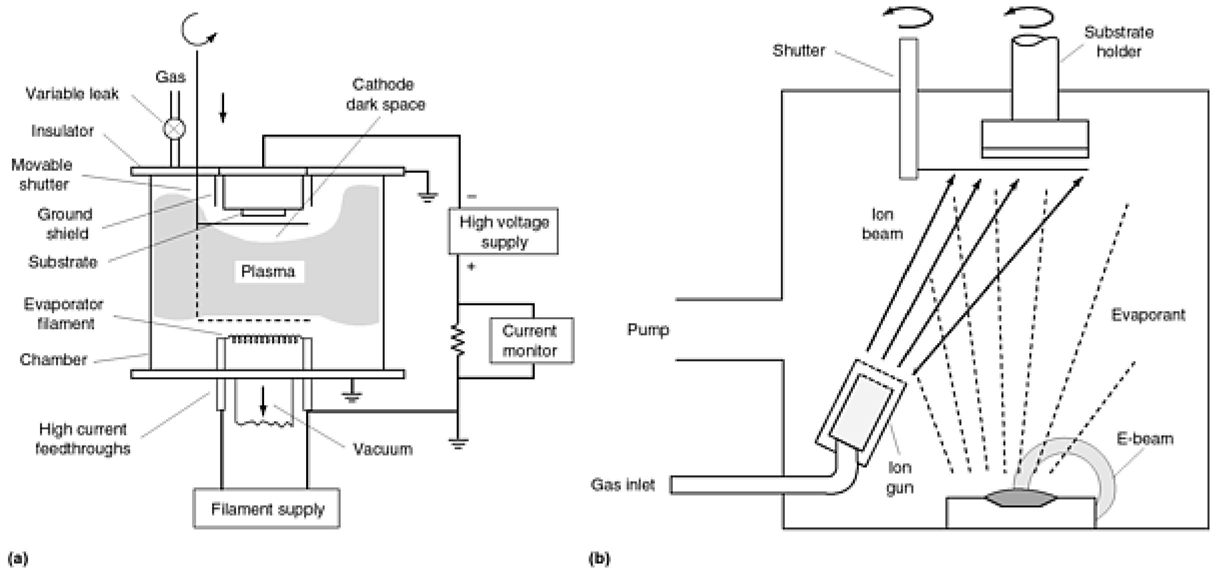


Fig. 2 Schematic showing typical ion plating installations. (a) Plasma-based configuration with resistively heated vaporization source. (b) Vacuum-based configuration with electron-beam evaporation source

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References

1. D.M. Mattox, Fundamentals of Iron Plating, *J. Vac. Sci. Technol.,* Vol 10, 1973, p 47
2. D.M. Mattox, Ion Plating, Chapter 13, *Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Noyes Publications, 1990
3. D.M. Mattox, Chapter 6, *Deposition Processes for Films and Coatings,* 2nd ed., R. Bunshah, Ed., in press
4. N.A.G. Ahmed, in *Ion Plating Technology--Developments and Applications,* John Wiley & Sons, 1987
5. W.D. Westwood, Calculations of Deposition Rates in Diode Sputtering Systems, *J. Vac. Sci. Technol.,* Vol 15, 1978, p 1
6. R.E. Somekh, Thermalizing Collision Calculations, *Vacuum,* Vol 34, 1984, p 987
7. D.W. Hoffman, A Sputtering Wind, *J. Vac. Sci. Technol. A,* Vol 3 (No. 1), 1985, p 561
8. S.M. Rossnagel, Gas Density Reduction Effects in Magnetrons, *J. Vac. Sci. Technol. A,* Vol 6 (No. 1), 1988, p 19
9. A.N. Chester, Gas Pumping in Discharge Tubes, *Phys. Rev.,* Vol 169 (No. 1), 1968, p 172
10. D.M. Mattox, Film Deposition using Accelerated Ions, *Electrochem. Technol.,* Vol 2, 1964, p 295
11. D.M. Mattox, Discussion section, *J. Electrochem. Soc.,* Vol 115 (No. 12), 1968, p 1255
12. D.M. Mattox, "Apparatus for Coating a Cathodically Based Substrate," U.S. Patent 3,329,601, 4 July 1967

13. S. Aisenberg and R.W. Chabot, Physics of Ion Plating and Ion Beam Deposition, *J. Vac. Sci. Technol.,* Vol 10 (No. 1), 1973, p 104

Effects of Bombardment on Film Formation

Film Properties. The properties of a film of a material formed by any physical vapor deposition (PVD) process depend on four factors, namely:

- Substrate surface condition: morphology (roughness, inclusions, particulate contamination), surface chemistry (surface composition, contaminants), surface flaws, outgassing, and so on
- Details of the deposition process and system geometry: angle-of-incidence distribution of the depositing adatom flux, substrate temperature, deposition rate, gaseous contamination, and so on
- Details of film growth on the substrate surface: nucleation, interface formation, interfacial flaw generation, energy input to the growing film, surface mobility of the depositing adatoms, growth morphology of the film (i.e., roughness), gas entrapment, reaction with deposition ambient (including reactive deposition processes), lattice defects produced, grain size and orientation, recoil implantation (atomic peening), and so on
- Postdeposition processing and reactions: reaction of film surface with the ambient, thermal, or mechanical cycling; corrosion; interfacial degradation; burnishing of soft surfaces; shot peening; encapsulation ("topcoat"); and so on

In order to have reproducible film properties, each of these factors must be controlled. Figure 3 depicts the effect of energetic particle bombardment on surfaces and the near-surface region (Ref 14). The near-surface region is defined as the region of physical penetration by the bombarding species and is about 1 nm/keV (10 Å/keV). These effects include:

- Reflection of some of the impinging high-energy particles as high-energy neutrals
- Generation of collision cascades in the near-surface region
- Physical sputtering
- Generation of lattice defects
- Trapping of the bombarding species
- Stuffing of atoms into the lattice by recoil processes
- Recoil implantation of surface species
- Enhanced chemical reactivity (bombardment-enhanced chemical reactivity)
- Enhanced diffusion in the surface region
- Heating of the near-surface region

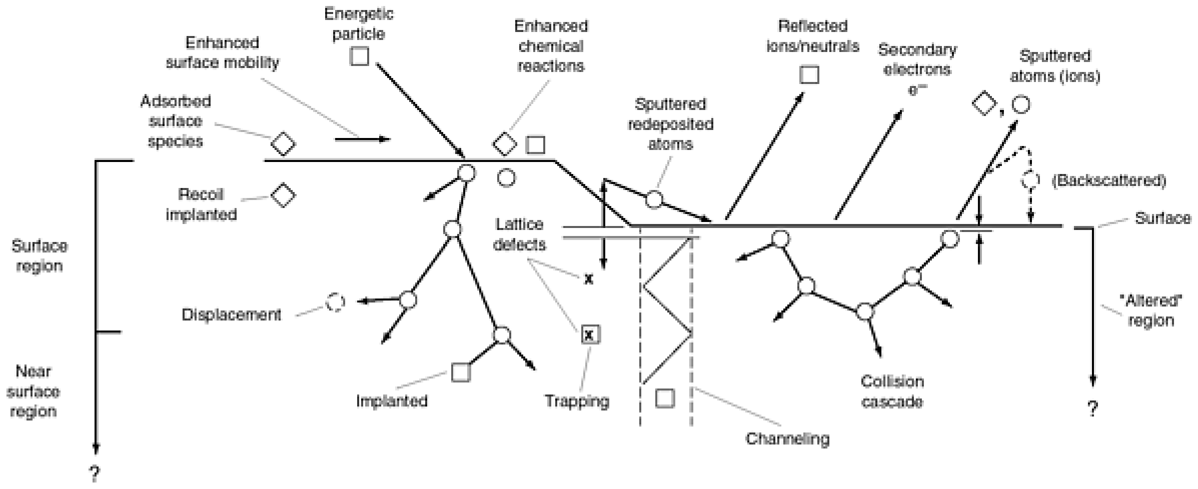

Fig. 3 Schematic showing interactions in the near-surface region and on a surface during massive energetic

particle bombardment. Source: Ref 14

Most of the bombarding energy is given up in the near-surface region in the form of heat. In a growing film that is being concurrently bombarded by energetic particles, the surface and near-surface region is continually being buried and bombardment effects are trapped in the growing film (Ref 14, 15).

Surface Preparation. Bombardment of the substrate surface by energetic particles prior to the deposition of the film material allows in situ cleaning of the surface (Ref 16). Any surface placed in contact with a plasma will assume a negative potential with respect to the plasma (self-bias), due to the more rapid loss of electrons to the surface compared to the loss of ions to the surface. This sheath potential will accelerate ions across the sheath to bombard the surface. The sheath potential that is developed depends on the flux and energy of the electrons striking the surface. For a weakly ionized direct current (dc) plasma, the sheath potential will be several volts. For a system where electrons are accelerated to the surface, the self-bias can be many tens of electron volts. When the surface is conductive, a dc potential can be applied directly to the surface (applied bias). If the surface is nonconductive, a radio frequency (rf) potential can be applied to the surface to give a periodic high negative potential (applied bias) to the surface.

For inert gas ions with less than about 25 eV (4 aJ) energy, cleaning by bombardment is in the form of desorption of volatile materials ("ion scrubbing"). For reactive gases such as hydrogen or oxygen, the cleaning is in the form of reaction with contaminants such as hydrocarbons and desorption of volatile reaction products such as CO or CH_3. Energetic reactive ions produce etching of the surface by reacting with the substrate surface material and producing a volatile compound ("plasma etching") (for example, $SiCl_4$ from bombardment of silicon with an energetic Cl-containing ion from a vapor such as CCl_4) (Ref 17, 18). More energetic inert particles produce physical sputtering ("sputter cleaning").

This in situ cleaning or surface preparation allows good interfacial contact for adhesion (Ref 19) and the generation of ohmic contacts to semiconductor materials. If done at low bombarding energies, the cleaning of semiconductor materials can be done without introducing surface defects that affect the electronic properties of the surface/interface (Ref 20). Bombardment can also make the surface more "active" by the generation of reactive sites and defects. For example, unbombarded silicon surfaces metallized with aluminum show no interdiffusion, but the bombarded surface gives rapid diffusion (Ref 21).

Bombardment can also be used to change the surface properties such as morphology (roughening) or chemical composition. For example, bombardment of a carbide surface by hydrogen ions results in the decarburization of a thin surface layer to produce a metallic surface on the carbide (Ref 22), and bombardment from a nitrogen plasma can be used to plasma nitride a steel surface prior to the deposition of a titanium nitride film (Ref 23, 24).

Nucleation. In ion plating, it is important that bombardment of the substrate surface during the surface preparation stage be continued into the deposition stage, where adatoms (atoms adsorbed on a surface so they will migrate over the surface) are continually being added to the surface. This prevents the surface from being recontaminated. Nucleation of adatoms on the surface is modified by concurrent energetic particle bombardment. This modification can be due to a number of factors, including cleaning of the surface, the formation of defects and reactive sites on the surface, recoil implantation of surface species, and the introduction of heat into the near-surface region (Ref 14, 25). Generally, this modification of nucleation increases the nucleation density. In addition, where there is high energy bombardment, sputtering and redeposition allow nucleation and film formation in areas that would not otherwise be reached by the depositing adatoms.

Interface Formation. Bombardment enhances the formation of a diffusion- or compound-type interface on the "clean" surface if the materials are mutually soluble, or it enhances the formation of a pseudodiffusion-type of interface, due to the energetic particle bombardment, if the materials are insoluble (Ref 14). Interface formation is aided by defect formation and the deposition of energy (heat) directly into the surface without the necessity for bulk heating (Ref 26, 27). In some cases, the temperature of the bulk of the material can be kept very low while the surface region is heated by the bombardment. This allows the development of a very high temperature gradient in the surface region, which limits diffusion into the surface (Ref 28). Ion bombardment along with a high surface temperature can cause all of the depositing material to be diffused into the surface, producing an alloy or compound coating.

Film Growth. Energetic particle bombardment during the growth of the film can modify a number of film properties, including (Ref 14):

- Density

- Bulk morphology
- Surface morphology
- Grain size
- Crystallographic orientation
- Electrical resistivity
- Porosity

The changes in film properties are due to a number of factors, including

- Input of energy into the surface region during deposition
- Forward sputtering and redeposition of deposited atoms that densify the film
- Bombardment-enhanced chemical reaction
- Sputtering of loosely bonded contaminants and unreacted reactive species

Surface Coverage. The macroscopic and microscopic surface coverage of a deposited film on a substrate surface can be improved by the use of concurrent bombardment during film deposition. The macroscopic ability to cover complex geometries depends mostly on scattering of the depositing material in the gas phase (Ref 29, 30). On a more microscopic scale, sputtering and redeposition of the depositing film material will lead to better coverage on micron-sized and submicron-sized features (Ref 31, 32, 33, 34, 35, 36) and to reduced pinhole formation. On the atomic scale, the increased surface mobility, increased nucleation density, and erosion/redeposition of the depositing adatoms will disrupt the columnar microstructure and eliminate the porosity along the columns. As a result, the use of gas scattering, along with concurrent bombardment, increases the surface-covering ability and decreases the microscopic porosity of the deposited film material as long as gas incorporation does not generate voids.

Reactive Deposition. In reactive ion plating, codepositing species, or depositing species and gaseous species, react to form a nonvolatile compound film material (Ref 37). For example, depositing titanium atoms can react with "activated" gaseous nitrogen to form TiN, with codeposited carbon (Ref 38, 39) to form TiC, or with a combination to form TiC_xN_y. In plasma-based ion plating, the plasma activates reactive species and creates new species in the gas phase. The concurrent bombardment of the surface enhances chemical reaction (bombardment-enhanced chemical reactions) (Ref 40, 41, 42, 43), desorbs unreacted adsorbed species (Ref 44), and densifies the film (Ref 45). In general, it has been found necessary to have concurrent bombardment in order to deposit hard and dense coatings of materials. Figure 4 shows the relative effects of heating and concurrent bombardment on the resistivity of ion plated and non-ion plated TiN films (Ref 46, 47).

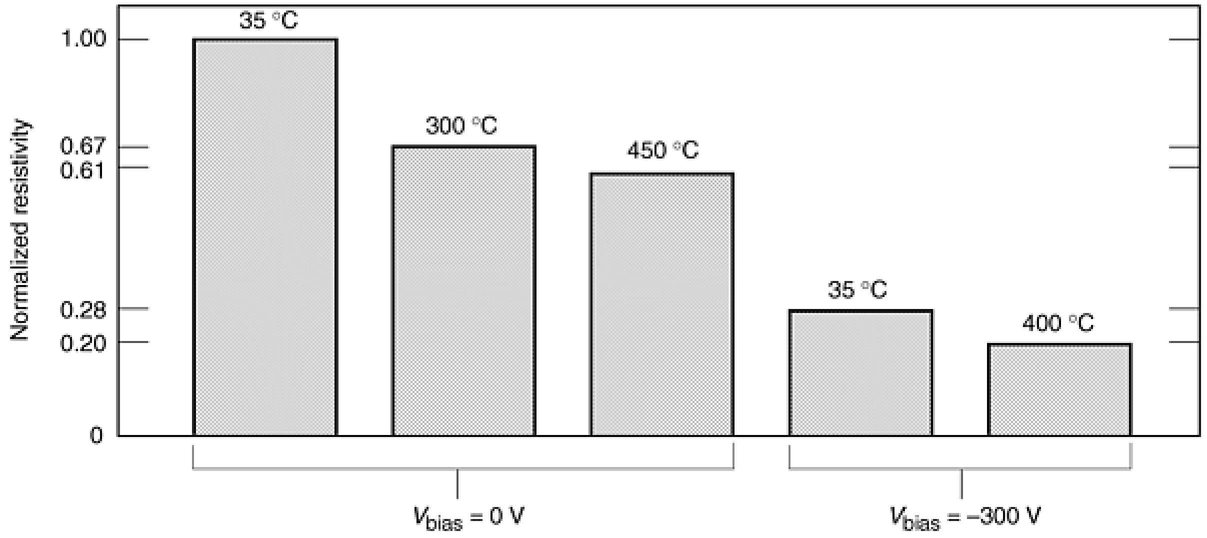

Fig. 4 Relative effect of deposition temperature and bias on reactively sputter-deposited titanium nitride. A lower resistivity rating indicates that the titanium film is more dense (that is, hard) and stoichiometric. Source:

Ref 46

In vacuum-based ion plating, the bombardment of the depositing film by energetic reactive gas ions enhances the chemical reaction (Ref 48, 49). In reactive deposition, the extent of the reaction depends on the plasma conditions, bombardment conditions, and the availability of the reactive species. By limiting the availability, the composition of a deposit can be varied. For example, in the reactive ion plating of TiN, by reducing the availability of the nitrogen in the plasma at the beginning of the deposition, an initial layer of titanium is deposited. The composition can then be graded to TiN by increasing the availability of nitrogen in the plasma, thus forming a "graded" interface.

Properties of Films Deposited by Ion Plating. The properties of films formed by processes depend on a number of factors. Because the ion plating process has more deposition parameter variables than other PVD processes, the film properties can be varied over a wide range, depending on the process parameters.

Film Adhesion. The adhesion of a deposited film to a surface depends on the deformation and fracture modes associated with the failure (Ref 19). Energetic particle bombardment prior to and during the initial stages of film formation can enhance adhesion by:

- Removing contaminant layers
- Changing the surface chemistry
- Generating a microscopically rough surface
- Increasing the nucleation density by forming nucleation sites (defects, implanted species, and recoil-implanted species)
- Increasing the surface mobility of adatoms
- Decreasing the formation of interfacial voids
- Introducing thermal energy and defects directly into the near-surface region, thereby promoting reaction and diffusion

Film adhesion can be degraded by the diffusion and precipitation of gaseous species to the interface. The adhesion can also be degraded by differences in the coefficient of thermal expansion of the film and substrate material in high-temperature processing, or the residual film growth stresses developed in low-temperature processing.

Residual Film Stress. Invariably, atomistically deposited films have a residual stress that may be tensile or compressive in nature and may approach the yield or fracture strength of the materials involved. Generally, vacuum-deposited films and sputter-deposited films prepared at high pressures (>0.7 Pa, or 5 mtorr) have tensile stresses that can be anisotropic, with off-normal angle of incidence depositions. In low-pressure sputter deposition and ion plating, energetic particle bombardment can give rise to high compressive film stresses due to the recoil implantation of surface atoms (Ref 50, 51, 52, 53, 54). This effect is sometimes called *atomic peening* and generally requires 20 to 30 eV (3 to 5 aJ) per deposited atom of additional energy from bombardment. Studies of vacuum-evaporated films with concurrent bombardment have shown that the conversion of tensile stress to compressive stress is very dependent on the ratio of bombarding species to depositing species. The residual film stress anisotropy can be very sensitive to geometry and gas pressure (Ref 55, 56) during sputter deposition, due to bombardment of high-energy reflected neutrals and the effect of gas-phase and surface collisions at higher pressures. Figure 5 shows the effect of gas pressure on residual film stress in postcathode magnetron sputter deposition of molybdenum.

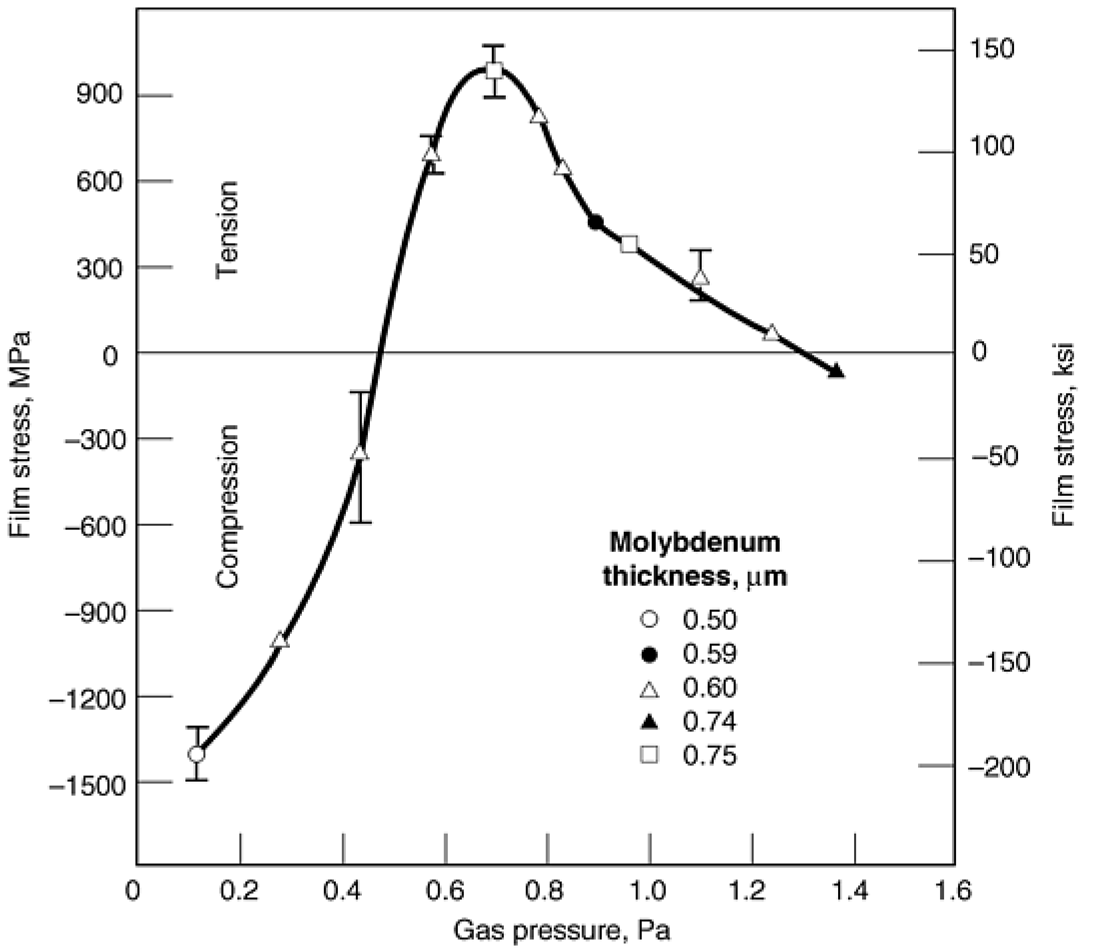

Fig. 5 Effect of gas pressure on residual stress in molybdenum films formed by postcathode magnetron sputter deposition. High compressive stress at low pressures is a result of reflected high-energy neutral bombardment. The low stress at high pressures is a result of columnar growth in a low-density film. Bars on points indicate range of values. Source: Ref 56

The lattice strain associated with the residual film stress represents stored energy, and this energy, together with a high concentration of lattice defects, can lead to:

- Lowering of the recrystallization temperature in crystalline materials
- A lowered strain point in glassy materials
- A high chemical etch rate
- Electromigration enhancement
- Room-temperature void growth in films
- Other such mass transport effects

Film Density. Under nonbombardment conditions at low temperature, the morphology of the deposited material is determined by geometrical effects with the film density being a function of the angle of incidence of the depositing particles. Under ion plating conditions, forward sputtering, sputtering and redeposition, increased nucleation density, and increased surface mobilities of adatoms on the surface under bombardment conditions can be important in disrupting the columnar microstructure and thereby increasing the film density and modifying film properties (Ref 57, 58). The bombardment also improves the surface coverage and decreases the pinhole porosity in a deposited film. This increased density and better surface coverage is reflected in film properties such as (Ref 59, 60, 61):

- Better corrosion resistance

- Lower chemical etch rate
- Higher hardness
- Lowered electrical resistivity of metal films
- Lowered gaseous and water vapor permeation through the film
- Increased index of refraction of dielectric coatings

However, it has been found that if the bombarding species is too energetic and the substrate temperature is low, high gas incorporation, defect concentration, residual stress, and the formation of voids can lead to poor-quality films.

Film Porosity. The porosity in atomistically deposited films results from:

- Incomplete surface coverage
- Deposition on particulate contamination that is subsequently dislodged
- Formation of a columnar film morphology
- Precipitation of voids at grain boundaries
- Precipitation of incorporated gases in the film

The increased surface-covering ability, densification of the film material, and disruption of the columnar morphology in ion plating decrease the film porosity unless bombardment gases are incorporated in the depositing film.

For more information about bombardment effects on film formation, see the article "Growth and Growth-Related Properties of Films Formed by Physical Vapor Deposition Processes" in this Volume.

References cited in this section

14. D.M. Mattox, Particle Bombardment Effects on Thin-Film Deposition: A Review, *J. Vac. Sci. Technol. A,* Vol 7 (No. 3), 1989, p 1105
15. J.M.E. Harper, J.J. Cuomo, R.J. Gambino, and H.R. Kaufman, Modification of Thin Film Properties by Ion Bombardment during Deposition, Chapter 4, *Ion Bombardment Modification of Surfaces--Fundamentals and Applications,* O. Aucello and R. Kelly, Elsevier, 1984
16. D.M. Mattox, Adhesion and Surface Preparation, Chapter 3, *Deposition Technologies for Films and Coatings,* R. Bunshah, Noyes Publications, 1982
17. D.M. Manos and D.L. Flamm, *Plasma Etching: An Introduction,* Academic Press, 1989
18. H.F. Winters, J.W. Coburn, and T.J. Chuang, Surface Processes in Plasma Assisted Etching Environments, *J. Vac. Sci. Technol. B,* Vol 1, 1983, p 469
19. D. Mattox, Thin Film Adhesion and Adhesive Failure--A Perspective, *Adhesion Measurement of Thin Films, Thick Films, and Bulk Coatings,* STP 640, ASTM, Feb 1978, p 54
20. J.L. Vossen, J.H. Thomas III, J.-S. Maa, and J.J. O'Neill, Preparation of Surfaces for High Quality Interface Formation, *J. Vac. Sci. Technol. A,* Vol 2, 1984, p 212
21. L.J. Brillson, Interfacial Chemical Reaction and Diffusion of Thin Metal Films on Semiconductors, *Thin Solid Films,* Vol 89, 1982, p 461
22. D.J. Sharp and J.K.G. Panitz, Surface Modification by Ion, Chemical and Physical Erosion, *Surf. Sci.,* Vol 118, 1982, p 429
23. A. Leland, K.S. Fancey, and A. Mathews, Plasma Nitriding in a Low Pressure Triode Discharge to Provide Improvements in Adhesion and Load Support for Wear Resistant Coatings, *Surf. Eng.,* Vol 7 (No. 3), 1991, p 207
24. S. Dressler, Single Cycle Plasma Nitriding--TiN Deposition for Alloy Steel Parts, *Ind. Heat.,* Vol 59 (No. 10), 1992, p 38

25. R. Miranda and J.M. Rojo, Influence of Ion Radiation Damage on Surface Reactivity, invited review, *Vacuum,* Vol 34 (No. 12), 1984, p 1069
26. A. Matthews and D.T. Gethin, Heating Effects in Ionization-Assisted Processes, *Thin Solid Films,* Vol 117, 1984, p 261
27. A. Matthews, A Predictive Model for Specimen Heating during Ion Plating, *Vacuum,* Vol 32 (No. 6), 1982, p 311
28. R.T. Johnson, Jr. and D.M. Darsey, Resistive Properties of Indium and Indium-Gallium Contacts to CdS, *Solid State Electron.,* Vol 11, 1968, p 1015
29. K.S. Fancey and J. Beynon, The Front:Back Thickness Ratio of Ion-Plated Films, *Vacuum,* Vol 34, 1984, p 591
30. K.S. Fancey and A. Mathews, Ion Plating Processes: Design Criteria and System Optimization, *Surf. Coat. Technol.,* Vol 36, 1988, p 233
31. Y. Homma and S. Tsunekawa, Planar Deposition of Aluminum by RF/DC Sputtering with RF Bias, *J. Electrochem. Soc.,* Vol 132, 1985, p 1466
32. C.Y. Ting, V.J. Vivalda, and H.G. Schaefer, Study of Planarized Sputter-Deposited SiO_2, *J. Vac. Sci. Technol.,* Vol 15, 1978, p 1105
33. D.W. Skelley and L.A. Gruenke, Significant Improvement in Step Coverage using Bias Sputtered Aluminum, *J. Vac. Sci. Technol. A,* Vol 4 (No. 3), 1986, p 457
34. J.K.G. Panitz, B.L. Draper, and R.M. Curlee, A Comparison of the Step Coverage of Aluminum Coatings Produced by Two Sputter Magnetron Systems and a Dual Beam Ion System, *Thin Solid Films,* Vol 166, 1988, p 45
35. R.N. Tait, T. Smy, and M.J. Rett, Simulation and Measurement of Density Variation in Mo Films Sputter Deposited over Oxide Steps, *J. Vac. Sci. Technol. A,* Vol 8 (No. 3), 1990, p 1593
36. D.M. Mattox, *Trans. Soc. Auto. Eng.,* Vol 78, 1969, p 2175
37. D.M. Mattox, Surface Effects in Reactive Ion Plating, *Appl. Surf. Sci.,* Vol. 48/49, 1991, p 540
38. A. Inspektor, U. Carmi, A. Raveh, Y. Khait, and R. Avni, Deposition of Pyrocarbon in a Low Temperature Environment, *J. Vac. Sci. Technol. A,* Vol 4 (No. 3), 1986, p 375
39. R. Avni, U. Carmi, A. Inspektor, and I. Rosenthal, The Role of Hydrogen in the Radical Polymerization Mechanisms of Hydrocarbon and Chlorosilanes in a Low Pressure Microwave Plasma, *J. Vac. Sci. Technol. A,* Vol 3 (No. 4), 1985, p 1813
40. W.D. Westwood, Reactive Sputter Deposition, Chapter 9, *Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes Publications, 1990
41. H.F. Winters, J.W. Coburn, and T.J. Chuang, Surface Processes in Plasma Assisted Etching Environments, *J. Vac. Sci. Technol. B,* Vol 1, 1983, p 469
42. G.A. Lincoln, M.W. Geis, S. Pang, and N. Efremeow, Large Area Ion Beam Assisted Etching of GaAs with High Etch Rates and Controlled Anisotropy, *J. Vac. Sci. Technol. B,* Vol 1, 1983, p 1043
43. H.P.W. Hey, B.G. Sluijk, and D.G. Hemmes, Ion Bombardment: A Determining Factor in Plasma CVD, *Solid State Technol.,* Vol 33 (No. 4), 1990, p 139
44. L.I. Maissel and P.M. Schaible, Thin Films Formed by Bias Sputtering, *J. Appl. Phys.,* Vol 36, 1965, p 237
45. M. Fukutomi, M. Fujitsuka, and M. Okada, Comparison of the Properties of Ion-Plated Titanium Carbide Films Prepared by Different Activation Methods, *Thin Solid Films,* Vol 120, 1984, p 283
46. A.J. Aronson, Sputtering Thin-Film Titanium Nitride, *Microelectron. Manuf. Test.,* Vol 11, 1988, p 25
47. K. Ahn, M. Wittmer, and C.Y. Ting, Investigation of TiN Films Reactively Sputtered using a Sputter Gun, *Thin Solid Films,* Vol 107, 1983, p 45
48. J.M.E. Harper, J.J. Cuomo, and H.T.G. Henzell, Synthesis of Compound Films by Dual Beam Deposition I. Experimental Approach, *J. Appl. Phys.*, Vol 58, 1985, p 550
49. J.J. Cuomo, Synthesis by Reactive Ion Beam Deposition, Conf. Proc., *Ion Plating and Implantation: Applications to Materials,* R.F. Hochman, Ed., American Society for Metals, 1986

50. J.A. Thornton and D.W. Hoffman, Stress Related Effects in Thin Films, *Thin Solid Films,* Vol 171, 1989, p 5
51. A.J. Perry, The State of Residual Stress in TiN Films Made by Physical Vapor Deposition Methods: State of the Art, *J. Vac. Sci. Technol. A,* Vol 8 (No. 3), 1990, p 1351
52. A.J. Perry, A Further Study of the State of Residual Stress in TiN Films Made by Physical Vapor Deposition Methods, *J. Vac. Sci. Technol. A,* Vol 8 (No. 4), 1990, p 3186
53. D.W. Hoffman and J.A. Thornton, Internal Stresses in Sputtered Chromium, *Thin Solid Films,* Vol 40, 1977, p 355
54. D.W. Hoffman and M.R. Gaerttner, Modification of Evaporated Chromium by Concurrent Ion Bombardment, *J. Vac. Sci. Technol.,* Vol 17, 1980, p 425
55. D.M. Mattox and R.E. Cuthrell, Residual Stress, Fracture and Adhesion in Sputter-Deposited Molybdenum Films, Symp. Proc., *Adhesion in Solids,* Vol 119, D.M. Mattox, J.E.E. Baglin, R.E. Gottschall, and C.D. Batich, Ed., Materials Research Society, 1988
56. R.E. Cuthrell, D.M. Mattox, C.R. Peeples, P.L. Dreike, and K.P. Lamppa, Residual Stress Anisotropy, Stress Control and Resistivity in Post Cathode Magnetron Sputter-Deposited Molybdenum Films, *J. Vac. Sci. Technol. A,* Vol 6 (No. 5), 1988, p 2914
57. D.W. Hoffman and R.C. McCune, Microstructural Control of Plasma-Sputtered Refractory Coatings, Chapter 21, *Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes Publications, 1990, p 483
58. R.D. Bland, G.J. Kominiak, and D.M. Mattox, Effects of Ion Bombardment during Deposition on Thick Metal and Ceramic Deposits, *J. Vac. Sci. Technol.,* Vol 11, 1974, p 671
59. C.V. Macchioni, Mechanical Properties of High Deposition Rate SiO_2 Films, *J. Vac. Sci. Technol. A,* Vol 8 (No. 3), 1990, p 1340
60. S. Benhenda, J.M. Guglielmacci, M. Gillet, L. Hultman, and J.-E. Sundgren, Effect of Substrate Bias on the Protective Properties of TiN Films Grown by Reactive Magnetron Sputtering onto Copper Substrates, *Appl. Surf. Sci.,* Vol 40, 1989, p 121
61. H.K. Pulker, Ion Plating as an Industrial Manufacturing Method, *J. Vac. Sci. Technol. A,* Vol 10 (No. 4), 1992, p 1669

Sources of Substrate Potential

The most common versions of ion plating use a potential on the substrate surface to accelerate ions to the surface. The potential on the surface can be applied by several methods.

Applied Bias (dc). A dc potential can be applied directly to an electrically conducting surface. Bombardment will be relatively uniform over flat surfaces where the equipotential field lines are conformal to the surface, but it will vary greatly if the field lines are curved, because ions are accelerated normal to the field lines. The dc discharge that is generated will fill the chamber volume if the pressure is sufficiently high. For pressures too low to establish a dc discharge, a magnetron configuration can be used to enhance the plasma over the surface of a web strip passing over the magnetron surface.

In the application of a dc potential, often the applied voltage and measured current (power expressed in watts/cm^2) to the surface is used as a process parameter and control variable. However, it must be realized that the bombarding ions generally have not been accelerated to the full applied potential due to the position of their formation, charge exchange collisions, and the physical collisions in the gas. The measured current consists of the incident ion flux (the ions may be multiply charged) and the loss of secondary electrons from the surface. The cathode power is a useful process parameter to maintain reproducibility only if parameters such as gas composition, gas pressure, system geometry, and so on are kept constant.

Applied Bias (rf). An rf potential (e.g., 13.56 MHz) must be applied to a surface if the surface is an insulator. Otherwise, charge buildup on the surface will result in arcing over the surface or through the insulating layer if it is thin (Ref 62). When applying an rf potential, the potential of the surface in contact with the plasma will vary continuously, although it will always be negative with respect to the plasma. The dc component of the bias will depend on the presence of blocking capacitance in the circuit and whether a dc bias supply is present. The energy of the ions that bombard the

surface will depend on the frequency of the rf source and the gas pressure. Maximum bombardment energy will be attained at low frequencies and low gas pressures. When using rf sputtering as a vapor source, a different rf frequency and power may be used on the substrate (Ref 63).

The rf bias has the advantage that it can establish a discharge in the space between the electrodes at a pressure lower than that required in a dc bias. It has the limitation that the rf electrode is like a radio antenna, and the plasma density formed over the surface depends on the shape of the substrate/fixture system. In some cases, the substrate/fixture should be surrounded by a "cage" to smooth out the electric field and give a more uniform plasma density. In all cases, ground shields should be kept well away from the rf electrode, and in the case of an insulator, the insulator should completely cover the rf electrode.

Applied Bias--dc plus rf. A dc potential and an rf potential can be applied at the same time if an rf choke is used in the dc circuit to prevent the rf from entering the dc power supply. By applying a dc bias, the insulating surface is exposed to bombardment for a longer period of time during the rf cycle.

Self-Bias. A negative self-bias is induced on an insulating or floating surface due to the higher mobility of the electrons compared to that of the ions. The higher the electron energy, the higher the negative self-bias generated. Figure 6 shows a technique for inducing a high self-bias by accelerating electrons away from a source and magnetically confining them so that they must bombard a substrate surface. It is possible to generate a positive self-bias if the electrons are prevented from bombarding the surface by using a magnetic field, because ions can reach the surface by scattering and diffusion. For example, substrates in a postcathode magnetron sputtering system can have a positive self-bias.

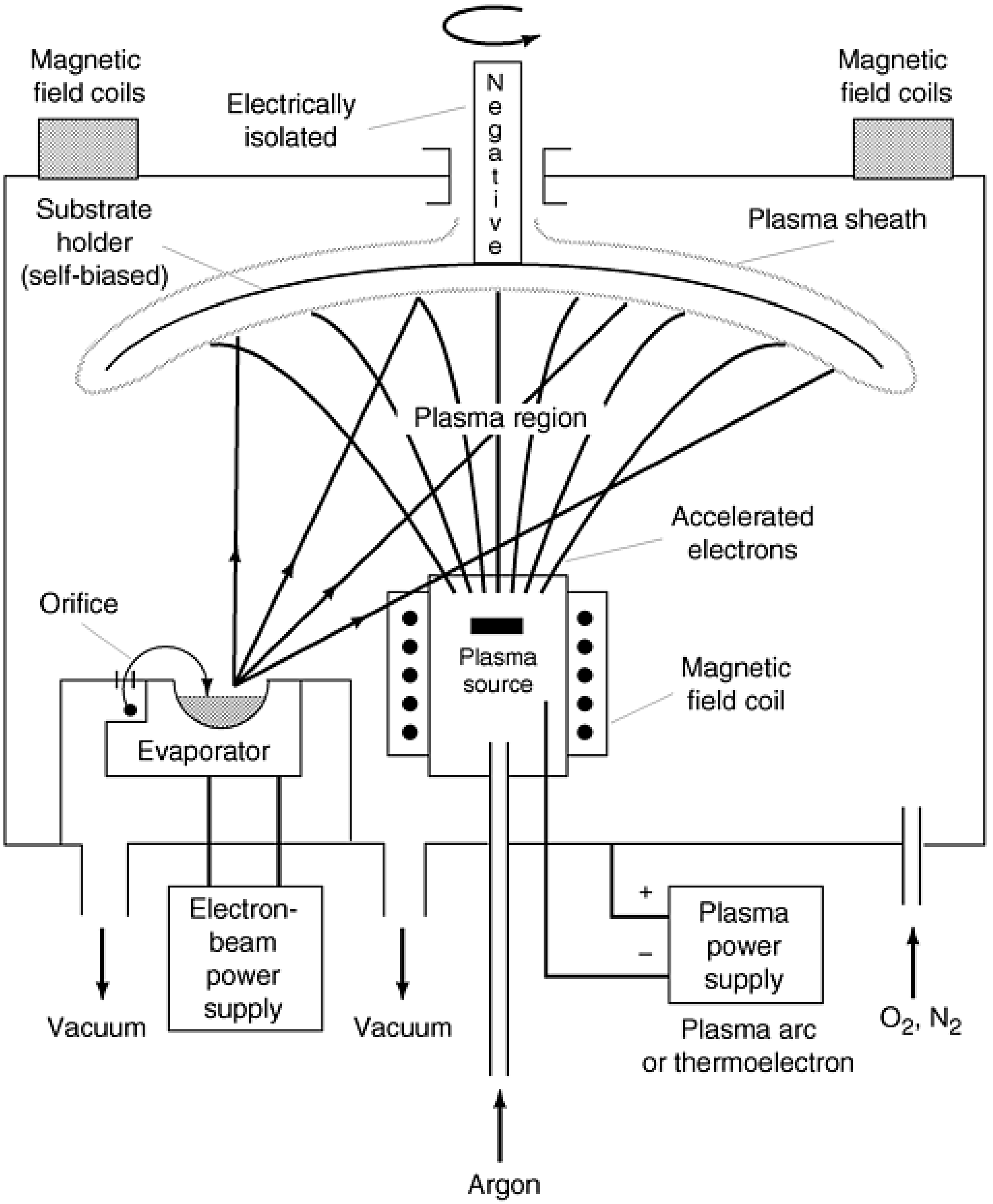

Fig. 6 Generation of a high self-bias and a plasma using accelerated electrons, an electrically isolated substrate holder, and a confining magnetic field. The vaporization source is a differentially pumped e-beam evaporator.

References cited in this section

62. J.S. Logan, RF Diode Sputter Etching and Deposition, Chapter 5, *Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes Publications, 1990

63. H.-D. Lowe, H.H. Goto, and T. Ohmi, Control of the Energy and Flux in a Dual Radio Frequency Excitation Magnetron Sputtering Discharge, *J. Vac. Sci. Technol. A,* Vol 9 (No. 6), 1991, p 3090

Sources of Bombarding Species

The energetic species used to bombard the growing film can be either ions or neutrals, although acceleration of charged ions is the most common way to obtain a controlled bombardment.

Plasmas. A common source of energetic bombarding species is ions accelerated from an inert or reactive gas plasma. The plasma can be formed using a number of configurations. The most common configuration is the dc diode with an

electrically conductive substrate serving as the cathode. When the substrate or depositing film is an electrical insulator, the plasma can be formed by making the substrate an rf electrode in an rf plasma system.

Bombardment can be enhanced by having a superimposed rf and dc potential on the substrate. In some cases, the plasma can be formed by the electrons used to vaporize the source material (Ref 64, 65, 66, 67, 68).

In some cases, auxiliary plasmas are used to provide the ions. Often these auxiliary plasmas are formed using a hot electron-emitting filament (Ref 69), a hollow cathode (Ref 70, 71), or a plasma arc source. The electrons can be confined with a magnetic field, as shown in Fig. 7.

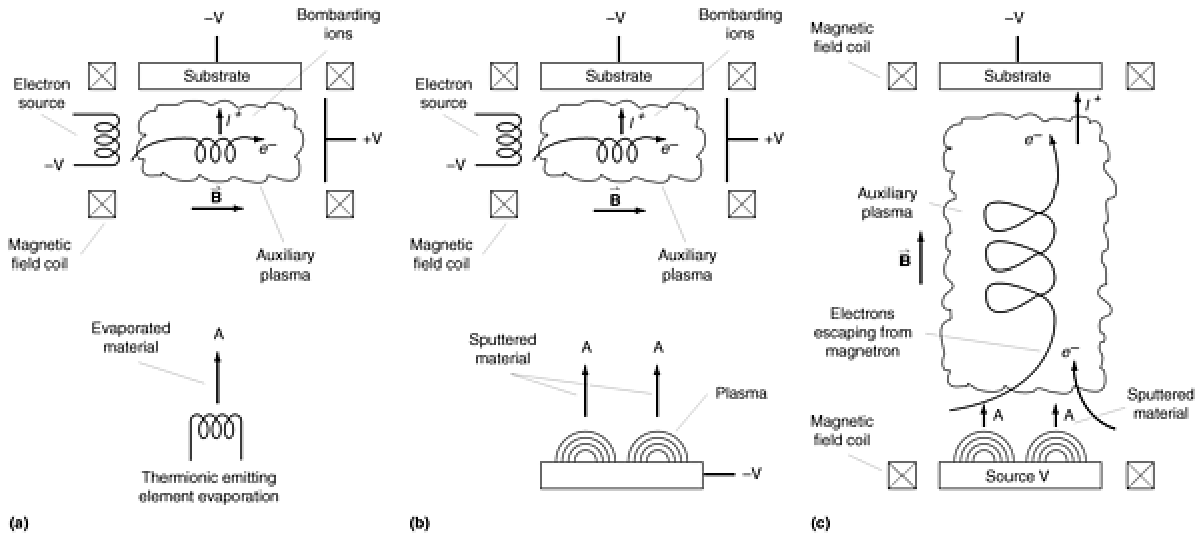

Fig. 7 Schematic showing selected methods used to provide a plasma near the substrate. (a) Hot cathode configuration. (b) Magnetically confined plasma configuration. (c) Unbalanced magnetron configuration

Gas Ions and Film Ions Generated by Arc Sources. Low-voltage, high-current arcs are a source of ions. If the arc is in a vacuum, then the vaporized electrode material is highly ionized and is often multiply charged (Ref 72, 73). In a vacuum, a positive space charge in the plasma between the electrodes accelerates the ions away from the electrodes. If the gas pressure is low, the ion can bombard a surface with appreciable energy. An arc can also be established with a gas present to generate a *plasma arc*. In a plasma arc, both the vaporized material (film ions) and gaseous species are ionized and can be accelerated to bombard the growing film. The ions from the arc can be used to sputter clean the surface at a high particle energy. If the accelerating voltage is high enough, the ion bombardment can prevent any net deposition on the substrate (Ref 65, 74).

High Energy Neutrals. In sputter deposition, ions bombarding a sputtering cathode can be neutralized and be reflected with an appreciable portion of their incident energy. If the gas pressure is low (~< 0.4 Pa, or 3 mtorr, as shown in Fig. 1), the high-energy reflected neutrals can bombard the growing film and affect the film properties (Ref 75, 76).

High-energy neutrals are also formed by charge exchange processes in the higher-pressure dc diode plasma configurations where the substrate is the cathode (Ref 77, 78, 79, 80).

References cited in this section

64. H.K. Pulker, "Methods of Producing Gold-Color Coatings," U.S. Patent 4,254,159, 3 March 1981
65. G. Mah, P.S. Mcleod, and D.G. Williams, Characterization of Silver Coatings Deposited from a Hollow Cathode Source, *J. Vac. Sci. Technol.*, Vol 11, 1974, p 663
66. S. Komiya and K. Tsuroka, Thermal Input to Substrate during Deposition by Hollow Cathode Discharge, *J.*

Vac. Sci. Technol., Vol 12, 1975, p 589

67. S. Komiya, Physical Vapor Deposition of Thick Cr and Its Carbide and Nitride Films by Hollow-Cathode Discharge, *J. Vac. Sci. Technol.,* Vol 13, 1976, p 520
68. Y.S. Kuo, R.F. Bunshah, and D. Okrent, Hot Hollow Cathode and Its Application in Vacuum Coating: A Concise Review, *J. Vac. Sci. Technol. A,* Vol 4, 1983, p 397
69. T.C. Tisone and P.D. Cruzan, Low Voltage Triode Sputtering with a Confined Plasma. Part II: Plasma Characteristics and Energy Transport, *J. Vac. Sci. Technol.,* Vol 12 (No. 5), 1975, p 1058
70. D.T. Lason and H.L. Draper, Characterization of the Be-Ag Interfacial Region of Silver Films Deposited onto Beryllium using a Hot Hollow Cathode Discharge, *Thin Solid Films,* Vol 107, 1983, p 327
71. J.J. Rocca, J.D. Meyer, M.R. Farrell, and G.J. Collins, Glow-Discharge-Created Electron Beams: Cathode Materials Electron Gun Designs and Technological Applications, *J. Appl. Phys.,* Vol 56 (No. 3), 1984, p 790
72. R.L. Boxman and S. Goldsmith, Cathode-Spot Arc Coating: Physics, Deposition and Heating Rates and Some Examples, *Surf. Coat. Technol.,* Vol 33, 1987, p 153
73. R.L. Boxman and S. Goldsmith, Characterization of a 1 kA Vacuum Arc Plasma Gun for Use as a Metal Vapor Deposition Source, *Surf. Coat. Technol.,* Vol 44, 1990, p 1024
74. W.D. Sproul, P.J. Rudnik, K.O. Legg, W.-D. Munz, J. Petrov, and J.E. Greene, Reactive Sputtering in the ABS System, *Surf. Coat. Technol.,* Vol 56, 1993, p 179
75. S.M. Rossnagel, Energetic Particle Bombardment of Films during Magnetron Sputtering, *J. Vac. Sci. Technol. A,* Vol 7 (No. 3), 1989, p 1025
76. D.W. Hoffman, Intrinsic Resputtering--Theory and Experiment, *J. Vac. Sci. Technol. A,* Vol 8 (No. 5), 1990, p 3707
77. J.P. van der Slice, Ion Energies at the Cathode of a Glow Discharge, *Phys. Rev.,* Vol 131, 1963, p 219
78. J. Machet, P. Saulnier, J. Ezquerra, and J. Gulle, Ion Energy Distribution in Ion Plating, *Vacuum,* Vol 33, 1983, p 279
79. P. Saulnier, A. Debhi, and J. Machet, Ion Energy Distribution in Triode Ion Plating, *Vacuum,* Vol 34 (No. 8), 1984, p 765
80. A. Bessaudou, J. Machet, and C. Weismantel, Transport of Evaporated Materials through Support Gas in Conjunction with Ion Plating: I, *Thin Solid Films,* Vol 149, 1987, p 225

Sources of Depositing Species

Thermal Vaporization. The various thermal vaporization sources can be used in ion plating. For plasma-based ion plating, the resistively heated sources are most often used. Low-energy electron-beam heating from hollow cathode sources and thermionic sources can be used, often with a magnetic confining field. This allows the electrons to heat the material to be vaporized and also to create the plasma. High-energy electron-beam heating can be used, but this requires isolating the electron-emitting filament from the plasma by the use of a conductance baffle with a hole to allow the electron beam to enter the plasma/crucible region (differentially pumped e-beam) (Ref 1, 81).

At high vaporization rates, gas phase nucleation generates ultrafine particles in the plasma (Ref 1). These particles become negatively charged, are suspended in the plasma, and do not deposit on the substrate. However, when the plasma is extinguished, the ultrafine particles will deposit on surfaces in the system.

Physical sputtering is often used as a source of depositing material. However, when using dc magnetron sputtering configurations, the plasma is confined in a region near the target and is not available as a supply of ions for substrate bombardment. In this case, the plasma used to supply these ions can be from an unbalanced magnetron configuration, the use of rf in conjunction with the dc magnetron, or the use of an auxiliary plasma source. A hot filament auxiliary plasma source and an unbalanced magnetron plasma source configurations are shown in Fig. 7(a) and 7(c), respectively.

Arc Vaporization. An arc can also be established with a gas present, giving a plasma arc. In a plasma arc, both the vaporized material and gaseous species are ionized (Ref 82, 83, 84). Either a solid cathodic arc surface or a molten anodic arc surface (Ref 85, 86) can be used. Ion species are then accelerated to the substrate under an applied bias. A problem with the cathodic arc vaporization source is that the arc causes the emission of molten globules (that is, macroparticles or macros) that deposit on the film surface. Various techniques are used to eliminate the globules from the plasma. Arc

vaporization sources are widely used in tool coating, even though they present a source of globules. The arc source and a sputtering source can be combined into one design (Ref 87). It has been found that by using the arc discharge for sputter cleaning, the cleaning and heating can be performed much faster than by using a dc diode discharge, due to the high ionization and the multiply charged heavy metal ions in the arc discharge (Ref 88). In addition, the surface smoothness is increased during arc-sputter cleaning (Ref 74). Figure 8 shows some arc-source ion plating configurations.

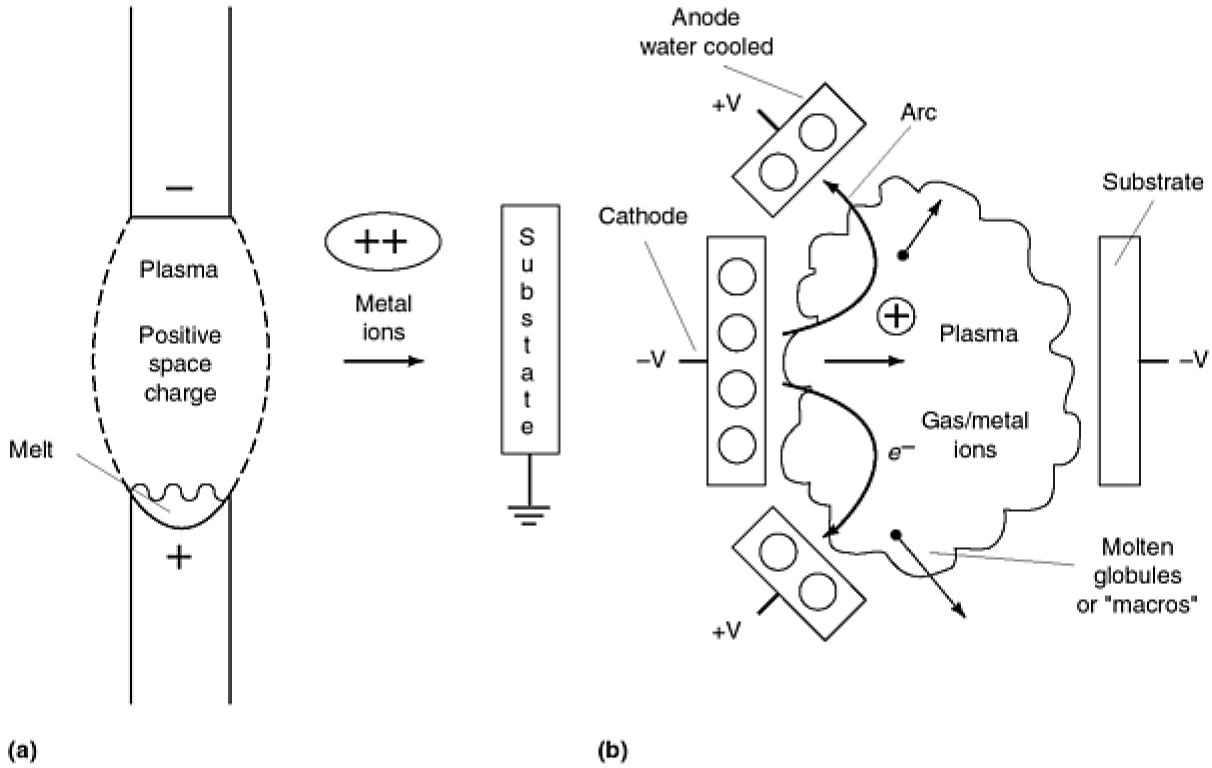

Fig. 8 Typical arc sources used in ion plating. (a) Vacuum arc/molten anode source. In the vacuum, the ions are accelerated away from the positive space charge in the plasma. (b) Cathodic arc vaporization source. In the plasma, the film ions are thermalized in the plasma, but both the film ions and the gas ions are accelerated to the substrate under an applied bias.

Chemical Vapor Precursor Gas. Gaseous chemical vapor precursor species containing the material to be deposited can be used as a deposition source. Using a chemical vapor precursor species in a plasma is very similar to plasma enhanced chemical vapor deposition (PECVD), in which the plasma is used to decompose the chemical species and to bias PECVD where ions from the plasma are accelerated to the substrate surface (Ref 43). Typical chemical vapor precursor gases are $TiCl_4$ for titanium, SiH_4 for silicon, and C_2H_4 for carbon, diamond-like carbon (DLC), and diamond.

The chemical vapor precursor may not be completely dissociated, so that it will deposit a compound material or material that has some of the original compound-forming material in it. For example, SiH_4 can be used to deposit amorphous silicon containing hydrogen. The chemical vapor precursor can be injected into the plasma (Ref 1, 89) in plasma-based ion plating or into a confined plasma ion source in vacuum-based ion plating (Ref 90, 91, 92).

Laser vaporization with concurrent ion bombardment has been used to deposit high-quality high-temperature superconductor films at relatively low substrate temperatures (Ref 93). Laser vaporization creates a large number of ions in the vapor "plume," and these can be accelerated to the substrate surface. This technique has been used to deposit hydrogen-free DLC films (Ref 94).

For more information about sources of depositing species, see the other articles in this Section.

References cited in this section

1. D.M. Mattox, Fundamentals of Iron Plating, *J. Vac. Sci. Technol.,* Vol 10, 1973, p 47
43. H.P.W. Hey, B.G. Sluijk, and D.G. Hemmes, Ion Bombardment: A Determining Factor in Plasma CVD, *Solid State Technol.,* Vol 33 (No. 4), 1990, p 139
74. W.D. Sproul, P.J. Rudnik, K.O. Legg, W.-D. Munz, J. Petrov, and J.E. Greene, Reactive Sputtering in the ABS System, *Surf. Coat. Technol.,* Vol 56, 1993, p 179
81. D.L. Chambers and D.C. Carmichael, Development of Processing Parameters and Electron-Beam Techniques for Ion Plating, *Society of Vacuum Coaters 14th Ann. Tech. Conf. Proc.,* 1971, p 13
82. J. Vyskocil, Cathodic Arc Evaporation in Thin Film Technology, *J. Vac. Sci. Technol.,* Vol 10 (No. 4), 1992, p 1740
83. J. Celis, J.R. Roos, E. Vancoille, S. Boelens, and J. Ebbering, Ternary (Ti,Al)N and (Ti,Nb)N Coatings Produced by Steered Arc Ion Plating, *Met. Finish.,* Vol 9 (No. 4), 1993, p 19
84. D. Sanders, Vacuum Arc-Based Processing, Chapter 18, *Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes Publications, 1990
85. H. Ehrich, B. Hasse, M. Mausbach, and K.G. Muller, The Anodic Vacuum Arc and Its Application to Coating, *J. Vac. Sci. Technol. A,* Vol 8 (No. 3), 1990, p 2160
86. H. Ehrich, B. Hasse, M. Mausbach, and K.G. Muller, Plasma Deposition of Thin Films Utilizing the Anodic Vacuum Arc, *IEEE Trans. Plas. Sci.,* Vol 18 (No. 6), 1990, p 895
87. W.D. Munz, F.J.M. Hauser, D. Schulze, and B. Buil, A New Concept for Physical Vapor Deposition Coating Combining the Methods of Arc Evaporation and Unbalanced-Magnetron Sputtering, *Surf. Coat. Technol.,* Vol 49, 1991, p 161
88. W.D. Sproul, *Surf. Coat. Technol.,* Vol 49, 1991, p 284
89. R. Culbertson and D.M. Mattox, *8th Conf. Tube Technology,* Institute of Electrical and Electronics Engineers, 1966, p 101-107
90. T. Mori and Y. Namba, Hard Diamondlike Carbon Films Deposited by Ionized Deposition of Methane Gas, *J. Vac. Sci. Technol. A,* Vol 1, 1983, p 23
91. S. Shanfield and R. Wolfson, Ion Beam Synthesis of Cubic Boron Nitride, *J. Vac. Sci. Technol. A,* Vol 1 (No. 2), 1983, p 323
92. F. Jansen, D. Kuhman, and C. Taber, Plasma Enhanced Chemical Vapor Deposition using Forced Flow through Hollow Cathodes, *J. Vac. Sci. Technol. A,* Vol 7 (No. 6), 1989, p 3176
93. J. Cheung and J. Horwitz, Pulsed Laser Deposition History and Laser-Target Interactions, *MRS Bull.,* Vol 17 (No. 2), 1992, p 30 (this issue is devoted to laser deposition)
94. F. Davanloo, E.M. Juengerman, D.R. Jander, T.J. Lee, and C.B. Collins, Laser Plasma Diamond, *J. Mater. Res.,* Vol 5 (No. 11), 1990, p 2394

Ion Plating Bombardment Parameters

A variety of ion plating configurations can be used (Fig. 9). Each configuration will have somewhat different parameters that need to be controlled. Ideally, the ion plating parameters that should be controlled are:

- Ion species and ionization state
- Particle energy
- Flux ratio
- Gas composition and mass flow
- Bombardment uniformity
- Substrate temperature
- Gas incorporation
- Fixturing

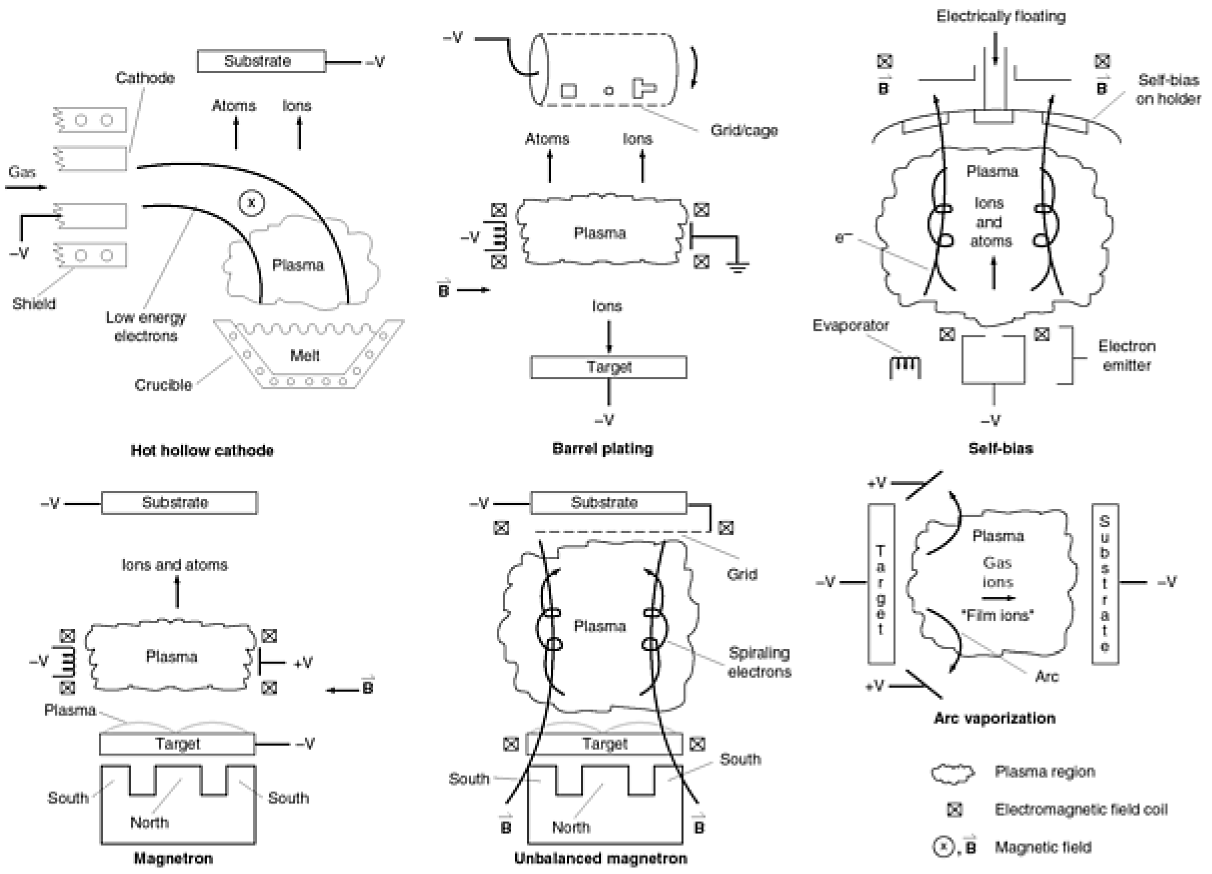

Fig. 9 Typical configurations used in ion plating

Ion Species. The mass of the bombarding species is important to the energy and momentum transferred during the collision. From the laws of conservation of energy and the conservation of momentum, the energy, *E*, transferred by the physical collision between hard spheres is given by:

$$E_t/E_i = 4M_tM_i \cos^2 j \,/(M_i + M_t)^2 \qquad \textbf{(Eq 1)}$$

where *E* = energy, *M* = mass, i = incident particle, t = target particle, and *j* = the angle of incidence as measured from a line joining their centers of masses. The maximum energy transfer occurs when $M_i = M_t$ and the motion is along a path joining the centers ($j = 0°$). In some cases, bombardment by self-ions (that is, ions of the target material) can result in self-sputtering. This occurs when atoms of the sputtered material become ionized and bombard the target.

The most common inert gas species used for plasma formation and ion bombardment is argon, because it is the least expensive of the inert gases. Krypton is sometimes used, and historically mercury was used. Common reactive gases used in plasmas are nitrogen and oxygen. A mixture of inert gas and reactive gas is often used to increase the momentum transfer efficiency in reactive deposition. Helium is sometimes mixed with other gases to increase the thermal conductivity of the gas mixture to aid in substrate cooling.

Particle Energy. The energetic particle energy and energy distribution are important parameters. The energy should be high enough to give appreciable energy transfer on collision, but it should not be high enough to be physically implanted and trapped in the depositing film where it can precipitate and form voids. Neither should it be high enough to cause excessive sputtering. For low-temperature deposition, the ion energy should not exceed about 300 eV (48 aJ). If the substrate is heated to 400 °C (750 °F) or greater, the energy can be increased, because the implanted ions are continually being rapidly desorbed. For low-pressure sputter deposition, the presence of high-energy reflected neutrals from the sputtering target can be an important parameter.

Flux Ratio. The ratio of depositing atoms to bombarding species is important to the film properties. Typically, to complete the disruption of the columnar morphology of the growing film and to obtain the maximum density and least microporosity, the energy deposited by the bombarding species should be about 20 eV (3 aJ) per depositing atom or about 20 to 40% resputtering (Ref 95, 96, 97).

Gas Composition and Mass Flow. Gas composition is an important processing variable in ion plating. In reactive deposition, the gas mass flow can be an important variable that is sensitive to the fixture/system geometry. The gas used for an inert plasma should be free of contaminants (for example, water vapor and oxygen) that will become activated in the plasma. Inert gases can be purified using heated reactive surfaces (for example, titanium or uranium chip beds). Reactive plasmas should be free of contaminants. For example, in reactive gases or gas mixtures, water vapor can be removed by cold traps using zeolite adsorbers.

Mixtures of gases can be used to deposit films having differing compositions and properties such as color. For example, titanium deposited in a nitrogen plasma to form titanium nitride is a gold color, but with a mixture of nitrogen and methane the color can be made bronze, rose, violet, or black as the TiC_xN_y varies in composition.

The gas distribution into the deposition system is an important factor in obtaining uniform bombardments over a surface and uniform activation of a reactive gas.

Bombardment Reproducibility. In vacuum-based ion plating, the ion and atom fluxes can be measured directly by using a Faraday cup ion collector and a mass deposition meter (for example, a quartz crystal deposition monitor). The presence of high-energy reflected neutrals from the sputtering target in the vacuum environment is difficult to measure and can be an unknown processing parameter when a sputtering source is used. In plasma-based ion plating, the ion flux and flux energy distribution are difficult to measure directly. In both vacuum-based and plasma-based ion plating bombardment and deposition, consistency, uniformity, and reproducibility are controlled by having a consistent vaporization source, system geometry, fixture motion, gas composition, gas flow, and substrate power (that is, voltage and current).

Fixturing is often the key to bombardment and deposition uniformity. Fixtures can be in the form of holders that move the substrates or move the deposition sources (Ref 98). Often a three-dimensional object is rotated in front of the deposition source to randomize the deposition angle of incidence, increase uniformity of bombardment, and give a more uniform morphology to the deposit (see the article "Growth and Growth-Related Properties of Films Formed by Physical Vapor Deposition" in this Volume). In some cases, especially when using an rf bias, irregularly shaped objects are surrounded by a grid that is electrically tied to the object, thus giving a smooth equipotential surface around the object. Figure 10 shows the use of a rotating "cage" to hold loose parts to be coated (Ref 99).

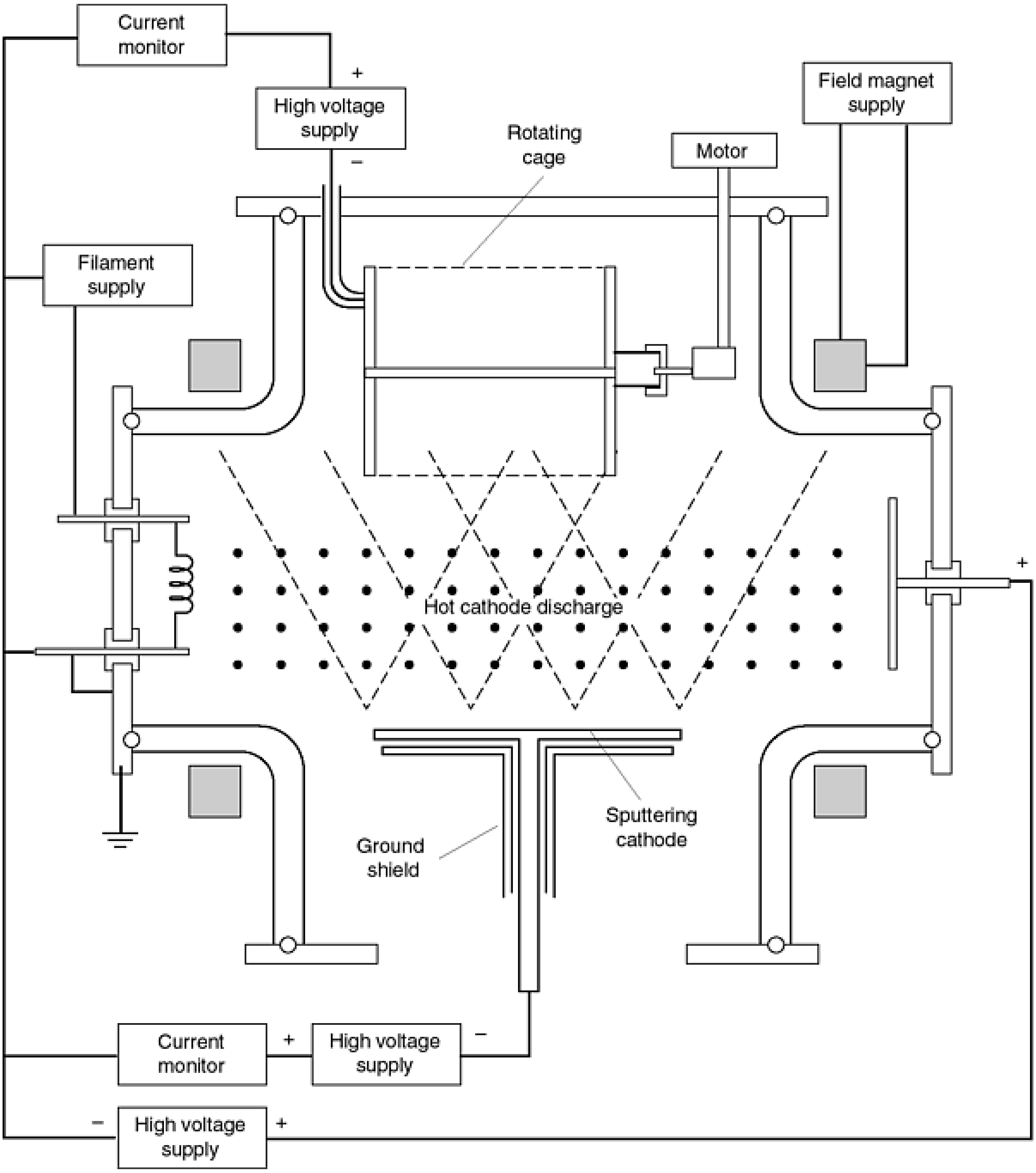

Fig. 10 Schematic showing key components of a barrel-plating configuration used in ion plating. The grid allows the acceleration of ions through the grid-holes to bombard the small parts enclosed within the rotating barrel (cage). Source: Ref 99

Substrate Temperature. In some cases, ion plated films are deposited without deliberate heating of the substrate. This is particularly advantageous when the substrate is thermally sensitive (for example, a plastic). In the extreme, the deposition can be periodic to allow cooling of the substrate between depositions. For example, the substrates can be mounted on a drum and alternately rotated in front of a deposition source and allowed to cool between depositions (Ref 100, 101, 102).

For the highest-density deposit and the most complete reaction, an elevated temperature is generally desirable (Ref 103). Substrate heating can be done by ion bombardment prior to and during deposition (Ref 74), but often a more controllable technique is to have an auxiliary heating source, such as a radiant heater or electron-bombardment heating. In tool coating, for example, the tool is often heated to just below the tempering temperature.

Gas Incorporation. At low substrate temperatures, bombarding gas can be incorporated into the growing film, particularly if the bombarding energy is high. To minimize gas incorporation, the bombarding energy should be kept low (that is, less than 300 eV, or 50 aJ), or a heavy bombarding particle (for example, krypton or mercury) can be used, or the substrate temperature can be kept high (that is, greater than 300 °C, or 570 °F). Low-temperature bombardment can be used to deliberately incorporate gas into the surface of a depositing film. In sputter-ion vacuum pumps, for example, trapping is used to pump inert gases and to incorporate insoluble light and heavy gases in depositing films (Ref 104, 105).

References cited in this section

74. W.D. Sproul, P.J. Rudnik, K.O. Legg, W.-D. Munz, J. Petrov, and J.E. Greene, Reactive Sputtering in the ABS System, *Surf. Coat. Technol.,* Vol 56, 1993, p 179
95. G.K. Hubler, D. Van Vechten, E.P. Donovan, and F.D. Correll, Fundamentals of Ion-Assisted Deposition. II. Absolute Calibration of Ion and Evaporant Fluxes, *J. Vac. Sci. Technol. A,* Vol 8 (No. 2), 1990, p 831
96. J.A. Thornton, The Influence of Bias Sputter Parameters on Thick Copper Coatings Deposited using a Hollow Cathode, *Thin Solid Films,* Vol 40, 1977, p 335
97. D.R. Brighton and G.K. Hubler, Binary Collision Cascade Prediction of Critical Ion-to Atom Arrival Ratio in the Production of Thin Films with Reduced Intrinsic Stress, *Nucl. Instrum. Method Phys. Res. B,* Vol 28, 1987, p 527
98. B.T. Nevill, Ion Vapor Deposition of Aluminum: An Alternative to Cadmium, *Plat. Surf. Finish.,* Vol 80 (No. 1), 1993, p 14
99. D.M. Mattox and F.N. Rebarchik, Sputter Cleaning and Plating Small Parts, *J. Electrochem. Technol.,* Vol 6, 1968, p 374
100. S. Schiller, U. Heisig, and K. Goedicke, Alternating Ion Plating--A Method of High Rate Ion Vapor Deposition, *J. Vac. Sci. Technol.,* Vol 12 (No. 4), 1975, p 858
101. J.W. Seeser, P.M. LeFebvre, B.P. Hichwa, J.P. Lehan, S.F. Rowlands, and T.H. Allen, Metal-Mode Reactive Sputtering: A New Way to Make Thin Film Products, *Society of Vacuum Coaters 35th Ann. Tech. Conf. Proc.,* 1992, p 229
102. "Magnetron Sputtering Apparatus and Process," U.S. Patent 4,851,095, 25 July 1989
103. K. Nakamura, K. Inagawa, K. Tsuruoka, and S. Komiya, Application of Wear-Resistant Thick Films Formed by Physical Vapor Deposition Processes, *Thin Solid Films,* Vol 40, 1977, p 155
104. D.M. Mattox and G.J. Kominiak, Incorporation of Helium in Deposited Gold Films, *J. Vac. Sci. Technol.,* Vol 8, 1971, p 194
105. J.J. Cuomo and R.J. Gambino, *J. Vac. Sci. Technol.,* Vol 14, 1977, p 152

Process Monitoring and Control

The equipment used for ion plating is very similar to that used in sputter deposition (see the article "Sputter Deposition" in this Volume). The exception is that in ion plating, the substrate is a sputtering target and often has a complex configuration that requires fixturing in order to obtain uniformity of bombardment, reactive gas availability, and film deposition. The plasma-based ion plating process is generally made reproducible by duplicating the geometry and process parameters used. The effects of the bombardment are generally determined by the property changes measured after deposition.

The amount of bombardment is often quoted as the amount of resputtering or the amount of energy per deposited atom that is added by the bombardment. Typically, for the maximum densification about 20 eV (3 aJ) per deposited atom must be added by bombardment. To avoid gas incorporation at low substrate temperatures, the bombardment energy should be less than 300 eV (50 aJ), which means that there must be about one high-energy particle to ten depositing atoms. Another measure of the bombardment is the resputtering rate of the film. Typically a resputtering rate of 20 to 30% is needed for full densification (Ref 96).

When using the IBAD configuration, the ion plating variables can often be measured directly. For example, in a grid-extraction ion gun, the ion energy is determined by the extraction grid voltages and the ion flux can be measured using a

Faraday cup. In the vacuum environment, the deposition rate can be easily monitored using a quartz crystal deposition monitor.

Reference cited in this section

96. J.A. Thornton, The Influence of Bias Sputter Parameters on Thick Copper Coatings Deposited using a Hollow Cathode, *Thin Solid Films,* Vol 40, 1977, p 335

Advantages and Limitations of Plasma-Based Ion Plating

Plasma-based ion plating is the most commonly used ion plating configuration.

Advantages of plasma-based ion plating (Ref 1, 2, 106) include:

- Excellent surface-covering ability ("throwing power") under the proper conditions
- Ability to have in situ cleaning of the substrate surface
- Ability to introduce heat and defects into the first few monolayers of the surface to enhance nucleation, reaction, and diffusion
- Ability to obtain good adhesion in many otherwise difficult-to-deposit systems
- Enhancement of reactive deposition process (activation of reactive gases, bombardment-enhanced chemical reaction, and adsorption of reactive species)
- Flexibility in tailoring film properties by controlling bombardment conditions (for example, morphology, density, and residual stress)
- Equipment requirements are equivalent to those of sputter deposition
- Source of depositing material can be from thermal vaporization, sputtering, or chemical vapor precursor gases

Limitations of plasma-based ion plating include:

- Many processing parameters must be controlled
- Contamination can be released from surfaces and "activated" in the plasma to become an important process variable
- To bombard growing films of electrically insulating materials, the surfaces must either attain a self-bias or must be biased with an rf potential
- Processing and "position equivalency" can be very dependent on substrate geometry and fixturing (that is, obtaining uniform bombardment and reactive species availability over a complex surface may be difficult)
- Bombarding gas species can be incorporated in the substrate surface and deposited film if too high a bombarding energy is used
- Substrate heating can be excessive
- High residual compressive growth stresses can be introduced into the film layer

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References cited in this section

1. D.M. Mattox, Fundamentals of Iron Plating, *J. Vac. Sci. Technol.,* Vol 10, 1973, p 47

2. D.M. Mattox, Ion Plating, Chapter 13, *Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Noyes Publications, 1990

106. H.K. Pulker, in *Coatings on Glass,* Elsevier, 1984, p 250

Applications of Ion Plating

Typical applications of the ion plating process include:

- Good adhesion between a film and substrate (for example, silver on steel for mirrors, silver on beryllium for diffusion bonding) (Ref 65)
- Electrical conductive layers (aluminum, silver, and gold) on plastics and semiconductors
- Low-shear solid film lubricants (for example, silver and gold) (Ref 107)
- Wear and abrasion-resistant coatings [for example, TiN, TiC_xN_y, $(Ti\text{-}Al)C_xN_y$, $Ti_{0.5}Al_{0.5}N$] on cutting tools (Ref 74), dies, molds, and jewelry
- Decorative coatings (TiN yields gold-colored deposit, TiC_xN_y yields rose-colored deposit, TiC yields black deposit, ZrN yields brass-colored deposit) applied to hardware, jewelry, guns (Ref 108), and cutlery
- Corrosion protection [aluminum on uranium (Ref 109); mild steel (Ref 110, 111) and titanium; carbon and tantalum on biological implants]
- Deposition of electrically conductive diffusion barriers (for example, HfN and TiN on semiconductor devices)
- Deposition of insulating films (for example, SiO_2 and ZrO_2)
- Deposition of optically clear, electrically conducting layers (indium-tin-oxide) (Ref 112)
- Deposition of permeation barriers on webs (Ref 113, 114, 115)

Ion plating has also been used to coat very large structural parts with aluminum for corrosion protection (replacing cadmium) (Ref 104).

Ion plating provides a means of modifying film properties that does not exist in other PVD techniques. This gives it a place in the range of PVD deposition techniques available for "surface engineering." Often the applications of ion plating are very substrate-specific, so that fixturing is a very important consideration in coating uniformity, unit cost, and cost-of-ownership for a specific application. The ability to devise an optimal fixture design is often the key to a successful process.

References cited in this section

65. G. Mah, P.S. Mcleod, and D.G. Williams, Characterization of Silver Coatings Deposited from a Hollow Cathode Source, *J. Vac. Sci. Technol.,* Vol 11, 1974, p 663

74. W.D. Sproul, P.J. Rudnik, K.O. Legg, W.-D. Munz, J. Petrov, and J.E. Greene, Reactive Sputtering in the ABS System, *Surf. Coat. Technol.,* Vol 56, 1993, p 179

104. D.M. Mattox and G.J. Kominiak, Incorporation of Helium in Deposited Gold Films, *J. Vac. Sci. Technol.,* Vol 8, 1971, p 194

107. T. Spalvins, A Review of Recent Advances in Solid Film Lubricants, *J. Vac. Sci. Technol. A,* Vol 5, 1987, p 212

108. E.S. Kincel, A Coat of Many Colors, *Gun World,* March 1993, p 23

109. D.M. Mattox and R.D. Bland, Aluminum Coating of Uranium Reactor Parts for Corrosion Protection, *J. Nucl. Mater.,* Vol 21, 1967, p 349

110. D.E. Muehlberger, Applications of Ion Vapor Deposited Aluminum Coatings, Conf. Proc., *Ion Plating and Implantation,* R.F. Hochman, American Society for Metals, 1986, p 75

111. B.T. Nevill, Ion Vapor Deposition of Aluminum: An Alternative to Cadmium, Plat. Surf. Finish., Vol 80 (No. 1), 1993, p 14

112. H.K. Pulker, in *Coatings on Glass,* Elsevier, 1984, p 253

113. M.I. Ridge, The Application of Ion Plating to the Continuous Coating of Flexible Plastic Sheet, *Thin Solid Films,* Vol 80, 1980, p 31

114. S. Schiller, M. Neumann, and V. Kirchoff, Progress in High-Rate Electron Beam Evaporation of Oxides for Web Coating, *Society of Vacuum Coaters 36th Ann. Tech. Conf. Proc.,* 1993, p 278

115. R.W. Philips, T. Markates, and C. LeGallee, Evaporated Dielectric Colorless Films on PET and OPP Exhibiting High Barriers toward Moisture and Oxygen, *Society of Vacuum Coaters 36th Ann. Tech. Conf. Proc.,* 1993, p 293

Ion-Beam-Assisted Deposition

Graham K. Hubler, Naval Research Laboratory; James K. Hirvonen, U.S. Army Research Laboratory

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Introduction

ION-BEAM-ASSISTED DEPOSITION (IBAD) refers to the process wherein evaporated atoms produced by physical vapor deposition (PVD) are simultaneously struck by an independently generated flux of ions. The extra energy imparted to the deposited atoms causes atomic displacements at the surface and in the bulk, as well as enhanced migration of atoms along the surface. These resulting atomic motions are responsible for improved film properties, including better adhesion and cohesion of the film, modified residual stress, and higher density, when compared with similar films prepared by PVD without ion bombardment. When the ion beam or the evaporant is a reactive species, compounds such as refractory silicon nitride ($Si_3 N_4$) can be synthesized at very low temperatures. Furthermore, adjustment of the ratio of reactive ions to atoms arriving at the substrate surface allows adjustment of the stoichiometry of solid solutions. Detailed reviews of the IBAD process can be found in Ref 1, 2, and 3.

Process Utilization. The feature that distinguishes IBAD from the other PVD processes discussed in this Section of the Volume is that the source of vapor and the source of energetic ions are separated into two distinct hardware items, as opposed to plasma-based techniques, such as direct current (DC), radio frequency (RF), and magnetron sputtering; plasma-enhanced chemical vapor deposition; and certain forms of ion plating in which both the evaporant flux and ion flux are derived by extraction from a plasma. Therefore, there is more control over the deposition parameters in the IBAD process, because the ion flux and the evaporant flux can be varied independently. The other major difference between the plasma techniques and IBAD is the higher pressure (0.13 to 13 Pa, or 10^{-3} to 10^{-1} torr) required by the operation of the plasma-based methods in order to sustain a plasma. Because IBAD techniques typically operate in the collision-free pressure regime, the evaporant and beam atoms follow straight-line paths to the substrate. This also limits IBAD to line-of-sight applications.

The two most common geometries used in IBAD processing are shown in Fig. 1. Details of the methods are described elsewhere (Ref 4, 5, 6). Normally, a broad beam from an ion source, such as a Kaufman-type ion gun, impinges on a substrate simultaneously with the deposited atoms. The PVD source is usually an electron-beam source, but it could also be a thermal source or a sputter target, in the case of dual-ion-beam sputtering. The simplest geometry for the generation of uniform films and the treatment of complex geometries is a small angle (<30°) between the vapor and ion sources.

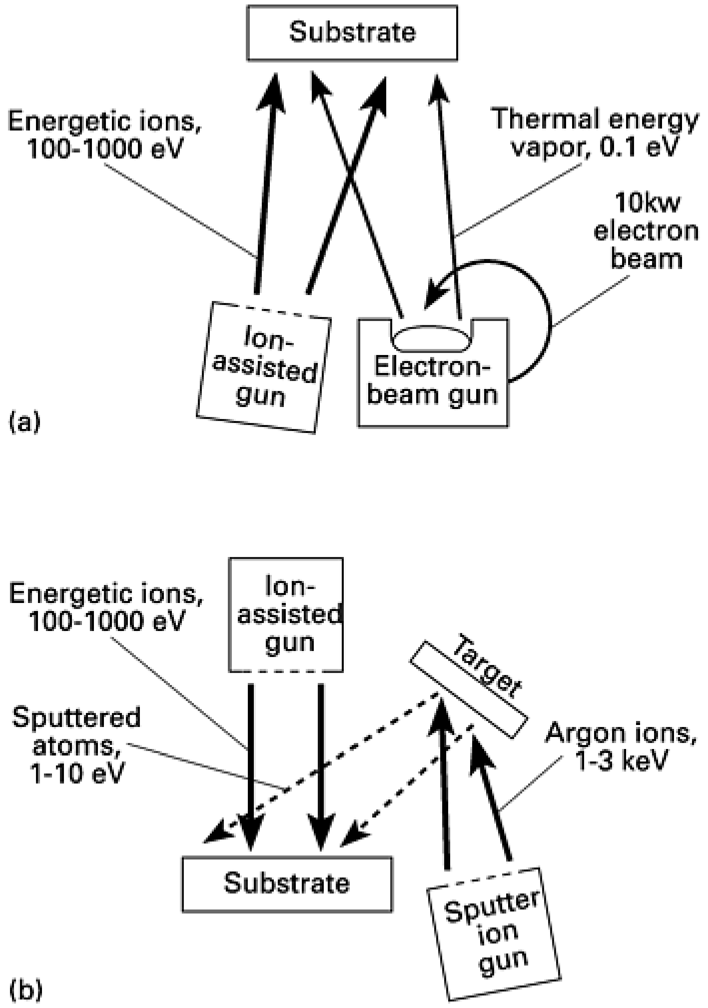

Fig. 1 Two common processing techniques. (a) Ion-beam-assisted deposition (IBAD). (b) Dual-ion-beam sputtering (DIBS)

Typical levels of ion-beam energy are between approximately 50 and 1000 eV for Kaufman-type ion guns. The ion beam has a uniform flux over a large area, depending on the diameter of the ion extraction apertures (typically, 30 to 80 mm, or 1.2 to 3.1 in.). The energy levels for beams from an ion implanter are 20 to 100 keV. Large areas are obtained by rastering the beam over the exposed surfaces. Research indicates that while the adhesion of IBAD films at low energies (500 eV to 3 keV) is excellent (Ref 7, 8, 9), an additional improvement in adhesion can sometimes be gained at higher energies (20 to 40 keV) if the film and substrate are not normally miscible. On the other hand, other properties, such as the absorption in optical films, increase as the energy increases because of greater displacement damage (Ref 10, 11, 12). Minimal absorption is obtained at energies below 500 eV. Therefore, for films intended for environmental protection, wear resistance, decorative coatings, and similar applications, a slight advantage might be derived from utilizing higher beam energies, although it would not normally be enough to warrant the greater expense of high-energy ion sources and beam-handling optics. However, for films intended for optical and microelectronics applications, lower energies are preferred in order to minimize beam damage resulting in optical absorption and the formation of electrically active defects.

For the low-energy range (50 to 1000 eV), inelastic collisions of the incident ions with the surface atoms deposit the energy into the surface according to the expression:

$$E \text{ (per film atom)} = R(E_b)$$

where R is the ratio of beam atoms to evaporant atoms arriving at the surface and E_b is the energy per atom in the ion beam. For the arrival of four beam atoms for every ten evaporant atoms (R = 0.4) and a beam energy of 200 eV, the average energy deposited in the surface for every film atom is 80 eV. This should be contrasted to the thermal energy of

evaporated film atoms without ion bombardment, which is E = 0.15 eV/atom. This parameter can be tightly controlled and independently varied over a wide range by changing the beam output of the ion source and the energy of the ion beam. In plasma-based techniques, there is a larger spread of energies of the energetic flux components, with unknown ratios of the ion to thermal atom flux. The independent control of these parameters is more limited.

Physical and Chemical Aspects. The physical processes that occur at the surface during the film formation of IBAD are shown in Fig. 2. The lower right portion of Fig. 2 shows a very dilute neutral plasma consisting of background gas ("g") at a thermal energy of 0.03 eV, which is present throughout the chamber, as well as vapor atoms ("v") with an energy of either 0.15 eV (produced by the electron-beam evaporator shown in Fig. 1a) or 1 to 10 eV (produced by the sputter source shown in Fig. 1b). The vapor atoms have a velocity vector directed toward the substrate and are confined to the region between the vapor source and the substrate. The gas and the vapor impinge on the film surface at individual rates that are determined by the chamber pressure and the evaporation rate, respectively. The lower left portion of Fig. 2 shows a 200 eV N^+ beam directed toward the substrate. Some of this charged plasma is charge-exchange neutralized in near collisions with the ambient gas atoms, resulting in an energetic 200 eV neutral N^0, which continues in the direction of the substrate, and a 0.03 eV N^+ charged atom that gets expelled from the positive column of charge represented by the ion beam. As a result of charge exchange, the neutralized (high-velocity) atoms will not be counted by the charge-collection system.

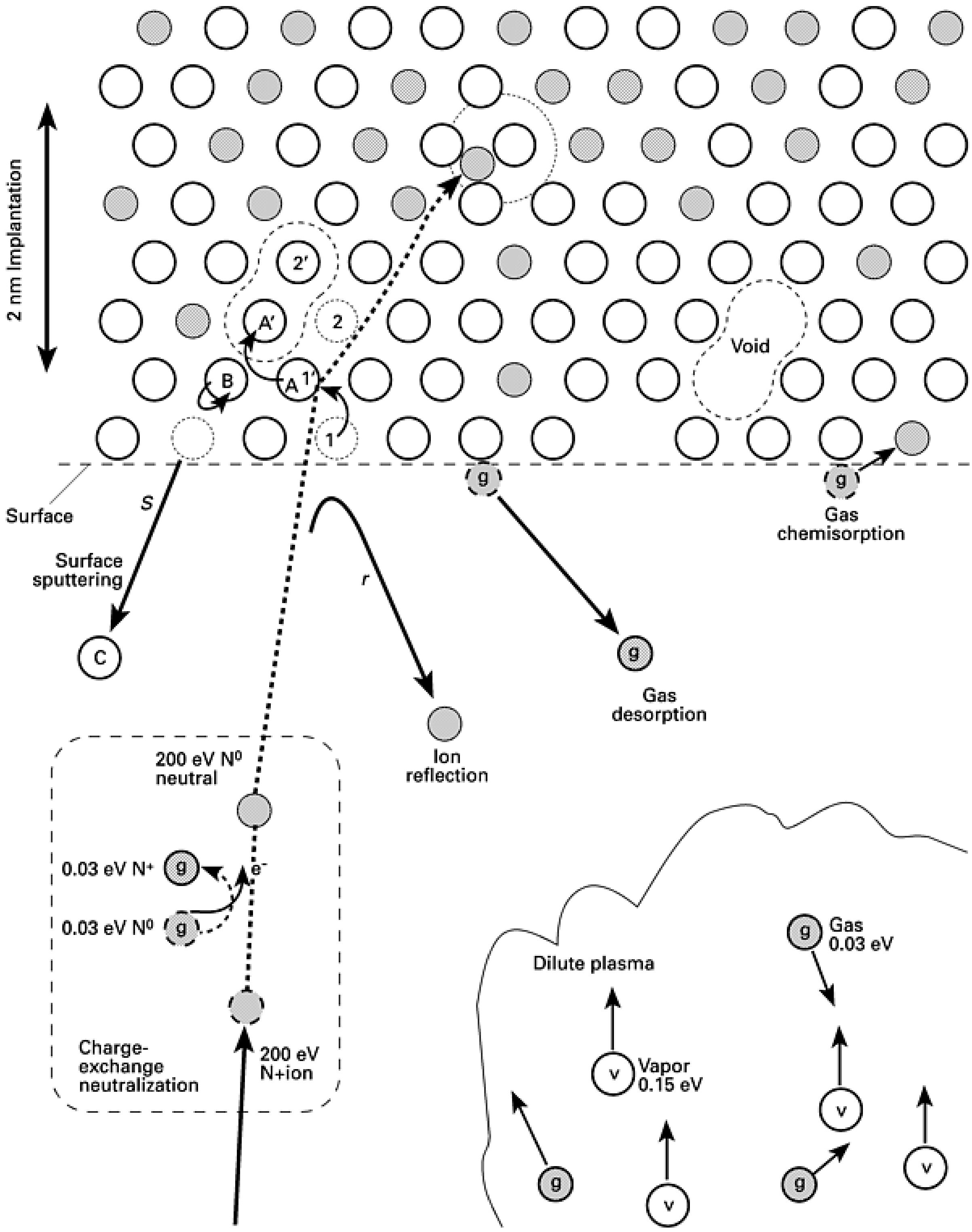

Fig. 2 Physical and chemical processes at the film-vacuum interface during ion-beam-assisted deposition and dual-ion-beam sputtering

In the central portion of Fig. 2, the ions, which consist of N^+ in this example, are either implanted into the first few atomic layers or reflected from the surface with a reflection coefficient, *r*. As a result of ion bombardment, some of the deposited and/or implanted atoms are sputtered from the surface with a sputtering coefficient, *S*. The sputtering process is shown as resulting from a three-step process, in which energy is transferred in a collision sequence, or cascade, from the ion to atom A, and then to atom B, which causes atom C to be sputtered. Additional surface processes shown are:

- The ion-stimulated thermal desorption of a physisorbed gas atom (binding energy ~0.05 eV) caused by a

thermal spike event in the vicinity of the ion impact

- The ion-stimulated chemisorption of the gas impurity to form chemical bonds with the deposited atoms (binding energy ~2 eV per bond)

The upper portion of Fig. 2 shows the processes that occur within the film. For this example, imagine that the vapor atoms are titanium and the ions are nitrogen. The large, open circles are titanium atoms condensed out of the vapor phase that form the film. They are more numerous near the surface because the nitrogen ions represented by the small, shaded circles have a finite range in the lattice of five atomic layers. In the deepest three layers shown, there are equal numbers of titanium and nitrogen atoms, giving stoichiometric titanium nitride. This also means that the rate of arrival of titanium atoms has been adjusted to be nearly equal to the rate of arrival of the nitrogen ions. Also shown in the near-surface region is a void that is formed in most metallic depositions at thermal energies. The random nature of the positions along the surface, where the vapor atoms land, coupled with the low mobility of the atoms after impact, leads to void formation.

The upper left portion of Fig. 2 represents the process of film densification. As the ion enters the lattice, it slows down upon inelastic collisions with other atoms in the lattice. The dashed line enclosing atoms A' and 2' indicates a void, identical to the one shown on the right, which was present prior to the arrival of the ion. In this schematic, the unprimed symbols are the atom positions before the ion collision, the primed symbols are their positions after the ion collision, and the faint dashed circles represent missing atoms after the collision is over. Upon entering the lattice, the ion strikes atom A, knocking it into one of the void positions (A'), but on the way, atom A also strikes atom B, whereupon its motion causes atom C to be sputtered, as already noted. Next, the ion knocks atom 2 into void position 2', leaving position 2 empty, and the thermal excitation of the ion impact causes atom 1 to jump into position 1', the position formerly held by atom A. Thus, before the collision, there were two atoms missing in the bulk, whereas after the collision, only one atom is missing, and the film has a net increase in density. Finally, the N ion comes to rest in an interstitial position, which represents a defect in the crystalline structure. This defect can be eliminated by a subsequent collision or it can remain in the film.

The atomic displacement mechanisms in the bulk of the film depicted in Fig. 2 are generic to any energetic deposition process. The plasma and surface processes depicted in that figure are conceptually simple, compared with the physical description of processes that occur in plasma-based deposition systems. For that reason, the production of reproducible films and graded composition films by IBAD is straightforward.

References

1. F.A. Smidt, *Int. Mater. Rev.,* Vol 135, 1990, p 61-128
2. J.K. Hirvonen, *Mater. Sci. Rep.,* Vol 6, 1991, p 215-274
3. G.K. Hubler, *Crit. Rev. in Surf. Chem.,* Vol 2 (No. 3), 1993, p 169-198
4. D. Van Vechten, G.K. Hubler, E.P. Donovan, and F.D. Correll, *J. Vac. Sci. Technol. A,* Vol 8, 1990, p 821
5. G.K. Hubler, D. Van Vechten, E.P. Donovan, and C.A. Carosella, *J. Vac. Sci. Technol. A,* Vol 8, 1990, p 831
6. J.M.E. Harper, J.J. Cuomo, and H.T.G. Hentzell, *J. Appl. Phys.,* Vol 58, 1985, p 550
7. M. Iwaki, *Mater. Sci. Eng. A,* Vol 115, 1989, p 369, and private communication
8. W. Ensinger and G. Wolf, *Mater. Sci. Eng. A,* Vol 116, 1989, p 1
9. G. Wolf, *Nucl. Instrum. Methods Phys. Res. B,* Vol 46, 1990, p 369
10. P.J. Martin, *J. Mater. Sci.,* Vol 21, 1986, p 1
11. P.J. Martin and R.P. Netterfield, in *Progress in Optics,* XXIII ed., E. Wolf, Ed., Elsevier, 1986, p 114
12. U.J. Gibson, Ion Beam Processing of Optical Thin Films, *Physics of Thin Films,* Vol 13, Academic Press, 1987, p 109

Processing Equipment

Laboratory. Most of the IBAD systems that exist in government, industry, and university laboratories are designed for sample sizes with diameters less than 30 mm (1.2 in.). These facilities are able to perform depositions on a small scale for limited batch sizes.

One common means of fabricating an IBAD system is to utilize commercially available electron-beam-source "box coaters" that are capable of large-area, high-volume coating applications and then modify them to accept commercially available low-energy, high-current ion guns of various designs. Deposition rates are determined by the electron-beam-source evaporation rate and the required arrival ratio of ions to atoms for a particular coating. When the required arrival ratios are between 0.1 and 1.0, the maximum current of a Kaufman-type ion gun (~1 mA/cm^2) translates into deposition rates of about 40 to 4 μm/h (100 Å/s to 10 Å/s), respectively, for a system based on an electron beam source.

Production. Many applications require large areas to be coated. Linear ion guns are made with lengths up to 1000 mm (40 in.) and widths of 20 mm (0.8 in.), whereas circular-aperture ion guns have diameters ranging from 10 to 380 mm (0.4 to 15 in.). Systems that can handle workpieces with a 1 m (40 in.) diameter have been built. In nonoptical applications, where film uniformity is not as strict a requirement, very large areas could be coated using existing equipment by the routine manipulation of the workpieces.

Even larger surface areas can be handled by using continuous coating schemes. The primary obstacle to scale-up is the requirement of line-of-sight processing, especially for odd-shape parts. Cylinders can easily be coated, but it is not yet clear whether complex shapes, like gear teeth, can be uniformly and reliably coated. Figure 3(a) shows a scheme developed for the large-area, high-volume deposition of optical films, which could be adapted easily for sheet-metal applications (Ref 13). Figure 3(b) depicts a prototype large-area, high-volume system used for sheet steel (Ref 14), which will be discussed later.

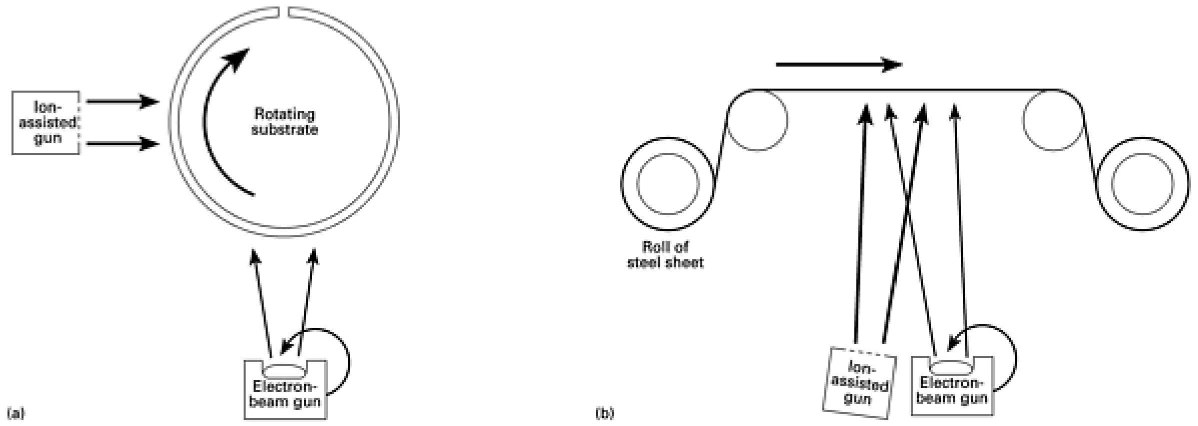

Fig. 3 Two methods used for large-area, high-volume implementation of ion-beam-assisted-deposition. (a) For optical films. (b) For steel sheet

Dual-ion-beam-assisted deposition (DIBS) systems, which utilize ion-beam sputter deposition, are also commercially available for use on substrates that are up to 120 mm (4.7 in.) in diameter. Some of these units are used for semiconductor applications, as well as for nonelectronic applications, such as the deposition of molybdenum disulfide films for friction reduction. In the case of sputter deposition, maximum deposition rates depend on the material to be deposited and are considerably less than for systems based on an electron beam. Ion-beam-sputtering systems are particularly suited to highly controlled, thin-film, multilayer coating applications, where up to six different sputtering targets can be sequentially moved into the sputter target position. High-quality, multilayer x-ray mirrors; laser mirrors; metallic multilayers; and other products have been manufactured using this method.

References cited in this section

13. Optical Coatings Laboratory, Inc., private communications, 1992

14. T. Takahashi, Y. Oikawa, T. Komori, I. Ito, and M. Hashimoto, *Surf. Coat. Technol.*, Vol 51, 1992, p 522

Processing Variables and Parameters

In general, there are three modes of IBAD. Several examples of the material systems that are deposited using each of the modes are given in Table 1. Mode 1 of this table identifies a simple type of ion assist, in which inert heavy ions, such as argon, are used to improve the properties of an elemental film or a compound film that undergoes congruent evaporation. In this case, it is important to minimize the amount of argon incorporated into the film, which increases with the arrival ratio, *R*, and the beam energy. Therefore, the lowest *R* value possible, consistent with obtaining the desired film properties, should be used. This mode also includes materials such as cerium oxide, which is typically slightly substoichiometric when simply deposited by evaporation. An ion assist with argon ions can be used for densification only, or oxygen ions can be used for densification and to restore stoichiometry.

Table 1 Three modes of film formation for ion-beam-assisted deposition (IBAD)

Vapor	Ion or ion/gas	Film
Mode 1: IBAD		
Ge	Ar	Ge
Ag	Ar	Ag
CeO_2	O	CeO_2
Ta_2O_3	O	Ta_2O_5
Mode 2: IBAD (Compound synthesis)		
Si	N	Si_3N_4
B	N	BN
Si	CH_4	SiC
Cu	O	Cu_2O
Mode 3: Reactive IBAD		
Ti	N/N	TiN
Ti	Ar/N	TiN
Nb	N/N	NbN
Al	O/O	Al_2O_3

Ge, germanium; Ar, argon; Si, silicon; N, nitrogen; Si_3N_4, silicon nitride; TiN, titanium nitride; Ag, silver; B, boron; CeO_2, cerium oxide; O, oxygen; CH_4, methane; SiC, silicon carbide; Nb, niobium; Ta_2O_3, tantalum oxide; Ta_2O_5, tantalum pentoxide; Cu, copper; Cu_2O, copper oxide; Al, aluminum; Al_2O_3, aluminum oxide

Mode 2 in Table 1 identifies an ion assist and compound synthesis group, in which there is little reaction probability of the ambient gas with the evaporant. All of the material that forms the compound in this deposition mode comes from the evaporation source, as well as directly from the ion beam.

Mode 3 in Table 1 covers compound synthesis that is possible only for very reactive materials. It can occur either with the gas associated with the ion beam (e.g., N_2 for titanium nitride) or when inert ions such as argon are used in conjunction with a secondary (background) gas supply of N_2. In the latter case, the purpose of the ions is to activate and control surface chemical reactions.

Table 2 is a selected compilation of materials that have been grown using IBAD processes. For application to metals, the oxides and pure metals are often used as corrosion-resistant coatings, whereas nitrides and some oxides are used as wear-resistant and corrosion-resistant coatings. The widespread application of these coatings for nonelectronic purposes is still new, but there is some evidence that the appropriate thickness for hard coatings for sliding wear resistance is 0.2 to 2 μm (8 to 80 μin.), and that for pin-hole-free corrosion-resistant coatings, a minimum thickness of 2 μm (80 μin.) is required. For abrasion-resistant coatings, very thick and hard coats can be deposited, although this has not been emphasized in the initial development of the technique. Optical coatings up to 15 μm (215 μin.) thick also have been deposited. Typical process parameters are shown in Table 3.

Table 2 Deposition and synthesis of inorganic compounds by ion-beam-assisted deposition (IBAD)

Material	Method	Evaporant	Ion	Energy, eV	*R*	Gas	Temperature		Comments	Ref
							°C	°F		
ZrO_2	IBAD	ZrO_2	Ar^+	600	0.82	. . .	20, 300	70, 570	. . .	15
ZrO_2	IBAD	ZrO_2	Ar^+/O_2^+	600/1200	0.33	O_2	20, 300	70, 570	Best films w/ O_2^+ cubic and monoclinic	16
ZrO_2	IBAD	ZrO_2	O_2^+/O^+	600/1200	0-10	. . .	25	75	. . .	17
ZrO_2	Reactive IBAD	ZrO_2	O_2^+	1200	. . .	O_2	275	525	. . .	18
TiO_2	Reactive IBAD	TiO, TiO_2	O_2^+	0-100	0.3-0.6	O_2	50-300	120-570	. . .	19, 20
TiO_2	Reactive IBAD	TiO	O^-	. . .	. . .	O_2	25	75	. . .	21
TiO_2	Reactive IBAD	Ti_2O_3	O_2^+	. . .	. . .	. . .	. . .	. . .	Amorphous	21
TiO_2	Reactive	TiO	O^+, O_2^+	30, 500	0-0.8	O_2	50-	120-	. . .	22

Material	Method	Evaporant	Ion	Energy, eV	*R*	Gas	Temperature		Comments	Ref
							°C	°F		
	IBAD						100	210		
TiO_2	Reactive IBAD	TiO, TiO_2	O_2^+	30, 500	0-1.3	O_2	50-100	120-210	. . .	23, 24
TiO_2	Reactive IBAD	TiO	O_2^+	600	0.3-0.9	O_2	25	75	. . .	25
TiO_2	Reactive IBAD	TiO_2	O_2^+	300	0.1-0.4	O_2	175	345	Optimum R = 0.2	26
SiO_2	Reactive IBAD	SiO	O^-	. . .	. . .	O_2	290	555	. . .	21
SiO_2	Reactive IBAD	SiO	Ar^+	600	0.03	O_2	25	75	. . .	25
SiO_2	Reactive IBAD	SiO	O^+, O_2^+	300, 500	0.25-1.7	O_2	50-100, 275	120-210, 525	Not sensitive to IBAD conditions	18, 22
Al_2O_3	Reactive IBAD	Al_2O_3	O_2^+	300-1000	0.08-0.8	O_2	275	525	Optimum R = 0.2 at 1000 eV	18
Al_2O_3	Reactive IBAD	Al_2O_3	O_2^+	300	1.33	O_2	125	255	. . .	27
Al_2O_3	Reactive IBAD	Al_2O_3	O_2^+	1200	0.6	O_2	20, 300	70, 570	. . .	28
Al_2O_3	Reactive IBAD	Al	O_2^+	500	0.16	O_2	25	75	. . .	29
CeO_2	Reactive IBAD	CeO_2	O_2^+	300, 600, 1200	1.9	O_2	20, 300	70, 570	. . .	30
CeO_2	Reactive IBAD	CeO_2	O_2^+	1200	0.84	O_2	20, 300	70, 570	. . .	31
HfO_2	Reactive IBAD	HfO_2	O_2^+	300	0.25	O_2	300	570	. . .	32
Ta_2O_5	Reactive	Ta_2O_5	O_2^+	1200	2.6	O_2	300	570	. . .	31

Material	Method	Evaporant	Ion	Energy, eV	*R*	Gas	Temperature		Comments	Ref
							°C	°F		
	IBAD									
Ta_2O_5	Reactive IBAD	Ta_2O_5	O_2^+	300-1000	0.08-1.4	O_2	275	525	Optimum *R* = 0.6 at 300 eV	18
Ta_2O_5	Reactive IBAD	Ta_2O_5	O_2^+	300	2.8	O_2	125	255	. . .	27
VO_2	IBAD	V	O_2^+	600	. . .	. . .	800-600	175-1110	. . .	32
MgF_2	IBAD	MgF_2	Ar^+	125-1000	0.04	. . .	25	75	High *E*-preferential sputtering of F	33
MgF_2	Reactive IBAD	MgF_2	Freon (C_2F_6)	80-1400	0.05-0.1	C_2F_6	25	75	Low *E* best	34, 35
MgF_2	IBAD	MgF_2	O_2^+	350-750	0.12-0.25	O_2	20, 300	70, 570	Crystalline	36
MgF_2	IBAD	MgF_2	Ar^+, O_2^+	300	0.3-0.34	. . .	25	75	. . .	37
LaF_3	IBAD	LaF_3	Ar^+, O_2^+	300, 500	0.22-0.57	. . .	25	75	*R* = 0.05, O_2^+ optimum	37, 38
Cryolite	IBAD	Na_3AlF_6	Ar^+, O_2^+	200, 300	0.25-0.75	. . .	25	75	*R* = 0.75 at 300 eV O_2^+ optimum	37
ThF_4	IBAD	ThF_4	Ar^+	300	0.05-0.35	. . .	25	75	. . .	39
Si_3N_4	Dual-ion-beam sputter	Si	N^+, N_2^+	680	2.05	N_2	<200	<390	Partially amorphous	40, 41
Si_3N_4	Reactive IBAD	Si	N_2^+	60, 100	2.1	N_2	25	75	. . .	42
Si_3N_4	IBAD	Si	N_2^+	500	0-1.33	. . .	25	75	Corrosion protection, optical properties	43, 44

Material	Method	Evaporant	Ion	Energy, eV	*R*	Gas	Temperature		Comments	Ref
							°C	°F		
Si_3N_4	IBAD	Si	N_2^+	20,000-100,000	0-1	. . .	<200	<390	Oxidation protection	45
Si_3N_4	IBAD	Si	N_2^+	100	0-1.3	. . .	<100	<210	Multilayer x-ray mirrors	46
Si_3N_4	IBAD	Si	N	500-1000	0-1.4	N_2	<100	<210	Process characterization	4, 5
$Si_{(1-x)}N_x$	Reactive IBAD	Si	N_2^+	1000	0-1.3	N_2	<70	<160	Amorphous films	47
SiON	IBAD	Si	O_2^+, N_2^+	3000	. . .	. . .	300	570	. . .	41
SiNH	IBAD	Si	NH_3	500	0-1.4	NH_3	<100	<210	Optical films	48
AlN	Dual-ion-beam sputter	Al	N_2^+	100-500	0-2.6	N_2	25	75	AlN at $R = 1$	6
AlN	IBAD	Al	N_2^+	200-1000	0.5	N	100	210	Oriented films	49
AlN	Reactive IBAD	Al	N_2^+	250-1000	0.5-2.7	N_2	100	210	. . .	50
AlN	IBAD	Al	N_2^+	75, 500	1.05, 1.7, 3.4	. . .	25	75	. . .	29
AlON	Reactive IBAD	Al	N_2^+	750	0.7-1.0	O_2	100	210	. . .	51
AlON	IBAD	AlN	O_2^+, N_2^+	300	. . .	. . .	300	570	. . .	41
TiN	Reactive IBAD	Ti	Ti^+, N^+	30/40,000	0.001-0.6	N_2	25-700	75-1290	. . .	52
TiN	Reactive IBAD	Ti	N	12,000	. . .	N_2	. . .	. . .	Structure	53
TiN	Reactive IBAD	Ti	N_2^+	5000	0-1	N_2	. . .	. . .	. . .	54

Material	Method	Evaporant	Ion	Energy, eV	*R*	Gas	Temperature		Comments	Ref
							°C	°F		
TiN	Reactive IBAD	Ti	N_2^+	1000	0.01-0.03	N_2	. . .	. . .	. . .	55
TiN	Reactive IBAD	Ti	N_2^+	10-30,000	1.0	N_2	300	570	. . .	56
TiN	Reactive IBAD	Ti	N^+, N_2^+	20,000	1.0	N_2	35	95	. . .	57
TiN	Bias magnetron	Ti	$Ar^+ + N_2^+$	2-200	0.4-1.0	N_2	300-600	570-1110	. . .	51
TiN	Dual-ion-beam sputter	Ti	N_2^+	200	0.25	N_2	400	750	Ti_3N_4 forms with excess N	58
TiN	IBAD	Ti	N_2^+	30,000	0.12-0.77	. . .	100-300	210-570	. . .	59
TiN	Reactive IBAD	Ti	N_2^+	500	0-1.1	N_2	25	75	Process parameters	44
TiN	Reactive IBAD	Ti	Ar^+	12,000	1	N_2	<250	<480	Comparison with other techniques	60, 61
TiN	Ion plating	Ti	$N^+ + N^+$	200	. . .	N_2	<100	<210	Batch processing of sheet metal	14
TiN	IBAD	Ti	N^+	20,000	0.37-1.1	. . .	. . .	. . .	. . .	62
TiN	IBAD	Ti	$N^+ + N_2^+$	20,000	1.0	. . .	200-300	390-570	Extensive data	63
TiN	Reactive IBAD	Ti	N_2^+	40,000	0-0.3	N_2	<100	<210	Oriented films	64
TiN	Reactive bias magnetron	Ti	N_2^+	300-500	4.1	. . .	550-850	1020-1560	Single crystal, epitaxial	65
CrN	IBAD	Cr	N_2^+	20,000	0.5-2	N_2	. . .	. . .	Oriented films	66

Material	Method	Evaporant	Ion	Energy, eV	*R*	Gas	Temperature		Comments	Ref
							°C	°F		
CrN	IBAD	Cr	N_2^+	12,000	10^{-4}-0.1	. . .	25	75	High hardness	9
BN	Reactive IBAD	B	N_2^+	25-40,000	0.7	N_2	200	390	Some cubic BN	67
BN	IBAD	B	N_2^+	120,000	. . .	. . .	300	570	Ion-beam mixing	68
BN	IBAD	B	$N_2^+ + N^+$	200-1000	1.0	. . .	. . .	. . .	. . .	69
BN	IBAD	B	N_2^+	80-500	1.0-2.0	. . .	280-300	535-570	. . .	70
BN	IBAD	B	N_2^+	500	2.55	. . .	200	390	. . .	71
BN	IBAD	B	N_2^+	200	1	. . .	300	570	Cubic BN	72
BN	IBAD	B	N_2^+	250-2000	0-1.5	. . .	25	75	Hardness, stress	73
BN	IBAD	B	N_2^+	2000-20,000	. . .	N_2	. . .	. . .	Cubic BN	74
TiC	IBAD	Ti, C	Ar^+	100,000	0.01	. . .	25	75	*R*=Ar/Ti ratio	75
TiC	Ion plating	TiC	Ar^+	200	. . .	. . .	<100	<210	Batch processing of sheet metal	14
ZrN	Dual-ion-beam sputter	Zr	N_2^+	200	0.25	. . .	400	750	. . .	58
ZrN	Reactive IBAD	Zr	N_2^+	200-700	. . .	N_2	25	75	Coated shaver screens	76
ZrN	Reactive IBAD	Zr	N_2^+	30,000	1	N_2	<300	<570	Chemistry, microstructure	77
HfN	Dual-ion-beam sputter	Hf	N_2^+	200	0.25	. . .	400	750	Hf_3N_4 also formed	58

Material	Method	Evaporant	Ion	Energy, eV	*R*	Gas	Temperature		Comments	Ref
							°C	°F		
MoN	Reactive IBAD	Mo	N^+, N_2^+	40,000	1.0	N_2	25-500	75-930	B1 structure for 25 °C (77 °F)	78
MoN	IBAD	Mo	N_2^+	500-1000	0-1.2	N_2	<100	<210	Pure phases	79
NbN_xC_y	Dual-ion-beam sputter	Nb	N_2^+ +CH_4	50-100	. . .	N_2+CH_4	<60	<140	. . .	80
InSnO	Reactive IBAD	In_2O_3-9SnO_2	O_2^+	100	1.0	O_2	25-400	75-750	Amorphous <100	81
InSnO	Reactive IBAD	InSnO	O_2^+	1200	0.7-1.0	O_2	50-150	120-300	. . .	82
WSi_2	IBAD	W, Si	Ar^+	100-400	0.05-0.25	. . .	25-500	75-930	Amorphous at room temperature	83
CuO	IBAD	Cu	O_2^+	<200	0.01-0.1	O_2	25	75	Formed Cu_2O, CuO, Cu_5O_4	84
YBaCuO	Reactive IBAD	$YBa_2Cu_4O_x$	Ar^+ + 2O_2^+	50	. . .	O_2	560-640	1040-1180	. . .	85
YBaCuO	IBAD	BaF_2, Cu, Y	O^+, O_2^+	50	. . .	. . .	600	1110	Single-crystal epitaxial films	86
MoS_2	Dual-ion-beam sputter	MoS_2	Ar^+	1000	0.01-0.1	. . .	25	75	Low friction	87
DLC	IBAD	C	Ar^+, Ne^+	200-1000	0.05-0.7	. . .	<100	<210	. . .	88
DLC	Ion-beam sputter	C	Ar	1200	. . .	H_2	25	75	Few diamond crystals in amorphous C	89
DLC	Ion-beam deposition	. . .	C^+	10-175	. . .	. . .	<400	<750	. . .	90, 91
DLC	Ion-beam deposition	. . .	CH_4	100-1200	. . .	CH_4	25	75	Deposition rates microstructure	92

Material	**Method**	**Evaporant**	**Ion**	**Energy, eV**	***R***	**Gas**	**Temperature**		**Comments**	**Ref**
							°C	**°F**		
DLC	Ion-beam deposition	. . .	CH_4	500-1000	. . .	CH_4	25	75	Composition, applications	93
B	IBAD	B	Ar^+	6000	. . .	. . .	25	75	Low stress	94
B	IBAD	B	Ar^+	6000	10^{-4}-0.1	. . .	25	75	Corrosion protection, adhesion	9
B	IBAD	B	Ar^+	3000-15,000	0-0.1	. . .	. . .	. . .	Stress control	95
C	Ion-beam deposition	. . .	C^+	5-200	. . .	. . .	25	75	X-ray mirrors	96
C	IBAD	C	Ar^+	. . .	. . .	. . .	. . .	. . .	Densification	97
Al	IBAD	Al	He, Ne, Ar, Kr, Xe	200-20,000	0-0.3	. . .	. . .	. . .	Thorough study	98
Al	IBAD	Al	Ar^+	50-2000	0.001-0.1	. . .	25	75	Oriented films	99
Si	Ion-beam deposition	. . .	Si^+	5-200	. . .	. . .	25	75	X-ray mirrors	96
Cr	IBAD	Cr	Ar^+	3000-15,000	0-0.1	. . .	. . .	. . .	Stress control	95
Cr	IBAD	Cr	N_2^+	60,000	0.1	. . .	. . .	. . .	Turbine blade coatings	100
Cr	IBAD	Cr	Ar^+	11,500	. . .	. . .	25	75	Low stress	8
Cr	IBAD	Cr	Ar^+	6000	. . .	. . .	25	75	Low stress	94
Cr	IBAD	Cr	Ar^+	60-800	0-1.5	. . .	25	75	Stress, resistivity	101, 102
Fe	IBAD	Fe	Ar^+	60-800	0-1.5	. . .	25	75	Stress, resistivity	101, 102

Material	**Method**	**Evaporant**	**Ion**	**Energy, eV**	***R***	**Gas**	**Temperature**		**Comments**	**Ref**
							°C	**°F**		
Permalloy	IBAD	Fe-Ni	Ar^+	300	. . .	. . .	. . .	. . .	Low stress	103
Co	IBAD	Co	Ar^+	60-800	0-1.5	. . .	25	75	Stress, resistivity	101, 102
Ni	IBAD	Ni	Ar^+	60-800	0-1.5	. . .	25	75	Stress, resistivity	101, 102
Ni	Ion-beam deposition	. . .	Ni^+	5-200	. . .	. . .	30	85	X-ray mirrors	96
Cu	IBAD	Cu	Ar^+	60-800	0-1.5	. . .	25	75	Stress, resistivity	101, 102
Cu	IBAD	Cu	Ar^+	. . .	. . .	. . .	. . .	. . .	On polytetrafluoroethylene	104
Cu	IBAD	Cu	Ar^+	. . .	. . .	. . .	. . .	. . .	. . .	105
Nb	IBAD	Nb	Ar^+	60-800	0-1.5	. . .	25	75	Stress, resistivity	101, 102
Ag	IBAD	Ag	Ar^+	. . .	. . .	. . .	. . .	. . .	On polytetrafluoroethylene	104
Ag	IBAD	Ag	Ar^+	. . .	. . .	. . .	. . .	. . .	. . .	106
Ta	IBAD	Ta	Ar^+	60-800	0-1.5	. . .	25	75	Stress, resistivity	101, 102
W	Ion-beam deposition	. . .	W^+	5-200	. . .	. . .	25	75	X-ray mirrors	96
W	IBAD	W	Ar^+	60-800	0-1.5	. . .	25	75	Stress, resistivity	101, 102
Au	IBAD	Au	Ar^+	. . .	. . .	. . .	. . .	. . .	On polytetrafluoroethylene	104
Au	IBAD	Au	Ar^+	. . .	. . .	. . .	. . .	. . .	On glass	107

Material	Method	Evaporant	Ion	Energy, eV	*R*	Gas	Temperature		Comments	Ref
							°C	°F		
Au	IBAD	Au	Ar^+	. . .	. . .	. . .	. . .	. . .	On glass	94
Au	IBAD	Au	Ar^+	300	0-1	. . .	25-250	77-480	Good adhesion	108

Source: Ref 1

Table 3 Typical values of ion-beam-assisted deposition process variables

Variable	Value
Vapor deposition rate, μm/h (μin./h)	1-40 (40-1600)
Chamber base pressure, Pa (torr)	226×10^{-7} (2×10^{-7})
Operating pressure, Pa (torr) (with backfill gas), Pa (torr)	0.003 to 0.03 (2×10^{-5} to 2×10^{-4}) 0.007 to 0.03 (5×10^{-5} to 2×10^{-4})
Ion current, mA/cm^2 (mA/in.^{2}) Fraction-exchange neutralized	0.1-2 (0.6-13) 0.05-0.40
Arrival ratio	0.1-1.5
Substrate temperature, °C (°F)	<100 (<210)

References cited in this section

1. F.A. Smidt, *Int. Mater. Rev.,* Vol 135, 1990, p 61-128
4. D. Van Vechten, G.K. Hubler, E.P. Donovan, and F.D. Correll, *J. Vac. Sci. Technol. A,* Vol 8, 1990, p 821
5. G.K. Hubler, D. Van Vechten, E.P. Donovan, and C.A. Carosella, *J. Vac. Sci. Technol. A,* Vol 8, 1990, p 831
6. J.M.E. Harper, J.J. Cuomo, and H.T.G. Hentzell, *J. Appl. Phys.,* Vol 58, 1985, p 550
8. W. Ensinger and G. Wolf, *Mater. Sci. Eng. A,* Vol 116, 1989, p 1
9. G. Wolf, *Nucl. Instrum. Methods Phys. Res. B,* Vol 46, 1990, p 369
14. T. Takahashi, Y. Oikawa, T. Komori, I. Ito, and M. Hashimoto, *Surf. Coat. Technol.,* Vol 51, 1992, p 522
15. P.J. Martin, R.P. Netterfield, W.G. Sainty, G.J. Clark, W.A. Lanford, and S.H. Sie, *Appl. Phys. Lett.,* 1983, Vol 43, p 711
16. P.J. Martin, R.P. Netterfield, and W.G. Sainty, *J. Appl. Phys.,* Vol 55, 1984, p 235
17. K.-H. Muller, R.P. Netterfield, and P.J. Martin, *Phys. Rev. B,* Vol 35, 1987, p 2934
18. J.J. McNally, F.L. Williams, and J.R. McNeill, *Proc. SPIE,* Vol 678, Society of Photo-Optical Instrumentation Engineers, 1986, p 151

19. H. Kuster and J. Ebert, *Thin Solid Films,* Vol 70, 1980, p 43
20. J. Ebert, *Proc. SPIE,* Vol 325, Society of Photo-Optical Instrumentation Engineers, 1982, p 29
21. T.H. Allen, *Proc. SPIE,* Vol 325, Society of Photo-Optical Instrumentation Engineers, 1982, p 93
22. J.R. McNeil, A.C. Barron, S.R. Wilson, and W.C. Herrmann, Jr., *Appl. Opt.,* Vol 23, 1984, p 552
23. J.R. McNeil, G.A. Al-Jumaily, K.C. Jungling, and A.C. Barron, *Appl. Opt.,* Vol 24, 1985, p 486
24. G.A. Al-Jumaily, S.R. Wilson, A.C. Barron, J.R. McNeil, and B.L. Doyle, *Nucl. Instrum. Methods Phys. Res. B,* Vol $\frac{7}{8}$, 1985, p 906
25. P.J. Martin, H.A. Macleod, R.P. Netterfield, C.G. Pacey, and W.G. Sainty, *Appl. Opt.,* Vol 22, 1983, p 178
26. F.L. Williams, J.J. McNally, G.A. Al-Jumaily, and J.R. McNeil, *J. Vac. Sci. Technol. A,* Vol 5, 1987, p 2159
27. F.L. Williams, R.D. Jacobson, J.R. McNeil, G.J. Exarhos, and J.J. McNally, *J. Vac. Sci. Technol. A,* Vol 6, 1988, p 2020
28. L.N. Binh, R.P. Netterfield, and P.J. Martin, *Appl. Surf. Sci.,* Vol 22/23, 1985, p 656
29. R.P. Netterfield, K.-H. Muller, D.R. McKenzie, M.J. Goonan, and P.J. Martin, *J. Appl. Phys.,* Vol 63, 1988, p 760
30. R.P. Netterfield, W.G. Sainty, P.J. Martin, and S.J. Sie, *Appl. Opt.,* Vol 24, 1985, p 2267
31. J.J. McNally, G.A. Al-Jumaily, S.R. Wilson, and J.R. McNeil, *Proc. SPIE,* Vol 540, Society of Photo-Optical Instrumentation Engineers, 1985, p 479
32. F.C. Case, *J. Vac. Sci. Technol. A,* Vol 6, 1988, p 2010
33. U.J. Gibson and C.M. Kennemore, III, *Thin Solid Films,* Vol 124, 1985, p 27
34. U.J. Gibson and C.M. Kennemore, III, *Proc. SPIE,* Vol 678, Society of Photo-Optical Instrumentation Engineers, 1986, p 130
35. C.M. Kennemore, III and U.J. Gibson, *Appl. Opt.,* Vol 23, 1984, p 3608
36. P.J. Martin, W.G. Sainty, R.P. Netterfield, D.R. McKenzie, D.J.H. Cockayne, S.H. Sie, O.R. Wood, and H.G. Craighead, *Appl. Opt.,* Vol 26, 1987, p 1235
37. J.D. Targove, M.J. Messerly, J.P. Lehan, C.C. Weng, R.H. Potoff, H.A. Macleod, L.C. McIntyre, Jr., and J.A. Leavitt, *Proc. SPIE,* Vol 678, Society of Photo-Optical Instrumentation Engineers, 1986, p 115
38. J.D. Targove, J.P. Lehan, L.J. Lingg, H.A. Macleod, J.A. Leavitt, and L.C. McIntyre, Jr., *Appl. Opt.,* Vol 26, 1987, p 3733
39. G.A. Al-Jumaily, L.A. Yazlovitsky, T.A. Mooney, and A. Smajkiewicz, *Appl. Opt.,* Vol 26, 1987, p 3752
40. C. Weissmantel, *Thin Solid Films,* Vol 32, 1976, p 11
41. H.J. Erler, G. Reisse, and C. Weissmantel, *Thin Solid Films,* Vol 65, 1980, p 233
42. R.P. Netterfield, P.J. Martin, and W.G. Sainty, *Appl. Opt.,* Vol 25, 1986, p 3808
43. P.W. Natishan, E. McCafferty, E.P. Donovan, D.W. Brown, and G.K. Hubler, *Surf. Coat. Technol.,* Vol 51, 1992, p 30
44. G.K. Hubler, C.A. Carosella, E.P. Donovan, D. Van Vechten, R.H. Bassel, T.D. Andraeadis, M. Rosen, and G.P. Mueller, *Nucl. Instrum. Methods Phys. Rev. B,* Vol 46, 1990, p 384
45. Y. Chen, S. Liu, Z. Shang, C. Xu, Y. Zheng, X. Liu, and S. Zou, *Surf. Coat. Technol.,* Vol 51, 1992, p 227
46. G.K. Hubler, C.A. Carosella, P.G. Burkhalter, R.K. Feitag, C.M. Cotell, and W.D. Coleman, *Nucl. Instrum. Methods Phys. Res. B,* Vol 59/60, 1991, p 268
47. E.P. Donovan, D.R. Brighton, G.K. Hubler, and D. Van Vechten, *Nucl. Instrum. Methods Phys. Res. B,* Vol 19/20, 1987, p 983
48. G.K. Hubler, E.P. Donovan, and G.K. Hubler, *Nucl. Instrum. Methods Phys. Res.,* in press
49. K. Ogata, Y. Andoh, S. Sakai, and F. Fujimoto, *Nucl. Instrum. Methods Phys. Res. B,* Vol 59/60, 1991, p 229
50. J.D. Targove, L.J. Lingg, J.P. Lehan, C.K. Hwangbo, H.A. Macleod, J.A. Leavitt, and L.C. McIntyre, Jr.,

in Materials Modification and Growth Using Ion Beams, U.J. Gibson et al., Ed., *Proc. Mater. Res. Soc. Symp.,* Vol 93, 1987, p 311

51. N. Savvides and B. Window, *J. Vac. Sci. Technol. A,* Vol 4, 1986, p 504
52. R.A. Kant, B.D. Sartwell, I.L. Singer, and R.G. Vardiman, *Nucl. Instrum. Methods Phys. Res. B,* Vol $\frac{7}{8}$, 1985, p 915
53. W. Ensinger and B. Rauschenbach, *Nucl. Instrum. Methods Phys. Res. B,* Vol 80/81, 1993, p 1409
54. Y. Nakagowa, S. Ohtani, M. Mikoda, and T. Takagi, *Nucl. Instrum. Methods Phys. Res. B,* 1993
55. R.A. Kant, S.A. Dillich, B.D. Sartwell, and J.A. Sprague, *Proc. Mater. Res. Soc. Symp.,* Vol 128, 1989, p 427
56. M. Satou, Y. Andoh, K. Ogata, Y. Suzuki, K. Matsuda, and F. Fukjimota. *Jpn. J. Appl. Phys.,* Vol 24, 1985, p 656
57. T. Sato, K. Ohata, N. Asahi, Y. Ono, Y. Oka, I. Hashimoto, and K. Arimatsu, *Nucl. Instrum. Meth. Phys. Res. B,* Vol 19/20, 1987, p 644
58. B.O. Johansson, H.T.G. Hentzell, J.M.E. Harper, and J.J. Cuomo, *J. Mater. Res.,* Vol 1, 1986, p 443
59. M. Kiuchi, K. Fujii, T. Tanaka, M. Satou, and F. Fujimoto, *Nucl. Instrum. Methods Phys. Res. B,* Vol 33, 1988, p 158
60. W. Ensinger, A. Schroer, and G.K. Wolf, *Surf. Coat. Technol.,* Vol 51, 1992, p 217
61. W. Ensinger, A. Schroer, and G.K. Wolf, *Nucl. Instrum. Methods Phys. Res. B,* Vol 80/81, 1993, p 445
62. S. Nakashima, M. Fukushima, M. Haginoya, K. Ohata, I. Hashimoto, and K. Terakado, *Mater. Sci. Eng. A,* Vol 115, 1989, p 197
63. K. Hayashi, J. Sugiyama, K. Fukutani, and J. Kittaka, *Mater. Sci. Eng. A,* Vol 115, 1989, p 349
64. W. Xi, L. Xianghuai, C. Youshau, Y. Genging, Z. Zuyao, Z. Zhihand, H. Wei, and Z. Shichang, *Nucl. Instrum. Methods Phys. Res. B,* Vol 59/60, 1991, p 272
65. L. Hultman, V. Helmersson, S.A. Barnett, J.-E. Sundgren, and J.E. Greene, *J. Appl. Phys.,* Vol 61, 1987, p 552
66. K. Sugiyama, K. Hayashi, J. Sasaki, U. Ichiko, and Y. Hashiguchi, *Nucl. Instrum. Methods Phys. Res. B,* Vol 80/81, 1993, p 1376
67. M. Satou, K. Yamaguchi, Y. Andoh, Y. Suzuki, K. Matsuda, and F. Fujimoto, *Nucl. Instrum. Methods Phys. Res. B,* Vol 7/8, 1985, p 910
68. R.J. Bricault, P. Sioshansi, and S.N. Bunker, *Nucl. Instrum. Methods Phys. Res. B,* Vol 21, 1987, p 586
69. Y. Andoh, K. Ogata, and E. Kamijo, *Nucl. Instrum. Methods Phys. Res. B,* Vol 33, 1988, p 678
70. W.G. Sainty, P.J. Martin, R.P. Netterfield, D.R. McKenzie, D.J.H. Cockayne, and D.M. Dwarte, *J. Appl. Phys.,* Vol 64, 1988, p 3980
71. C.A. Carosella, G.K. Hubler, D. Van Vechten, and E.P. Donovan, in Processing and Characterization of Materials Used in Ion Beams, L.E. Rehn et al., Ed., *Proc. Mater. Res. Soc. Symp.,* Vol 128, 1989, p 79
72. N. Tanabe and M. Iwaki, *Nucl. Instrum. Methods Phys. Res. B,* Vol 80/81, 1993, p 1349
73. D. Bouchier and W. Moller, *Surf. Coat. Technol.,* Vol 51, 1992, p 190
74. S. Nishiyama, N. Kuratani, A. Ebe, and K. Ogata, *Nucl. Instrum. Methods Phys. Res. B,* Vol 80/81, 1993, p 1485
75. S. Pimbert-Michaux, C. Chabrol, M.F. Denanot, and J. Delafond, *Mater. Sci. Eng. A,* Vol 115, 1989, p 209
76. S. Kiyama, H. Hirano, Y. Domoto, K. Kuramoto, R. Suzuki, and M. Osumi, *Nucl. Instrum. Methods Phys. Res. B,* Vol 80/81, 1993, p 1388
77. X.-Y. Wen and Z.-L. Zhang, *Surf. Coat. Technol.,* Vol 51, 1992, p 252
78. F. Fujimoto, Y. Nakane, A.M. Satou, F. Komori, K. Ogata, and Y. Andoh, *Nucl. Instrum. Methods Phys. Res. B,* Vol 19/20, 1987, p 791
79. E.P. Donovan, G.K. Hubler, P. Mudholkar, and L. Thompson, *Surf. Coat. Technol.,* in press
80. L.-J. Lin and D.E. Prober, *Appl. Phys. Lett.,* Vol 49, 1986, p 416

81. P.J. Martin, R.P. Netterfield, and D.R. McKenzie, *Thin Solid Films,* Vol 137, 1986, p 207
82. J.A. Dobrowolski, F.C. Ho, D. Menagh, R. Simpson, and A. Waldorf, *Appl. Opt.*, Vol 26, 1987, p 5204
83. D.S. Yee, J. Floro, D.J. Mikalsen, J.J. Cuomo, K.Y. Ahn, and D.A. Smith, *J. Vac. Sci. Technol. A,* Vol 3, 1985, p 2121
84. C.R. Guarnieri, S.D. Offsey, and J.J. Cuomo, reported in S.M. Rossnagel and J.J. Cuomo, *MRS Bull.*, Vol 12, Feb-Mar 1987, p 40
85. J. Fujita, T. Yoshitake, A. Kamujo, T. Satoh, and H. Igarashi, *J. Appl. Phys.,* Vol 64, 1988, p 1292
86. K. Moriwqaki, Y. Enomoto, S. Kubo, and T. Murakami, *Jpn. J. Appl. Phys.*, Vol 27, 1988, p L2075
87. L.E. Seitzman, I.L. Singer, R.N. Bolster, and C.R. Gossett, *Surf. Coat. Technol.*, Vol 51, 1992, p 232
88. K. Ogata, Y. Andoh, and E. Kamijo, *Nucl. Instrum. Methods Phys. Res. B,* Vol 33, 1988, p 685
89. M. Kitabatake and K. Wasa, *J. Vac. Sci Technol. A,* Vol 6, 1988, p 1793
90. S.R. Kasi, H. Kang, and J.W. Rabalais, *J. Vac. Sci. Technol. A,* Vol 6, 1988, p 1788
91. Y. Kifshitz, S.R. Kasi, and J.W. Rabalais, in Processing and Characterization of Materials Used in Ion Beams, L.E. Rehn et al., Ed., *Proc. Mater. Res. Soc. Symp.,* Vol 128, 1989, p 101
92. R.A. Kant and G.K. Hubler, *Surf. Coat. Technol.,* Vol 51, 1992, p 242
93. R.L.C. Wu, *Surf. Coat. Technol.,* Vol 52, 1992, p 258
94. P.J. Martin, W.G. Sainty, and R.P. Netterfield, *Vacuum,* Vol 35, 1985, p 621
95. M. Borth, W. Ensinger, V. Hoffman, and G.K. Wolf, *Nucl. Instrum. Methods Phys. Res. B,* Vol 59/60, 1991, p 254
96. I. Katoaka, *Surf. Coat. Technol.,* Vol 51, 1992, p 273
97. J. Ullmann, G.K. Wolf, and W. Moller, *Nucl. Instrum. Methods Phys. Rev. B,* Vol 80/81, 1993, p 1507
98. S. Sakai, K. Ogata, and Y. Andoh, *Nucl. Instrum. Methods Phys. Res. B,* Vol 59/60, 1991, p 288
99. S. Masaki, H. Kobayashi, and H. Morisaki, *Nucl. Instrum. Methods Phys. Res. B,* Vol 59/60, 1991, p 292
100. C.J. Bedell, H.E. Bishop, G. Dearnaley, and J.E. Despout, *Nucl. Instrum. Methods Phys. Res. B,* Vol 59/60, 1991, p 245
101. R.A. Roy, D.S. Yee, and J.J. Cuomo, *Proc. Mater. Res. Soc. Symp.,* Vol 128, 1989, p 23
102. R. Roy, *Surf. Coat. Technol.,* Vol 51, 1992, p 203
103. P.H. Wocjiechowski, *J. Vac. Sci Technol. A,* Vol 6, 1988, p 1924
104. I.H. Loh, J.K. Hirvonen, J.R. Martin, P. Revesz, and C. Boyd, *Proc. Mater. Res. Soc. Symp.,* Vol 108, 1988, p 241
105. F. Parmigiani, E. Kay, T.C. Huang, and J.D. Swalen, *Appl. Opt.,* Vol 24, 1985, p 3335
106. F. Parmigiani, E. Kay, T.C. Huang, J. Perrin, W. Jurich, and J.D. Swalen, *Phys. Rev. B,* Vol 33, 1986, p 879
107. S.S. Nandra, F.G. Wilson, and C.D. Des Forges, *Thin Solid Films,* Vol 107, 1983, p 335
108. A.J. Kellock, J.E.E. Boglin, T.T. Bordin, and J.G. Pronko, *Nucl. Instrum. Methods Phys. Res. B,* Vol 59/60, 1991, p 249

Coating Properties

Adhesion. Because an ion gun is available in an IBAD system, substrates are normally sputter cleaned prior to deposition. This promotes improved bond formation between the substrate and the film. However, there are additional benefits from bombardment during deposition. One is that the surface is sputter cleaned of contaminants at the same time the substrate is exposed to the fluxes and is continuously cleaned during deposition. Another benefit is that there is atom movement across the interface caused by ballistic collisions such that film atoms are driven a few atomic layers into the substrate and substrate atoms are mixed into the film. This promotes the completion of interfacial bonding and also produces a robust, nonabrupt interface several atomic layers thick. The adhesive strength of these IBAD interfaces is typically 10 to 100 times higher than for the same films deposited at thermal energies with an electron beam or other PVD source without ion assistance. This bonding is enhanced for coating/substrate systems exhibiting high atomic miscibility.

Some of the systems that show adhesion improvement when deposited by IBAD are gold on copper (Ref 107), gold and silicon on glass (Ref 94), aluminum on iron (Ref 8), titanium nitride on steel (Ref 52), and copper, silver, and gold on polytetrafluoroethylene (Ref 104). Many more combinations have yet to be investigated. An excellent review (Ref 109) of the adhesion improvement of films by post-deposition bombardment gives further insight into the mechanisms of adhesion enhancement.

Stress. Most deposited thin films retain a residual compressive or tensile stress that limits the thickness that can be deposited. The accumulated stress either ruptures the interface bonds, causing delamination, or exceeds the cohesive forces of the material, causing film disintegration. Studies have shown that in most cases, a judicious combination of ion-bombardment parameters and substrate temperature can be chosen that will produce very small residual stresses in the coating. Therefore, conditions can normally be found where there are no thickness limitations to applications of IBAD coatings. This is a very important property for industrial applications.

Examples of low-stress films deposited by IBAD include chromium on glass by 11.5 keV argon bombardment (Ref 8), tungsten on silicon by 400 eV argon bombardment (Ref 101), boron and chromium on iron by 6 keV argon bombardment (Ref 94), and permalloy (iron-nickel) films on polypyromelitimide using 300 eV argon bombardment (Ref 103).

Density. An extremely important practical attribute of IBAD is the increase in film density, when compared with PVD films deposited without the aid of energetic ions. Such PVD films typically contain voids or columnar structures that produce a 10 to 20% density deficit relative to the bulk material. This is especially true for covalently bonded semiconductors and refractory metals. It is well established that the energetic ion beam applied to the film in the IBAD process can eliminate the voids and produce essentially bulk-density films. The mechanism for this densification is related to atomic displacements in the collision cascades, enhanced surface and bulk diffusion, recoil implantation, and ion mixing mechanisms (Ref 1, 2, 3).

Information on the densification of metal films is sparse and gives a mixed picture of whether or not IBAD causes densification. Gold films were found to be more dense (Ref 107), as were carbon films (Ref 97), but copper (Ref 105) and silver (Ref 106) films were found to be less dense. There is ample evidence for densification with semiconductors and oxides. The energy dependence for densification was studied for argon ions from 65 eV to 3 keV, and it was found that an arrival ratio of 0.1 at the low-energy level or 0.0003 at the high-energy level produced bulk-density germanium films (Ref 3, 110). For zirconium oxide films, IBAD using oxygen or argon ions produced nearly bulk-density films, when compared with evaporated films (Ref 16). In general, densification is found to occur in films deposited with an ion assist.

Microstructure. The effects of ion beams on the microstructure of films are numerous and complicated. For this reason, only some general observations are noted here. Most covalently bonded materials, such as semiconductors and silicon nitride or silicon carbide ceramics, are amorphous when deposited at room temperature. Silicon and germanium will be crystalline above the temperature of approximately 0.4 T_m, which is the melting temperature in degrees kelvin. Using IBAD, this characteristic temperature for achieving crystallinity can be lowered by approximately 200 K, because the atomic motion induced by the energetic atoms serves the same purpose as high substrate temperature (Ref 111).

Metals and ionic materials tend to be polycrystalline. In general, the ion beam decreases the grain size at low temperatures, but can increase it at higher temperatures, where annealing effects overcome the damage caused by the ion beam (Ref 102). The general observation that IBAD films are more ductile than bulk materials that usually contain larger grains has been attributed to this smaller grain size.

The orientation of films can be altered such that textured films are commonplace. The degree of texturing depends on beam angle, beam energy, beam flux, and substrate temperature (Ref 49). At high ion/atom ratios, the texture is such that the most loosely packed planes, which are favorable for ion channeling, are parallel to the ion-beam direction. At low ion/atom ratios, forward scattering of film atoms causes a close-packed fiber texture in the film plane for near-normal ion incidence (Ref 112). In some cases, epitaxial films can be induced to grow with an ion assist where they would not in the absence of ions. Examples include copper and aluminum on silicon (Ref 113, 114).

Morphology. In general, IBAD films are very smooth. If the substrate is initially atomically smooth, then processing conditions can be found for most coating materials that produce a remarkably small deterioration in smoothness. For very rough surfaces, the line-of-sight coverage means that there may be shadowing effects where part of the surface is not covered. This would render an anticorrosion coating useless, but it is not necessarily detrimental to antiwear coatings. For substrates of intermediate roughness, IBAD coatings tend to produce a smoother surface. In some rare cases and with specific processing parameters, the surface is roughened by an IBAD film, usually for low-melting-point metal films.

References cited in this section

1. F.A. Smidt, *Int. Mater. Rev.,* Vol 135, 1990, p 61-128
2. J.K. Hirvonen, *Mater. Sci. Rep.,* Vol 6, 1991, p 215-274
3. G.K. Hubler, *Crit. Rev. in Surf. Chem.,* Vol 2 (No. 3), 1993, p 169-198
8. W. Ensinger and G. Wolf, *Mater. Sci. Eng. A,* Vol 116, 1989, p 1
16. P.J. Martin, R.P. Netterfield, and W.G. Sainty, *J. Appl. Phys.,* Vol 55, 1984, p 235
49. K. Ogata, Y. Andoh, S. Sakai, and F. Fujimoto, *Nucl. Instrum. Methods Phys. Res. B,* Vol 59/60, 1991, p 229
52. R.A. Kant, B.D. Sartwell, I.L. Singer, and R.G. Vardiman, *Nucl. Instrum. Methods Phys. Res. B,* Vol $\frac{7}{8}$, 1985, p 915
94. P.J. Martin, W.G. Sainty, and R.P. Netterfield, *Vacuum,* Vol 35, 1985, p 621
97. J. Ullmann, G.K. Wolf, and W. Moller, *Nucl. Instrum. Methods Phys. Rev. B,* Vol 80/81, 1993, p 1507
101. R.A. Roy, D.S. Yee, and J.J. Cuomo, *Proc. Mater. Res. Soc. Symp.,* Vol 128, 1989, p 23
102. R. Roy, *Surf. Coat. Technol.,* Vol 51, 1992, p 203
103. P.H. Wocjiechowski, *J. Vac. Sci Technol. A,* Vol 6, 1988, p 1924
104. I.H. Loh, J.K. Hirvonen, J.R. Martin, P. Revesz, and C. Boyd, *Proc. Mater. Res. Soc. Symp.,* Vol 108, 1988, p 241
105. F. Parmigiani, E. Kay, T.C. Huang, and J.D. Swalen, *Appl. Opt.,* Vol 24, 1985, p 3335
106. F. Parmigiani, E. Kay, T.C. Huang, J. Perrin, W. Jurich, and J.D. Swalen, *Phys. Rev. B,* Vol 33, 1986, p 879
107. S.S. Nandra, F.G. Wilson, and C.D. Des Forges, *Thin Solid Films,* Vol 107, 1983, p 335
109. J.E.E. Baglin, in *Ion Beam Modification of Insulators,* P. Mazzoldi and G. Arnold, Ed., Elsevier, 1986, p 585
110. E.H. Hirsch and I.K. Varga, *Thin Solid Films,* Vol 69, 1980, p 99
111. R.A. Zuhr, S.J. Pennycook, T.S. Noggle, N. Herbot, T.E. Hayes, and B.R. Appleton, *Nucl. Instrum. Methods. Phys. Res. B,* Vol 37/38, 1989, p 16
112. K.-H. Müller, *Phys. Rev. B,* Vol 35, 1987, p 7906
113. D.W. Brown, E.P Donovan, C.M. Cotell, and K.S. Grabowski, *Proc. Mater. Res. Soc. Symp.,* Vol 268, 1992, p 173
114. I. Yamada, H. Usui, S. Tanaka, and S. Wada, *Nucl. Instrum. Methods Phys. Res. B,* Vol 59/50, 1991, p 302

Advantages and Limitations

The IBAD process is a hybrid of PVD and ion implantation. It combines the advantages of both techniques, while eliminating most of the disadvantages of each. Table 4 lists the advantages and limitations of IBAD.

Table 4 Advantages and limitations of ion-beam-assisted deposition

Advantages, achievable benefits
Low deposition temperature
High adhesion

Control of stress level
Bulk density achievable
Control of microstructure (nanocrystalline; metastable crystalline or amorphous; textured; and epitaxial, for some materials)
Reproducible
Precise modulation of composition with depth
Highly versatile for metals, ceramics, semiconductors, dielectrics
Limitations
Moderately higher cost than physical vapor deposition
Line-of-sight processing
Technology in commercial infancy (limited vendors)

Even polymers with low melting points can be coated, because the deposition temperature can be maintained between room temperature and nearly 100 °C (210 °F). The properties of adhesion, stress, and density are superior to those of PVD films, and there is a high degree of control over the microstructure. Depending on the deposition parameters, films can be deposited as:

- Nanocrystalline
- Amorphous
- Textured crystalline or epitaxial (for some materials)
- Metastable crystalline

Finally, the composition, or crystalline phases, can be precisely modulated as a function of thickness to produce functionally gradient materials with properties such as graded hardness, coefficient of thermal expansion, refractive index, density, tensile strength, and stress.

Applications

In order to place IBAD processing in the proper context with respect to potential applications, examples of current and projected IBAD uses are described below. Applications are discussed in the areas of optical films, oxidation- and corrosion-protection coatings, and tribological coatings. Applications are quite extensive in the optical thin-film industry, where the primary advantage offered by IBAD is film densification. Refractive index stability and freedom from environmental degradation are thus direct benefits of using the IBAD process in these applications. Research in the area of wear- and corrosion-resistant coatings for metals and ceramics is in an early development stage.

Films deposited using dry, benign, energetic deposition techniques are also attractive for replacing wet electrochemical processes, such as chromium and cadmium plating, that can pollute the environment. As a result of research already conducted, corrosion and wear problems involving planar and cylindrical geometries of parts less than 1 m (40 in.) in size can already be addressed technically using these energetic-deposition techniques. The issue that needs further attention,

then, is how each technique and the economics thereof relates to the scale-up of specific applications and associated geometries.

Optical Films. As already stated, the IBAD process was promoted earliest by those workers interested in optical thin films. This involved, in turn, two kinds of applications: those in which densification is the primary concern and those in which graded refractive index profiles are required.

For applications involving densification, low-energy argon or oxygen ions are typically used to bombard the optical thin films during deposition (Ref 16). As a result, the density is increased, sometimes up to that of the bulk material. The primary attraction is not necessarily that the refractive index is increased to near-bulk values, but that the index value is stable under humidity and temperature variations, because there are no voids or pores in the film that adsorb water vapor. This simplifies optical-coating design and promotes better control and reproducibility in the fabrication process. Another benefit of using low-energy ions is that adhesion to the substrate is improved, which also helps to increase production yields.

The IBAD process is just starting to be used to fabricate graded index coatings for antireflection coatings, reflection filters, and mirrors (Ref 115). Some of these devices can be tens of microns thick, which means that stress control becomes very important. In general, low energies are desired for the deposition of optical films to reduce absorption caused by radiation damage.

Ion-Beam Deposition. Several groups are depositing diamond-like carbon (DLC) by either direct ion-beam deposition or sputter deposition of carbon in the presence of ion bombardment (Ref 90). Using a Kaufman-type ion source, methane is introduced into the plasma and, at energies between 100 and 1000 eV, DLC is deposited at rates between 0.1 and 1 nm/s (1 and 10 Å/s). Applications include hard, protective coatings for optics and windscreens on vehicles. Although DLC absorbs strongly in the visible range, coatings that are between 20 and 200 nm (200 and 2000 Å) in thickness remain transparent enough to be used as protective transmission coatings. As of 1994, commercial sources are available to produce these coatings over reasonably large areas (200 mm, or 8 in., in diameter). The advantages of these coatings include low porosity, high scratch hardness, and high adhesion to most substrates.

Aqueous Corrosion. The first industrial application of IBAD for purposes of wear or corrosion resistance appears to be the coating of electric razor screens with titanium nitride (Ref 7). In this case, the choice of IBAD processing was dictated by both the superior adhesion of the films and a decreased number of pin holes, combined with low-temperature deposition on 316 stainless steel substrates. Because IBAD films are dense and have few pin holes, they are attractive for corrosion-protection applications.

Only a limited number of studies on the corrosion behavior of IBAD coatings have been made, but the early results look promising. Platinum, titanium carbide, titanium nitride, boron, diamond-like carbon, chromium nitride, boron nitride, chromium oxide, silicon nitride, and silicon coated on metals using the IBAD process provide excellent corrosion resistance (Ref 7, 8, 9, 43, 45, 116).

One company (Ref 13) has set up a processing line that coats steel sheet continuously with aluminum, titanium nitride, or aluminum oxide for decorative panel applications. Figure 3(b) depicts the apparatus. Part of the cost of the process is recovered by the use of inexpensive steel substrate and coating materials. The resulting films are adherent and more ductile than bulk materials, because of the microcrystalline or amorphous structures. Therefore, they can yield with the metal sheet so that some working of the metal should be possible after the coating is applied.

High-Temperature Oxidation. Work on achieving oxidation protection with IBAD coatings is also very new. Only a few results are in the literature describing the use of chromium nitride (Ref 100), titanium nitride (Ref 100), and silicon nitride (Ref 76) to protect titanium alloys. This seems to be a promising area for further research.

Ion-Induced Chemical Vapor Deposition (CVD). Several researchers have used reactive IBAD (mode 3 of Table 1) to produce unique hydrocarbon or ceramic films (Ref 117). In this process, a gas is introduced into the chamber, the substrate is cooled to induce condensation of the gas, and an ion beam strikes the surface. During the process, hydrocarbon bonds are broken, volatile species are released, and a coating is produced. For silicone oil vapor, the films can range from very low friction solid lubricants to very hard, corrosion-resistant silicon oxycarbide (SiO_xC_y) coatings, depending on the arrival ratio of ions to vapor-condensed atoms. This process is similar to CVD, in which the high temperature of the substrate provides the energy to initiate chemical reactions that are responsible for film formation. In

the ion-beam case, the same or similar reactions can be beam-induced at room temperature, opening the possibility of depositing CVD-like films on polymers and other temperature-sensitive substrates.

Friction and Wear. The IBAD process is being used to deposit solid-lubricant coatings, such as molybdenum disulfide. Advantages are that the coatings adhere to the substrate and have a longer lifetime as a result of densification (better coherence) (Ref 87, 118).

Hard coatings, such as titanium nitride, are by far the most extensively studied (Ref 1). The hardness of these coatings can be varied over a large range by microstructure control (Ref 55). The ductility of these films, even for the highest hardness, is much larger than that for bulk material or CVD titanium nitride films. Boron nitride is also a coating that is readily deposited by IBAD and has good wear characteristics (Ref 119). The IBAD technique is the only one, as of 1994, that is capable of depositing cubic boron nitride that is theoretically as hard as diamond (Ref 72). Currently, molybdenum disulfide, titanium nitride, and ion-stimulated CVD of silicone are the most developed materials for tribological applications.

References cited in this section

1. F.A. Smidt, *Int. Mater. Rev.,* Vol 135, 1990, p 61-128
7. M. Iwaki, *Mater. Sci. Eng. A,* Vol 115, 1989, p 369, and private communication
8. W. Ensinger and G. Wolf, *Mater. Sci. Eng. A,* Vol 116, 1989, p 1
9. G. Wolf, *Nucl. Instrum. Methods Phys. Res. B,* Vol 46, 1990, p 369
13. Optical Coatings Laboratory, Inc., private communications, 1992
16. P.J. Martin, R.P. Netterfield, and W.G. Sainty, *J. Appl. Phys.,* Vol 55, 1984, p 235
43. P.W. Natishan, E. McCafferty, E.P. Donovan, D.W. Brown, and G.K. Hubler, *Surf. Coat. Technol.,* Vol 51, 1992, p 30
45. Y. Chen, S. Liu, Z. Shang, C. Xu, Y. Zheng, X. Liu, and S. Zou, *Surf. Coat. Technol.,* Vol 51, 1992, p 227
55. R.A. Kant, S.A. Dillich, B.D. Sartwell, and J.A. Sprague, *Proc. Mater. Res. Soc. Symp.,* Vol 128, 1989, p 427
72. N. Tanabe and M. Iwaki, *Nucl. Instrum. Methods Phys. Res. B,* Vol 80/81, 1993, p 1349
76. S. Kiyama, H. Hirano, Y. Domoto, K. Kuramoto, R. Suzuki, and M. Osumi, *Nucl. Instrum. Methods Phys. Res. B,* Vol 80/81, 1993, p 1388
87. L.E. Seitzman, I.L. Singer, R.N. Bolster, and C.R. Gossett, *Surf. Coat. Technol.,* Vol 51, 1992, p 232
90. S.R. Kasi, H. Kang, and J.W. Rabalais, *J. Vac. Sci. Technol. A,* Vol 6, 1988, p 1788
100. C.J. Bedell, H.E. Bishop, G. Dearnaley, and J.E. Despout, *Nucl. Instrum. Methods Phys. Res. B,* Vol 59/60, 1991, p 245
115. E.P. Donovan, D. Van Vechten, A.D.F. Kahn, C.A. Carosella, and G.K. Hubler, *Appl. Opt.,* Vol 28, 1989, p 2940
116. E. McCafferty, G.K. Hubler, P.M. Natishan, P.G. Moore, R.A. Kant, and B.D. Sartwell, *Mater. Sci. Eng.,* Vol 86, 1987, p 1
117. Y. Itoh, S. Hibi, T. Hioki, and J. Kawamoto, *J. Mater. Res.,* Vol 6, 1991, p 871
118. H. Kuwano and K. Nagai, *J. Vac. Sci. Technol. A,* Vol 4, 1986, p 2993
119. K. Miyoski, D.H. Buckley, and T. Spalvins, *J. Vac. Sci. Technol. A,* Vol 3, 1985, p 2340

Future Trends

As a surface modification technique, IBAD is attractive because it retains the best features of PVD and ion implantation and eliminates the worst features. The application of IBAD films as wear- and corrosion-resistant coatings for metals and ceramics is just beginning. Because relatively thick coatings (i.e., many microns) of controlled composition and stress are achievable, it is expected that IBAD processing will be accepted into those application areas that currently use conventional PVD techniques without ion assistance.

Health and Safety

There are no special health concerns associated with these techniques. The considerations are identical to those for conventional electron-beam evaporation sources and sputtering targets. The techniques involve very little solid waste of benign elemental materials.

Arc Deposition

David M. Sanders, Joseph W. Glaser, and Steven Falabella, Lawrence Livermore National Laboratory

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Introduction

THE VACUUM ARC is a form of electrical discharge that is sustained primarily on the electrons and ions that originate from the electrodes used to produce the arc. The value of using vacuum arc deposition to produce coatings stems from the copious quantity of ions of electrode material composition that are generated during the discharge. Because the output of the vacuum arc is highly ionized, it is possible to control both the trajectory of the coating material during its transit from source to part and the energy with which ions impinge on that part. This level of control can be contrasted to competing vacuum coating technologies, such as electron-beam evaporation and magnetron sputtering, where the atoms of coating material travel from the source to the part to be coated in an electrically neutral state.

Adjusting the deposition energy can produce coatings that have greater density, purity, and adhesion. Under favorable circumstances, the quenching of ions can produce coatings with structures that have unusual properties, such as the extremely hard and smooth amorphous diamond coatings that will be described in this article. Although the use of ion trajectory control to improve coating properties has not been extensively explored, it has been used to overcome the major drawback of the cold cathodic arc process: the production of micron-scale particles of electrode material, or macroparticles. Macroparticle formation and the approaches used for removal are described in Ref 1, 2, and 3.

Due to the ion charge state, vapor produced by vacuum arc techniques is typically more reactive than that produced using evaporative or sputter techniques. This increased reactivity can lead to compound coatings in which better stoichiometry is produced when deposition occurs in the presence of a reactive gas. For instance, when compared with electron-beam evaporation and magnetron sputtering, the cathodic arc can produce stoichiometric titanium nitride over a much wider range of nitrogen partial pressures (Ref 4). This can be particularly important when depositing compound coatings on complex shapes.

The most widely used type of vacuum arc is a cathodic arc with a cooled cathode. Because the source material remains solid, it can operate in any orientation. This avoids the difficulties associated with the reactivity of liquid metals. Once the arc is initiated, it self-focuses into a small spot at which the heat and the electron flux are sufficient to vaporize and ionize the cathode material and liberate enough electrons to sustain the discharge. The arc currents are typically 100 A, whereas the ion currents fraction is approximately 10% of that.

Acknowledgements

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References

1. H. Randhawa and P.C. Johnson, A Review of Cathodic Arc Plasma Processing. *Surf. Coat. Technol.,* Vol 31, 1987, p 308-318
2. D.M. Sanders, Vacuum Arc-Based Processing, *Handbook of Plasma Processing Technology Fundamentals, Etching, Deposition, and Surface Interactions,* S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes, 1990, p 419-446
3. D.M. Sanders, D.B. Boercker, and S. Falabella, Coating Technology Based on the Vacuum Arc--A Review, *IEEE Trans. Plasma Sci.,* Vol 18 (No. 6), 1990, p 883-894

4. D.N. Poppov, T.D. Uzunov, and E.I. Dimitrov, Influence of the Nitrogen Partial Pressure on the Composition and Color of Titanium Nitride Coatings Obtained by Reactive Magnetron Sputtering and Reactive Arc Evaporation, *Bulg. J. Phys.* (Bulgaria), Vol 13 (No. 5), 1986, p 470-476

Process Utilization

Arc sources can be classified according to the duration of operation, the type of electrode that provides the metal vapor, and whether the arc comprises discrete spots or is distributed over a larger area of the electrode. There are pros and cons associated with using each type of arc. For example, in a pulsed cathodic arc source, the arc duration is typically short enough that direct cathode cooling is not needed, which simplifies the design and makes it easier to change target materials. In addition, the confinement of the arc spot to the cathode surface is not problematic, because the short arc duration typically means that there is not enough time for the arc spot to leave the cathode surface. Short arc durations also permit deposition of materials, such as silicon, that are vulnerable to cracking because of relatively poor thermal conductivity, coupled with a negative resistivity coefficient with respect to temperature, which slows arc spot motion. However, pulsed sources that have low duty cycles also have correspondingly low integrated coating rates.

Continuous cathodic arc sources are typically sustained by a low-voltage, high-current power supply, such as an arc welding supply. In this arc mode, the arc spots that appear to move rapidly on the negative electrode are actually separate arcing events that occur in rapid succession. The rate of apparent motion of the arc spot(s) is a strong function of:

- Cathode composition
- The presence and composition of any working gases
- The component of any magnetic fields parallel to the cathode surface

Continuous cathodic arc sources typically provide higher coating rates, but the cathode must be designed to dissipate the heat generated by the arc. Because the heat is concentrated in a small spot, direct water cooling is usually required. This leads to difficulty in changing cathodes and limits the use of some low thermal conductivity materials. In addition, arc confinement is essential, because damage to support components and contamination of the coating can occur if the arc spot leaves the cathode surface. More details on arc initiation, confinement, and other aspects of cathodic arc source design are provided in Ref 1, 2, and 3.

The cold cathodic arc source typically produces droplets of cathode material (macroparticles). These macroparticles result from the extreme localized heating of the cathode, which is due to the high current densities that are found in cold cathode arcs (10^4 to 10^8 A/cm^2). Unless the macroparticles can be removed from the plasma stream, they become lodged in the coating and are usually considered to be defects.

Macroparticle Filtering. An extensive body of knowledge that describes the filtering of these macroparticles in cases where such defects are unacceptable is now available. Two useful sources are Ref 5 and 6. Although the design of macroparticle filters is also beyond the scope of this article, one example is shown in Fig. 1. Briefly, this approach uses magnetic fields in order to constrain arc-produced electrons to follow a curved path from cathode to workpiece. This sets up an electrostatic field that channels the ions through the filter. The macroparticles, however, follow straight-line trajectories into baffles and are stopped. Although there are numerous designs for such filters, they all lose at least half of the desired coating material during transit through the filter, which leads to a corresponding decrease in deposition rate.

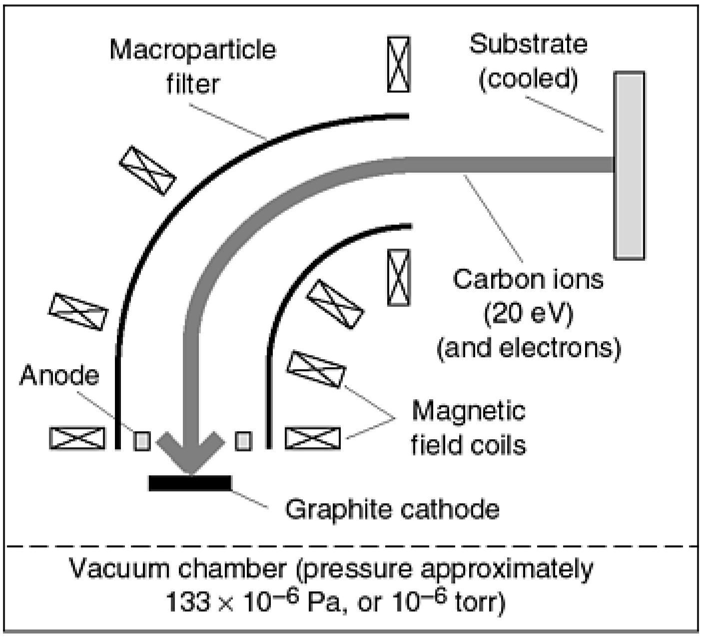


Fig. 1 Generic filter for removing macroparticles from a cathodic arc

A second general approach, which is appropriate in cases where a small number of macroparticles can be tolerated, is given by Coll (Ref 7). The cathode is placed behind a magnet structure that focuses the ion stream strongly at the coil location and then diverges outwardly toward the workpiece location. Arc confinement is provided by the magnetic field from the focusing coil (Fig. 2). The focusing action is thought to vaporize any macroparticles that pass through the plasma, reducing their number substantially. The source, however, requires a background gas pressure on the order of 1 Pa to operate, which can affect coating quality.

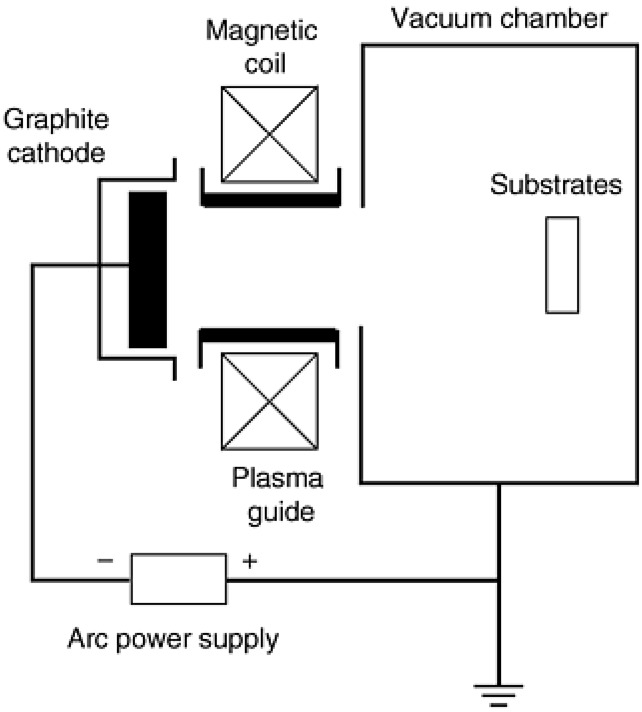


Fig. 2 Approach for reducing number of macroparticles from a cathodic arc

A third approach for avoiding macroparticles is to use an arc source that does not produce them. A broad class of such sources is based on a different type of arc, which is characterized by a much lower current density (~10 A/cm^2). This is about five orders of magnitude lower than that found in cold cathode arcs. The same arc currents are made possible because the arc is distributed over a much larger area of the electrode, which leads to the term ***distributed discharge arc*** (Ref 8). Although such distributed discharge arcs have been reported for both electrodes, most of the investigations to date have been on arcs that vaporize the positive electrode or anode.

Arc Source Types. Anodic arc sources can be classified according to the method by which ionization electrons are supplied (Ref 3). The sources can be hot filament (Ref 9), hollow cathode (Ref 10, 11, 12, 13), or cathodic arc (Ref 14, 15, 16). Typical configurations are shown in Fig. 3 and 4.

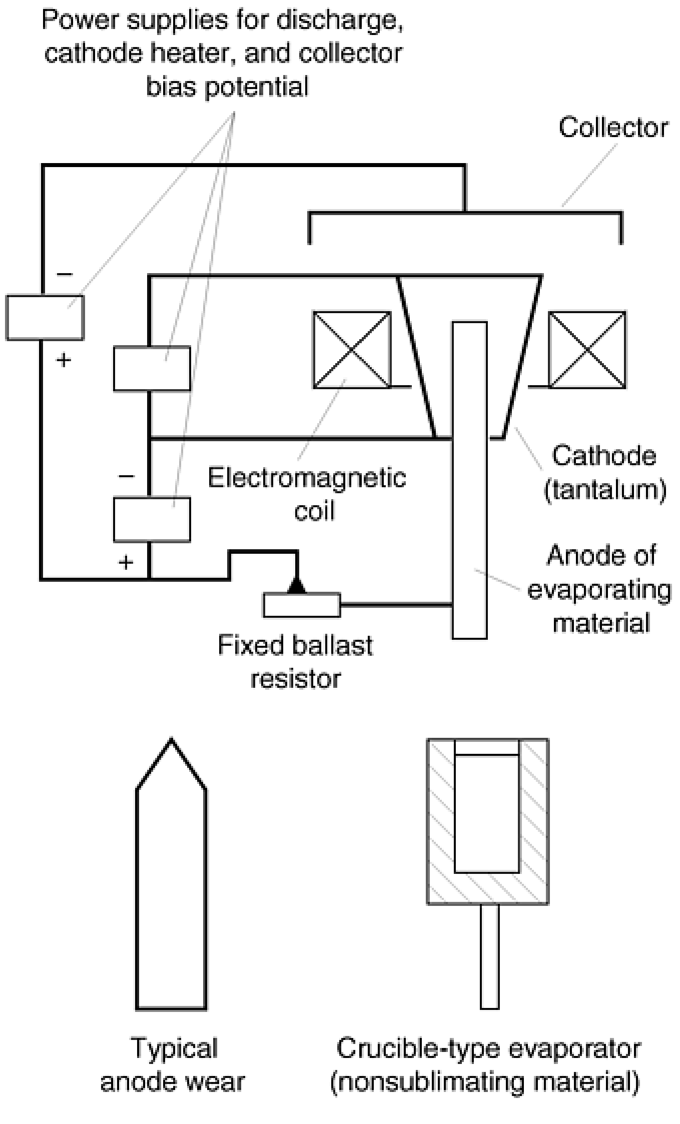


Fig. 3 Anodic arc device. Source: Based on Ref 11

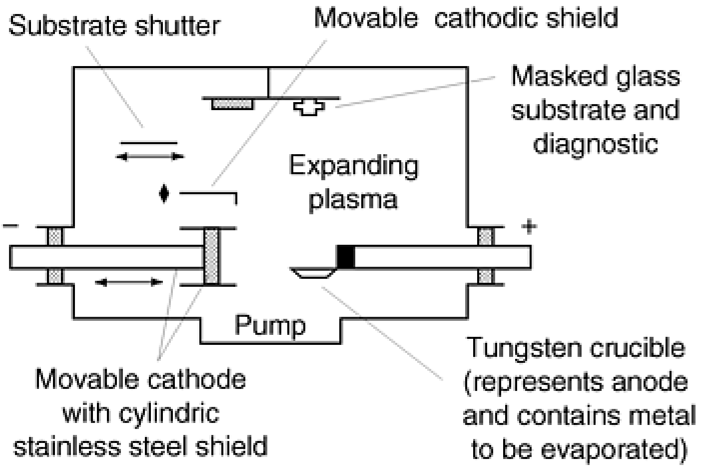


Fig. 4 Arc discharge apparatus. Source: Based on Ref 18

The hollow cathode arrangement described by Dorodnov (Ref 10, 11) operates as a self-sustaining arc (Fig. 3). The material to be evaporated, which forms the anode, is located within a hollow cathode. The anode material evaporates under a low-voltage (10-50 V), high-current (~100 A) electron beam, which, along with electrons trapped within the hollow cathode, ionizes the vapor (Ref 7). Because voltages are relatively low, sputtering of the cathode is minimized. Dorodnov reports using this source for chromium, carbon, magnesium, titanium, molybdenum, silicon, germanium, and copper (Ref 11). Saenko (Ref 13, 17) used this source to process substrates with diameters up to 150 mm (6 in.). Derkach and Saenko (Ref 12) incorporated a divergent plasma lens, which resulted in a 150 mm (6 in.) diameter copper vapor plasma with an ion-component beam uniformity of about 2%. The deposition rate was reported to be approximately 100 nm/s (4 μin./s).

The approach taken by Ehrich et al. (Ref 16) used a cathodic arc to supply ionization electrons to the vapor stream (Fig. 4). In this configuration, copper and zinc films were deposited at rates between 23 and 65 nm/s (0.9 and 2.6 μin./s) (below that reported by Dorodnov). The films were found to be homogeneous, with film purities up to 99.9% (Ref 14). The researchers determined an ion temperature of approximately 0.7 eV at plasma densities between 10^{15} and $10^{17}/m^3$ (Ref 18). These films were found to have densities that were lower than bulk material densities by 0 to 10%. Overall, this technique produced compact films with physical properties that were close to those of the bulk materials.

The use of shielding eliminated contamination of the deposited material that was due to cathodic bombardment (Fig. 4). This type of contamination, along with source contamination from the containment vessel, are issues that need to be addressed when designing this arc source. Dorodnov (Ref 11) suggests using a hearth made of the same material as that being evaporated. For vapors originating from sources that sublimate, such as carbon, actively cooled supports outside the heat-affected zone have been used. However, the relatively low evaporation rate (compared with the cathodic arc technique), short run times, and issues associated with filament lifetime have hindered the commercial development of the anodic arc source.

The utility of the anodic arc lies in its ability to generate a flow of predominant monocharged ions without macroparticles. This flow of single-charge-state ions facilitates deposition by allowing greater control of deposition energies. This can be contrasted with the cathodic arc, which produces multiple-charge-state ions. Deposition onto a biased substrate in the presence of multiple-charge-state ions may result in sputter damage to the substrate. Because the charge-state distribution in the anodic arc is nearly single valued, substrate sputtering can readily be controlled. Similarly, the monocharged nature of the anodic-arc-generated ions simplifies stream focusing and control. This facilitates usage in materials processing and as a plasma source in space research.

The rate of deposition, using arc technology in a laboratory environment can range from several angstroms/minute to 0.1 mm/s (4 mils/s) depending on the specific process chosen and the coating quality required. High-quality optical coatings of aluminum oxide and zirconium oxide have been produced using a cathodic arc with a macroparticle filter at rates of 35 μm/h and 20 μm/h, respectively (Ref 19).

References cited in this section

1. H. Randhawa and P.C. Johnson, A Review of Cathodic Arc Plasma Processing. *Surf. Coat. Technol.*, Vol 31, 1987, p 308-318
2. D.M. Sanders, Vacuum Arc-Based Processing, *Handbook of Plasma Processing Technology Fundamentals, Etching, Deposition, and Surface Interactions*, S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, Ed., Noyes, 1990, p 419-446
3. D.M. Sanders, D.B. Boercker, and S. Falabella, Coating Technology Based on the Vacuum Arc--A Review, *IEEE Trans. Plasma Sci.*, Vol 18 (No. 6), 1990, p 883-894
5. D.B. Boercker, S. Falabella, and D.M. Sanders, Plasma Transport in a New Cathodic Arc Ion Source--Theory And Experiment, *Surf. Coat. Technol.*, Vol 53 (No. 3), 1992, p 239-242
6. I.I. Aksenov et al., Plasma Flux Motion in a Toroidal Plasma Guide, *Plasma Phys. and Contrl. Fus.*, Vol 28 (No. 5), 1986
7. B.F. Coll et al., Diamond-Like Carbon Films Synthesized by Cathodic Arc Evaporation, *Thin Solid Films*, Vol 209 (No. 2), 1992, p 165-173
8. A.M. Dorodnov, Technical Applications of Plasma Accelerators, *Sov. Phys.-Tech. Phys.*, Vol 23 (No. 9), 1978, p 1058-1065
9. R. Buhl, E. Moll, and H. Daxinger, Method and Apparatus for Evaporating Material Under Vacuum Using Both Arc Discharge and Electron Beam, U.S. Patent, 4,448,802, 1984
10. A.M. Dorodnov, N.P. Kozlov, and N.V. Reshetnikov, Characteristics of Arc Anodes with Forced or Radiative Cooling, *High Temp.*, Vol 13 (No. 3), 1975, p 556-561
11. A.M. Dorodnov, A.N. Kuznetsov, and V.A. Petrosov, New Anode-Vapor Vacuum Arc with a Permanent Hollow Cathode, *Sov. Tech. Phys. Lett.*, Vol 5 (No. 8), 1979, p 418-419
12. A.A. Derkach and V.A. Saenko, Source of Metal-Vapor Plasma with Axial Anode, *Instrum. Exp. Tech.*, Vol 33 (No. 6), 1990, p 1421-1423
13. V.A. Saenko, Production of Plasma from Vapors of Solids, *Instrum. Exp. Tech.*, Vol 33 (No. 4), 1990, p 174-176
14. H. Ehrich, Vacuum Arcs with Consumable Anodes and Their Application to Coating, *Vak.-Tech.*, Vol 37 (No. 6), 1988, p 176-182
15. H. Ehrich, The Anodic Vacuum Arc. I. Basic Construction and Phenomenology, *J. Vac. Sci. Technol.*, Vol A6 (No. 1), 1988, p 134-138
16. H. Ehrich et al., Plasma Deposition of Thin Films Utilizing the Anodic Vacuum Arc, *IEEE Trans. Plasma Sci.*, Vol 18 (No. 6), 1990, p 895-903
17. V.A. Saenko, A.A. Derkach, and V.M. Poznikharenko, Discharge Chamber of Metal-ion Source, *Instrum. Exp. Tech.*, Vol 33 (No. 4), 1990, p 910-912
18. M. Mausbach, H. Ehrich, and K.G. Muller, Cu and Zn Films Produced with an Anodic Vacuum Arc, *Vacuum*, Vol 41 (No. 4-6), 1990, p 1393-1395
19. P.J. Martin, R.P. Netterfield, and T.J. Kinder, Ion-Beam-Deposited Films Produced by Filtered Arc Evaporation, *Thin Solid Films*, Vol 193 (No. 1-2), 1990, p 77-83

Processing Parameters

Besides the typical processing variables that characterize other vacuum deposition processes, vacuum arc deposition offers additional control of the arrival energy of coating ions. In the case of conductive or semiconductive coatings, this bias can be controlled using a direct-current power supply. The level of bias is limited at the upper end by thermal considerations, because the part being coated is heated by condensing ions. Many of the trends that exist for other ion plating processes also apply to vacuum arc deposition. The main difference is ion composition. In the case of vacuum arc deposition, the ions are the particles that form the coating. With most other ion plating processes, the majority of ions involved are ionized gas molecules. This distinction can become important when coating parts that have complex shapes during a reactive process.

Properties of Deposited Materials

Vacuum arc deposited coatings tend to have compressive stress that is due to the impact energy of ions on the part being coated. Titanium nitride can be deposited on cutting tools at relatively low temperatures and still maintain excellent adhesion and cutting characteristics.

The deposition of carbon films by the cathode arc presents a particularly interesting example. The carbon films produced by the deposition of ions of roughly 20 eV energy have a hardness of 40 to 100 GPa (6 to 15 × 10^6 psi), a modulus of 300 to 500 GPa (45 to 75 × 10^6 psi), and an optical transmission of 0.5 to 50 μm. The coating is amorphous, with primarily sp^3 bonding characteristic of crystalline diamond. It has a low coefficient of friction, 0.02 to 0.1, and a hydrogen content of less than 0.1%. This is an example of a material that can only be produced by the condensation of energetic ions.

Process Advantages, Limitations, and Applications

One advantage of vacuum arc technology is the relative safety afforded by the low-voltage power supplies, compared with the high-voltage supplies necessary for sputtering and electron-beam evaporation. A second advantage is the relatively benign environmental impact of this technology, compared with competing means for depositing refractory metals, such as chemical vapor deposition.

All types of vacuum arc deposition processes share the same potential for making commercially valuable coatings. However, cold cathode sources produce macroparticles that may need to be removed in certain applications. Although hot sources avoid the macroparticle problem, they have other design constraints that must be evaluated, such as crucible reactions and heating and cooling cycle times.

As of 1994, the most important applications of coatings produced by the vacuum arc process involve the reactive deposition of nitrides for extending the useful life of cutting tools, reducing wear and friction in parts of machines, and providing a gold color in certain decorative applications. In particular, the cold cathode cathodic arc and one form of anodic arc have been used extensively in commercial environments for coating cutting tools with titanium nitride.

Future Trends

As with any emerging technology, the vacuum arc will displace existing approaches only when a compelling advantage can be demonstrated. Situations in which extremely good adhesion is desired can represent opportunities for the vacuum arc process. Adhesion of copper to glass with bond strengths sufficient to fracture the glass during a pull test have been reported (Ref 20). Applications that require an efficient process for rapidly depositing refractory metal coatings can be opportune for the cathodic arc. This technology should be particularly attractive in situations where the presence of a small number of macroparticles does not present difficulties. It may also be attractive for producing hard, amorphous diamond coatings for various tribological applications. There are also numerous potential applications for corrosion-barrier coatings. Examples include coatings on fibers used in metal-matrix composites and protective coatings for turbine blades (Ref 1). Filtered arcs can produce very high-quality ceramic coatings at high deposition rates (Ref 21) because of the high reactivity of the ions.

References cited in this section

1. H. Randhawa and P.C. Johnson, A Review of Cathodic Arc Plasma Processing. *Surf. Coat. Technol.,* Vol 31, 1987, p 308-318

20. D.M. Sanders and E.A. Pyle, Magnetic Enhancement of Cathodic Arc Deposition, *J. Vac. Soc. Tech.,* Vol A5, 1987, p 2728-2731

21. P.J. Martin et al., Deposition of TiN, TiC, and TiO_2 Films by Filtered Arc Evaporation, *Surf. Coat. Technol.,* Vol 49 (No. 1-3), 1991, p 239-243

Ion Implantation

James K. Hirvonen, U.S. Army Research Laboratory; Bruce D. Sartwell, U.S. Naval Research Laboratory

Introduction

ION IMPLANTATION involves the bombardment of a solid material with medium-to-high-energy ionized atoms and offers the ability to alloy virtually any elemental species into the near-surface region of any substrate. This near-surface alloying can be performed irrespective of thermodynamic criteria such as solubility and diffusivity. These advantages, coupled with the additional possibility of low-temperature processing, have prompted explorations into applications in which the limitations of dimensional changes and possible delamination of conventional coatings are a concern. In almost all cases the modified region is within the outermost micrometer of the substrate, often only within the first few hundred angstroms (i.e., microinches) of the surface. Maximum. concentrations of several tens of atomic percent are usually achievable, although this depends on the ion-substrate combination.

During implantation, ions come to rest beneath the surface in less than 10^{-12} s. This rapid stopping time produces an ultrafast quench rate in the wake of the stopping ion. This allows many novel surface alloys or compounds unattainable by conventional (equilibrium) processing techniques to be produced at room temperature. These include substitutional solid solutions of normally immiscible or low-solubility elements. Such highly metastable and amorphous alloys often possess unique physical and chemical properties. Ion implantation has been used extensively in the semiconductor industry since the 1970s to introduce dopant atoms reproducibly into silicon wafers to modify electrical performance, and it is used routinely in several stages of integrated circuit production. It allows fabrication of electronic devices not producible by any other process, largely due to the highly reproducible control of dopant concentration levels over several orders of magnitude as compared to doping by thermal diffusion. Since the mid-1970s, the use of ion implantation and other closely related ion beam processes has expanded into a number of diverse application areas in the international research and development community. However, only relatively recently have applications in the industrial sector developed.

Research interests in metals have expanded from the initial friction and wear studies to include other areas, such as corrosion, oxidation, fatigue, and studies of basic metallurgical mechanisms (Ref 1, 2). In addition to metals, polymers and ceramics have been studied with the principal aims of increasing the conductivity of polymers (Ref 3) and improving the fracture toughness and tribological properties of ceramics (Ref 4).

On a commercial scale, the applications for ion implantation of metals continue to increase, at present mainly for antiwear treatment of high-value components. A large number of industrial trials have involved the implantation of nitrogen for improving the wear resistance of coated and uncoated tools and other precision components. Implantation appears to be an attractive technique for treating industrial components by stabilization of the microstructure (preventing a change in wear mode), by transformation to a wear-resistant mode, or by chemical passivation to prevent a corrosive wear mode (Ref 5).

References

1. J.K. Hirvonen, Ed., *Ion Implantation,* Academic Press, 1980
2. J.K. Hirvonen, *Surface Alloying by Ion, Electron, and Laser Beams,* L. Rehn, S.T. Picraux, and H. Wiedersich, Ed., ASM International, 1987, p 373-388
3. T. Venkatesan, *Proceedings of the Fourth International Conference on Ion Beam Modification of Materials,* B.M. Ulrich, Ed., 1985, p 461-467
4. C.J. McHargue, C.W. White, B.R. Appleton, G.C. Farlow, and J.M. Williams, *Ion Implantation and Ion Beam Processing of Materials,* G.K. Hubler, O.W. Holland, C.R. Clayton, and C.W. White, Ed., Elsevier, 1984, p 385-393
5. G.K. Hubler, *Surface Alloying by Ion, Electron, and Laser Beams,* L. Rehn, S.T. Picraux, and H. Wiedersich, Ed., ASM International, 1987, p 287-324

Fundamentals of the Ion Implantation Process

Figure 1 shows a schematic view of the path of an individual ion as it loses energy in a material, thereby forming a shallow surface-modified region. As indicated in the figure, the ion does not travel in a straight path to its resting place, due to collisions with the target atoms. Target atoms are displaced from their lattice sites with sufficient energy that they

can themselves displace additional target atoms, resulting in a collision cascade. These individual collisions with lattice atoms within a single collision cascade are shown in the insert at the bottom of Fig. 1.

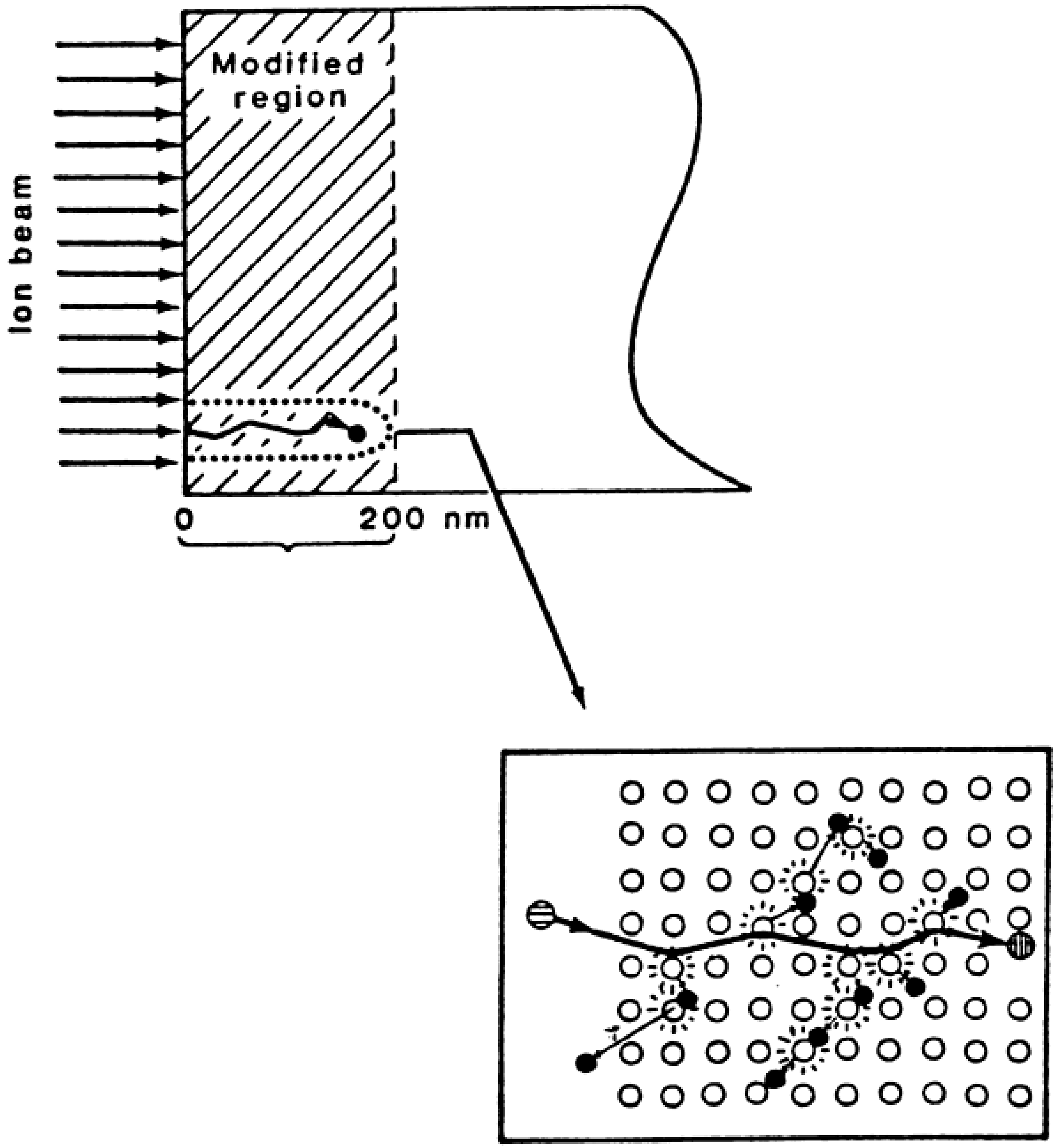


Fig. 1 Schematic view of ion implantation process (top) and depiction of the interactions with substrate atoms in a single collision cascade (bottom). Source: Ref 6

The actual integrated distance traveled by the ion is called the range, *R*. The net penetration of the ion into the material, measured as projected onto the original trajectory, is called the projected range. Ion implantation is a random process, normally producing a Gaussian-shaped impurity depth profile whose centroid is defined as the average projected range, R_p. The statistical nature of the scattering process gives rise to a distribution of ions around the projected range depth. The average fluctuation (standard deviation) in the projected range is called the range straggling, ΔR_p.

The ion energy directly affects both the range and the distribution of the implanted ions in a given substrate. At higher energies a greater spread in the ion distribution (a greater ΔR_p) is realized for a given dose, which is the number of implanted ions per unit area of the surface of the material (areal density), usually expressed as ions/cm^2. The areal dose (also called fluence) is a convenient unit of ion implantation because the actual volume concentration associated with an

implantation is a function of ion species, ion energy, and substrate material. For metals, beneficial doses can span the range of 10^{15} to 10^{18} ions/cm^2, depending on the application (see the section "Applications" in this article). The determination of the implanted atomic concentration (atoms/cm^3) requires relating the areal density of implanted atoms to their spatial extent. At low ion doses, the implant profile can normally be approximated as a Gaussian distribution centered about the projected range. Accordingly, the width of the distribution can be expressed by the standard deviation of the Gaussian distribution, ΔR_p. The expression for the peak concentration (N_p) of a Gaussian distribution is given in terms of the applied dose (N_A) and range straggling as:

$$N_p(atoms/cm^3) = \frac{N_A(atoms/cm^2)}{\sqrt{2}p\Delta R_p(cm)}$$

Figure 2 shows the projected range and range straggling for nitrogen ions implanted into iron versus the initial ion energy. The range distribution is shown as a Gaussian distribution with R_p and ΔR_p characteristic of the ion energy. For a given energy, a lighter ion such as nitrogen will penetrate farther and will undergo more large-angle scattering (leading to a broader distribution) than would a heavier ion such as chromium. Each implanted ion can displace hundreds to thousands of lattice atoms as it travels into the substrate surface. This results in a net damage distribution that is also normally Gaussian-shaped but is situated closer to the surface than the range distribution, because each ion creates damage between the surface and its final resting place in the lattice. This lattice damage can render ionic or covalently bonded lattices amorphous during implantation, whereas a nondirectionally bonded (metal) substrate can either self-anneal, with no residual damage, or else can retain point defects or extended defects (e.g., dislocations) resembling those of a heavily work-hardened metal or alloy. Ion implantation of certain species (e.g., phosphorus in iron) can stabilize amorphous structures in metals in a manner analogous to bulk rapid quench techniques such as splat cooling.

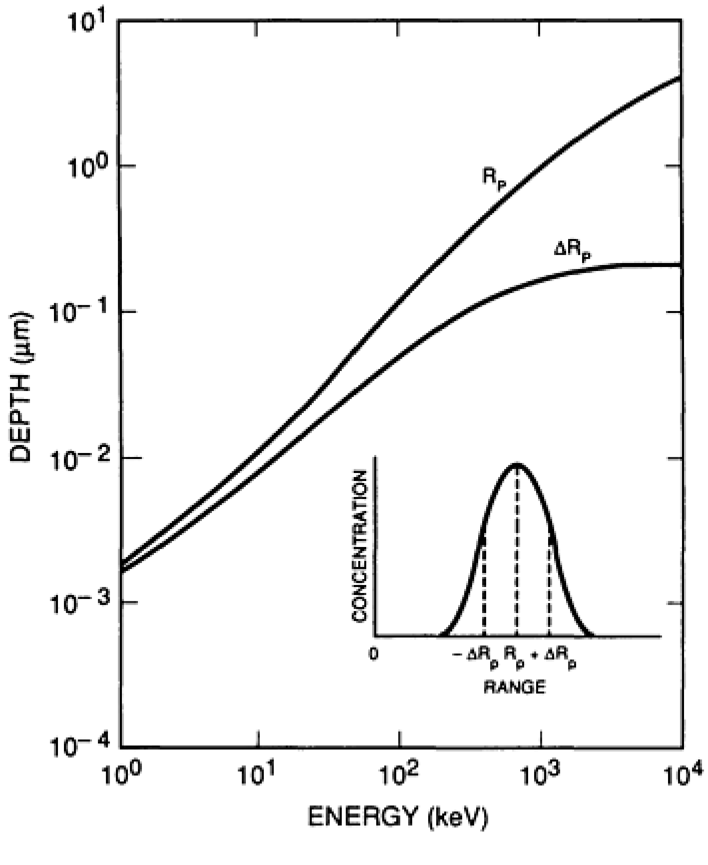
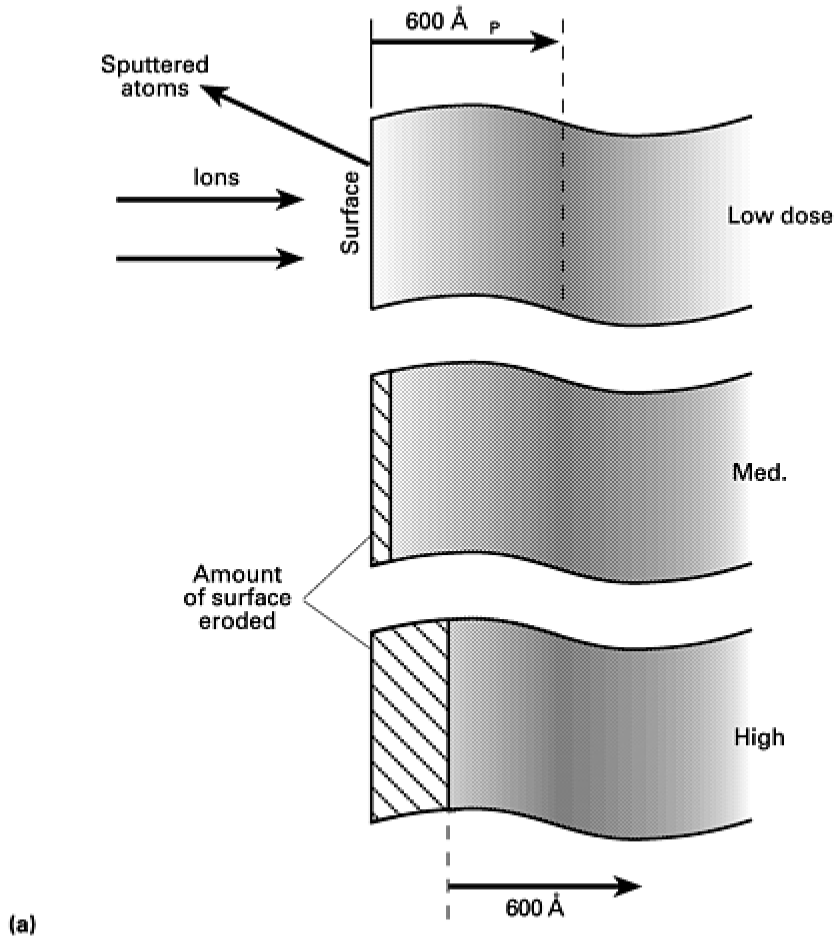


Fig. 2 The projected range, R_p, and range straggling, ΔR_p, of nitrogen ions implanted into iron vs. the initial ion energy. Source: Ref 6

As an ion penetrates a material, there is a certain probability that a surface atom will be ejected from its lattice site, because there is some momentum directed back toward the surface in a collision cascade that allows an atom to receive sufficient energy to overcome its surface-binding energy. This phenomenon is called sputtering and is analogous to the

erosion of materials by the impact of high-velocity particles. The ratio of the number of substrate atoms ejected per incident ion is commonly termed the sputtering coefficient, *S*. As a general rule, for a given substrate material, *S* will increase with increasing ion mass and will increase sharply at more oblique angles of incidence. For a given ion at normal incidence, *S* depends principally on the surface binding energy of the material, which can be related to its heat of sublimation. Therefore, for a given ion, *S* will decrease with increasing heat of sublimation for the substrate material. Values for *S* can range from less than 1 for the case of a light ion incident on a heavy substrate (e.g., nitrogen implanted into iron) to greater than 10 for very heavy ions in a lighter substrate (e.g., tantalum ions implanted into iron).

Figure 3(a) shows a schematic view of the evolution of the concentration depth profile of an implanted element for the case where *S* is greater than unity. In this particular example, the projected range of ions is shown as being 600 Å. This closely represents the implantation of 200 keV chromium ions into steel (or iron). At a low dose, the distribution is essentially Gaussian, as discussed earlier, and there is a low concentration of implanted atoms at the surface. However, as the dose increases and the surface is eroded, an increasing number of previously implanted atoms are exposed on the surface, and these near-surface atoms are subject to sputtering just as the target atoms are.



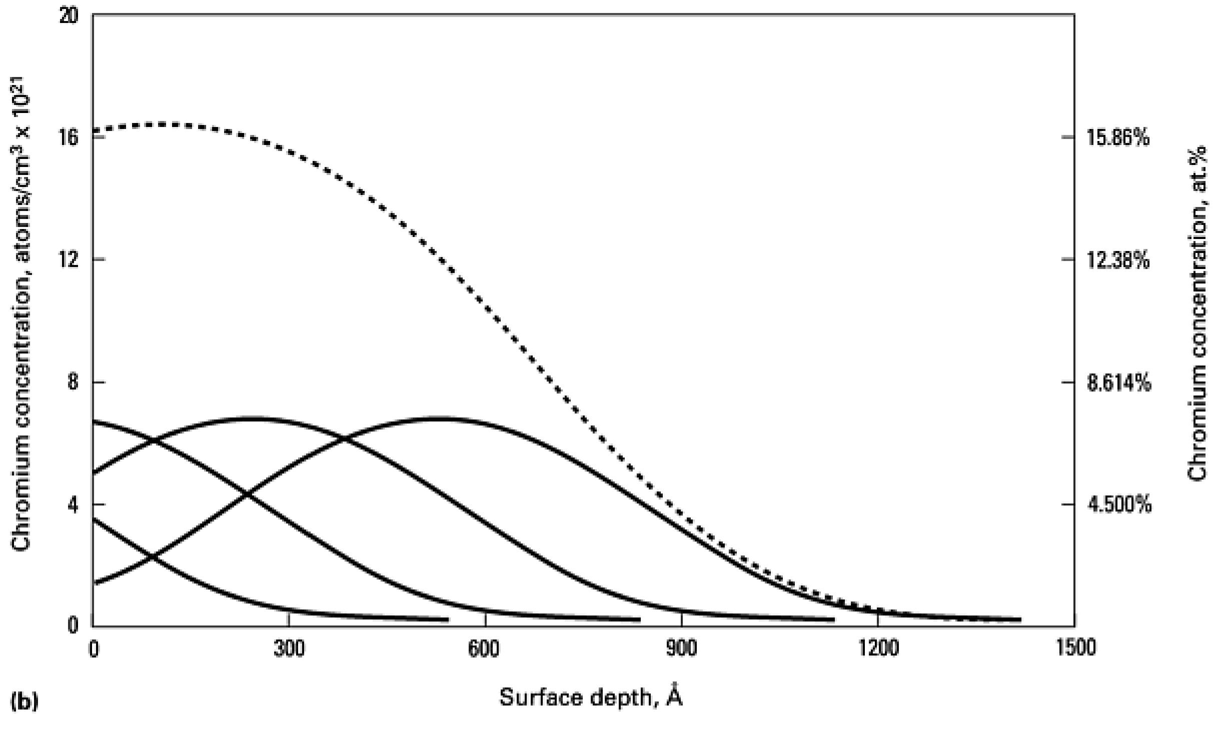


Fig. 3 (a) Schematic view of the development of implanted impurity profiles from low to high doses. Source: Ref 6. (b) Computer simulation of four consecutive 5 × 10^{16} Cr/cm^2 implantations at 200 keV energy into iron, accounting for sputter erosion of the surface for each implantation. The sum of the four individual profiles (the curve of dark squares) yields a distribution with a maximum near the receded surface. Source: Ref 7

At a particular dose level, called the saturation dose, a steady-state situation is established whereby the rate of removal of previously implanted atoms is equal to the arrival rate of energetic ions. The peak concentration of the implanted element distribution approaches the surface, as shown in Fig. 3(b), as the implanted dose increases and approaches the saturation dose. Generally, the maximum surface concentration of the surface element is equal to 1/(*S* + 1). For the example of 200 keV chromium ions in iron, *S* has a value of about 5 atoms/ion, so the maximum surface concentration of chromium would be about Å or 16 at.%. In this case, the steady-state dose would be approximately 2×10^{17} ions/cm^2. This behavior is quantitatively predicted by analytic models, as shown in Fig. 3(b), which illustrates the sputter removal of the surface and the surface enrichment of the implanted species resulting from successive (lower-dose) implantations.

For certain ion-substrate combinations and concentrations, chemical reactions with molecular species present in the vacuum chamber can be induced. An excellent example of this is titanium implantation into steel. At high titanium doses, highly reactive titanium atoms become exposed on the surface and react with the residual CO and CO_2 hydrocarbon molecules normally present in the vacuum chamber. When the partial pressure of carbon-containing molecules is 1×10^{-6} torr or higher, the implantation results in the formation of an amorphous Fe-Ti-C surface layer that has been shown to reduce friction and wear greatly (see the section "Applications" in this article). When the background pressure in the chamber is less than 10^{-6} torr, there are insufficient carbon-containing molecules to produce the carburized surface layer. A consequence of these surface chemical reactions is a considerably reduced sputtering yield because of the increase in the surface binding energy due to compound formation. This phenomenon has been exploited by deliberately introducing gases into the vacuum chamber during implantation. For example, for tantalum implantation into steel, where normally *S* is approximately 10, the introduction of oxygen into the chamber to 1×10^{-5} torr (partial pressure) reduces the sputtering by more than a factor of three, due to the formation of an almost pure Ta_2O_5 layer at the surface for a tantalum dose of 2×10^{17} ions/cm^2.

References cited in this section

6. G.K. Hubler, "Ion Beam Processing," Memorandum Report 5828, Naval Research Laboratory, 1987

7. S.N. Bunker and A.J. Armini, *Nucl. Instrum. and Methods in Phys. Res.,* Vol B39, 1989, p 7-10

Advantages and Limitations of the Ion Implantation Process

Table 1 gives the advantages and limitations of the implantation process for surface modification.

Table 1

Advantages	**Limitations**
Produces surface alloys independent of thermodynamic criteria	Limited thickness of treated material
No delamination concerns	High-vacuum process
No significant dimensional changes	Line-of-sight process
Ambient-temperature processing possible	Alloy concentrations dependent on sputtering
Enhance surface properties while retaining bulk properties	Relatively costly process; intensive training required compared to other surface treatment processes
High degree of control and reproducibility	Limited commercial treatment facilities available

The ability to use ion implantation to inject alloying species forcibly into the near-surface region of virtually any material, independent of thermodynamic criteria such as solid solubility and diffusivity, is an important feature for applying the process to basic metallurgical studies. For example, one can prepare supersaturated or metastable systems and study their return to equilibrium by suitable thermal annealing and observation of their microstructure. This application of ion implantation technology has been exploited to measure low-temperature diffusion, solid solubility, and trapping phenomena in alloys (Ref 8).

Because implanted near-surface layers are an integral part of the substrate, without an interface, they can sustain very high stresses without the occurrence of the delamination that plagues certain types of coatings, especially those deposited at low temperatures.

Strictly speaking, ion-implanted surfaces do experience a dimensional change, albeit on a microscopic level (typically less than 0.1 μm, or 4 μin.), due to erosion caused by sputtering. In addition, at doses greater than 10^{17} ions/cm^2 some degree of surface roughening may occur due to sputtering effects. The accumulation of insoluble implanted gaseous species may also cause surface blistering. However, from a practical engineering perspective it is normally accurate to portray implantation as a process that does not significantly affect substrate dimensions or topography.

Implantation processing can be carried out at near-ambient temperatures, but this depends on the thermal mass of the substrate, the relative ion beam power (W/cm^2) being delivered to the substrate, and, critically, the ability to conduct heat away from the substrate, because radiative cooling is negligible at desired processing temperatures. The latter factor depends on the thermal conductivity between the substrate and the fixturing to which it is attached in the vacuum chamber.

The limited thickness of the implanted layer (typically less than a micrometer) is an intrinsic limitation of the ion implantation process and is dictated by the physics of the energy loss processes. For applications requiring thicker surface-modified regions, it may be desirable to employ hybrid ion beam/coating processes. See the article "Ion-Beam-Assisted Deposition" in this Volume.

Ion implantation is intrinsically a vacuum process requiring background pressures of 10^{-5} torr or less. Manipulation of components, through the use of vacuum-compatible fixtures, and thermal heat sinking are often required to ensure both uniform dosage and adequate cooling to dissipate the imposed heat load on the component due to the energetic ion beam. This requirement poses some limitations on the types of substrates that can be implanted.

Directed beam ion implantation is a line-of-sight process. It lacks the so-called throwing power of certain other plasma-based coating processes, which can better treat irregular surface features due to multiple scattering of atoms (ions) within the higher-pressure plasma.

As discussed previously, implanted atoms are always in an intimate mixture with atoms of the original substrate, thus forming a surface alloy. However, because of sputtering, desired alloy concentrations may be unattainable for many ion-substrate combinations.

Reference cited in this section

8. S.M. Myers, *Ion Implantation*, Chapter 10, J.K. Hirvonen, Ed., Academic Press, 1980

Equipment and Processing Times

As of 1994, ion implantation processing technology is still a relatively specialized process compared to many conventional surface treatment techniques. Most implanters in use today for metals applications require highly trained operators because they were originally built for processing silicon wafers, which required very rigorous process control, Such implanters have been subsequently modified for more general use. Typically, the cost of processing components in these types of systems is higher per unit area than for conventional coatings or surface modification techniques.

Figure 4 is a schematic of a typical medium-current semiconductor implanter adapted for metals implantation. This implanter uses a versatile ion source capable of producing heavy metal ion beams of most elements by introducing metal vapor or a volatile compound of the element into the plasma discharge of the ion source. After the positive ions are

extracted from the ion source, they are mass analyzed by being passed through a 90° sector magnet. They are subsequently accelerated to their ultimate energy (typically 30 to 200 keV), then directed and scanned over the target.

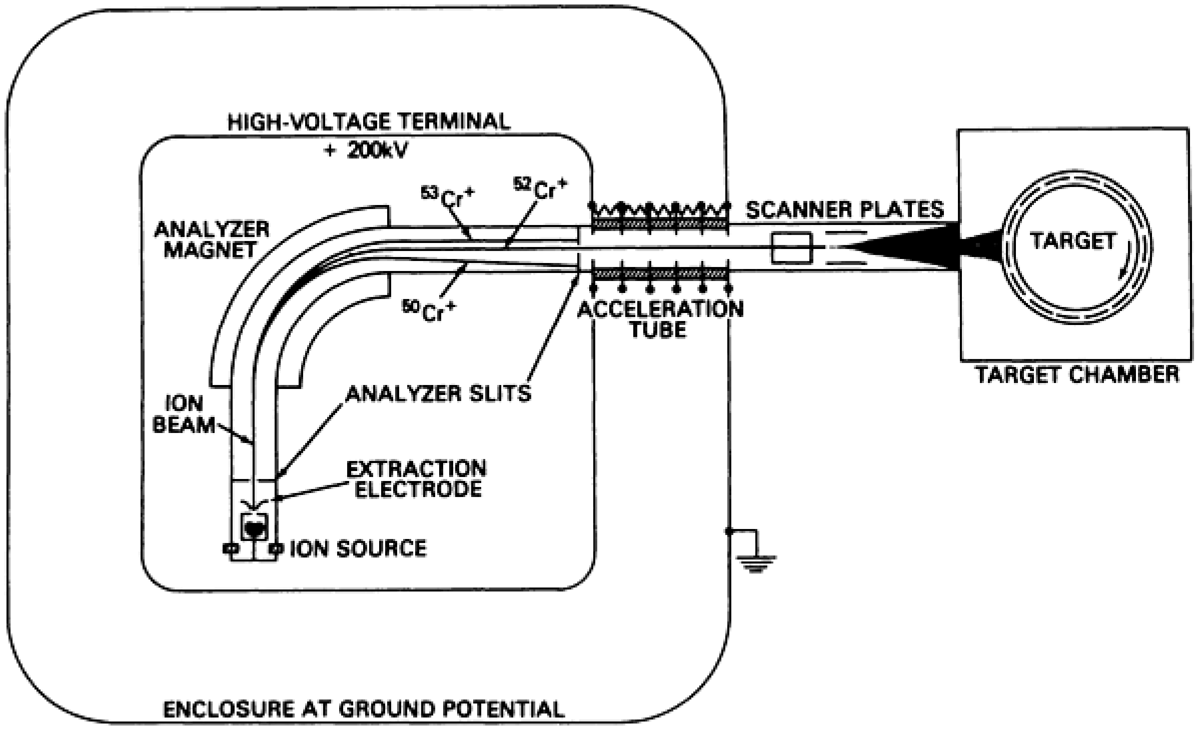


Fig. 4 Schematic of Naval Research Laboratory implantation facility for surface alloying. Mass analyzed $^{52}Cr^+$ beam being transported for the implantation of bearing components to improve their corrosion resistance. The footprint of this machine is about 2.5 × 4 m. Source: Ref 9

An implanter of this design can produce from 1 to 10 mA (6 to 60 × 10^{15} ions/s) of positive ion beam, depending on the size and design of the ion source. At an energy of 100 keV, this beam current corresponds to energy densities of 100 to 1000 W in the envelope of the beam. It is therefore imperative to either spread this beam energy over a large area or to ensure good thermal conductivity of the substrates to a heat sink in order to limit beam heating. Both of these approaches are used in practice. The actual processing times can be determined by knowing the area to be treated, the ion current intensity, and the geometrical factors involving manipulation of the substrates through the beam to ensure uniform surface coverage. For a stationary substrate, an average beam current of 1 mA will deliver 10^{17} ions in about 15 s, a typical ion dose required for each square centimeter of the substrate. The actual implantation time will therefore depend on the area over which the beam is scanned to ensure both dose uniformity and adequate cooling. Larger batch sizes help reduce beam heating and improve the economics of processing.

Several approaches have been taken to simplify and reduce the cost of implantation treatments, such as using alternative ion source designs when using mass analysis (Ref 10). Large-scale dedicated systems have also been built without mass analysis to implant nitrogen into fairly massive components. One such unit in the United Kingdom has a processing chamber that is more than 2 m in diameter and 2 m in length and has been used to implant components such as automobile camshafts, dies, and plastic molds weighing more than 500 kg. A similar system has been constructed in the United States (Ref 11). Another large-scale non-mass-analyzed unit, which has a target platen 2 ft in diameter, has been built and installed in a U.S. Army Aviation Depot for high-current (25 mA) nitrogen implantation of metal cutting tools (Ref 12).

A second approach, called plasma immersion ion implantation (PIII) or plasma source ion implantation (PSII) (Ref 13, 14), involves immersing the object to be implanted in a plasma and pulsing it to a high negative voltage (50 to 100 kV), thereby extracting the ions from the plasma. Because the plasma completely surrounds the component(s), the line-of-sight restriction of conventional ion implantation is greatly alleviated, with the result that more complex geometries can be implanted and/or less complicated fixturing can be used. A current restriction to this technique, however, is that it is limited to readily ionized plasma species (mainly gaseous elements such as nitrogen) and conducting substrates.

A third approach is to produce heavy ion beams from solids by using a metal vapor vacuum arc (MEVVA) discharge in a pulsed mode (Ref 15), yielding non-mass-analyzed ion beams extracted from a broad beam source (up to 50 cm in diameter). These sources have been demonstrated to produce up to 100 mA currents of metals. The commercial development of this source has been projected to yield low unit costs and high production throughput (Ref 16).

References cited in this section

9. F.A. Smidt and B.D. Sartwell, *Nucl. Instrum. and Methods in Phys. Res.*, Vol B6, 1985, p 70-77
10. B. Torp, B.R. Nielsen, D.M. Ruck, H. Emig, P. Spadtke, and B.H. Wolf, *Rev. Sci. Instruments*, Vol 61, 1990, p 595
11. G. Dearnaley, *Technology Today*, Vol 15 (No. 1), March 1994
12. S.N. Bunker, Implant Sciences Corp., Wakefield, MA, personal communication
13. J.R. Conrad, J.L. Radtke, R.A. Dodd, F.J. Worzala, and N.C. Tran, *J. Applied Phys.*, Vol 62, 1987, p 4591-4596
14. D.J. Rej and R.B. Alexander, *J. Vac. Sci. and Technol. B*, in press, 1994
15. I. Brown, *J. Vac. Sci. Technol. A*, Vol 11 (No. 4), 1993, p 1480
16. J.R. Treglio, A.J. Perry, and R.J. Stinner, *Surface and Coatings Technology*, Vol 65, 1994, p 184

Applications

Table 2 outlines some of the research and development applications that have been pursued using directed beam ion implantation technology. Of the properties listed, the tribological aspects of ion implantation have received the most attention (Ref 17). In spite of the relatively shallow penetration of implanted ions (typically nitrogen), implanted surfaces have often demonstrated a high degree of resistance to wear under mild abrasive or lubricated sliding conditions. This wear resistance is especially noteworthy in alloy surfaces that contain elements forming stable nitrides. Titanium and Co-Cr alloy orthopedic prostheses for hips and knees are among the most successful commercial applications of ion implantation components for wear resistance. In use, these components, shown in Fig. 5, articulate against an ultrahigh-molecular-weight polyethylene mating surface. Tests at several laboratories have indicated that wear reductions of 10× to 100× may be realized by the implantation of nitrogen ions into the alloy. To date tens of thousands of such components have been ion implanted prior to surgical implantation.

Table 2

Surface properties modified	**Substrates studied**	**Ions species used**	**Comments, references**
Wear	Steels, WC, Ti, Co/Cr alloys, TiN coatings, electroplated Cr	N, C 10-20 at.% $\geq 10^{17}$ ions/cm^2	Ti, Co/Cr alloys largest use commercially in orthopedic devices (Ref 5, 9, 17)
Friction	Steels	Ti plus C implants $\geq 10^{17}$ ions/cm^2	Dual implants give amorphous surface layer (Ref 18)
Fatigue	Ti alloys, steels	N, C $\geq 10^{17}$ ions/cm^2	Implantation effective for surface initiated fatigue (Ref 5)
Fracture toughness	Ceramics: Al_2O_3, TiN	Ar 10^{15}-10^{17}	Radiation damage critical, ion induced compressive stress helpful (Ref 4, 19)

		ions/cm^2	
Aqueous corrosion catalysis	Steels, Ti alloys, Pt	Cr, Ta, Cr plus P $\geq 10^{17}$ ions/cm^2	Ion implant can mimic "normal" alloys; amorphous and unique surface alloys possible (Ref 20)
Oxidation	Superalloys	Y, Ce $\geq 10^{15}$ ions/cm^2	Low effective doses; implanted species stay at metal-oxide interface (Ref 21, 22)
Electrical conductivity	Polymers	Ar, F 10^{12}-10^{17} ions/cm^2	Permits chain scissoning, doping; conductivity approaches disordered metal levels (Ref 3, 23)
Optical: Refractive index	Glasses, electrooptics	Li, Ar 10^{15}-10^{17} ions/cm^2	Chemical doping and lattice disorder both important (Ref 24, 25)

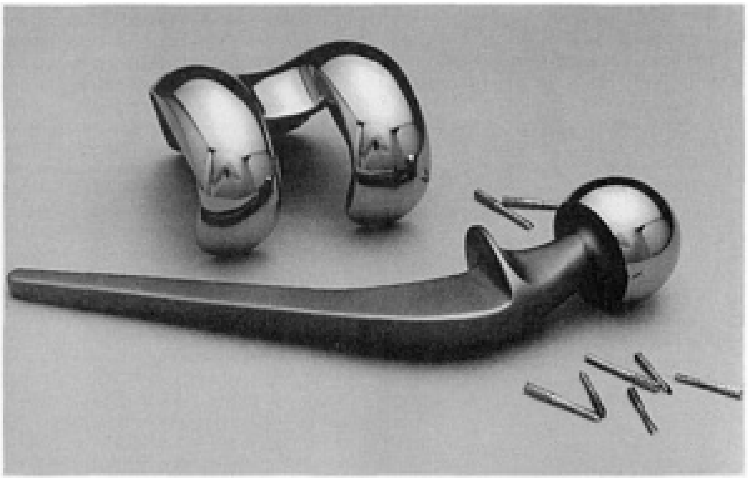


Fig. 5 Surgical prostheses of Ti-6Al-4V alloy of types being commercially ion implanted for wear benefits

Ion implantation is also being investigated as a means of improving the performance of certain types of coatings. Two examples are the implantation of nitrogen ions into (a) physical vapor deposited TiN coatings, such as on cutting inserts to increase their lifetimes, and (b) electroplated chromium to produce a CrN surface layer that inhibits the formation of microcracks, thus increasing the useful life of the electroplate. The latter use is of particular interest because of steadily increasing environmental concerns.

References cited in this section

3. T. Venkatesan, *Proceedings of the Fourth International Conference on Ion Beam Modification of Materials,* B.M. Ulrich, Ed., 1985, p 461-467
4. C.J. McHargue, C.W. White, B.R. Appleton, G.C. Farlow, and J.M. Williams, *Ion Implantation and Ion Beam Processing of Materials,* G.K. Hubler, O.W. Holland, C.R. Clayton, and C.W. White, Ed., Elsevier, 1984, p 385-393
5. G.K. Hubler, *Surface Alloying by Ion, Electron, and Laser Beams,* L. Rehn, S.T. Picraux, and H. Wiedersich, Ed., ASM International, 1987, p 287-324

9. F.A. Smidt and B.D. Sartwell, *Nucl. Instrum. and Methods in Phys. Res.,* Vol B6, 1985, p 70-77
17. J.K. Hirvonen, Ion Beam Processing for Surface Modification, *Annual Review of Material Science,* Vol 19, 1989, p 401-417
18. I.L. Singer and R.A. Jeffries, *Ion Implantation and Ion Beam Processing of Materials,* G.K. Hubler, O.W. Holland, C.R. Clayton, and C.W. White, Ed., Elsevier, 1984, p 673-678
19. C.J. McHargue and C.S. Yust, *J. Amer. Ceram. Soc.,* Vol 67 (No. 2), 1984, p 117
20. C.R. Clayton, *Surface Alloying by Ion, Electron, and Laser Beams,* L. Rehn, S.T. Picraux, and H. Wiedersich, Ed., ASM International, 1987, p 325-355
21. G. Dearnaley, *Nucl. Instr. Methods,* No. 182/183, 1981, p 899
22. M.J. Bennett and A.T. Tuson, *Mater. Sci. and Eng. A,* Vol 116, 1989, p 79-87
23. E.H. Lee, G.R. Rao, M.B. Lewis, and L.K. Mansur, *Nucl. Instrum. and Methods in Phys. Res.,* Vol B74, 1993, p 326
24. P.D. Townsend, *Journal of Physics E: Scientific Instruments,* Vol 10, 1977, p 197
25. C. Buchal, *Nucl. Instrum. and Methods in Phys. Res.,* Vol 68 (No. 1), 1992, p 355

Health and Safety

Ion implantation of gaseous elements, whether using conventional ion implantation or the PSII process, does not involve the use of any toxic or hazardous material and produces no effluent that requires special precautions. Semiconductor applications typically do use toxic gases for production of ion beams, and chlorine gas is sometimes used for producing heavy metal ion beams. However, implanters using a MEVVA, high-temperature, or sputtering heavy ion source do not require the use of toxic gases. The use of high voltages for ion acceleration and ion beam handling requires adequate training of personnel and proper design of equipment for shock protection and reduction of x-ray levels to within acceptable limits.

Future Trends

Commercial ion implantation processing is presently a service business directed toward high-value components whose lifetime extension warrants the processing costs. The largest markets are presently orthopedic devices and specialized tooling. However, a growing body of research and develoment workers are exploring the PIII process because of the attractive scaleup possibilities for large objects with complicated shapes. The ongoing development of high-current, heavy ion sources is also expected to open up new process applications. These include both high-temperature, versatile heavy ion sources (Ref 10) and MEVVA sources (Ref 15, 16) for applications not requiring mass analysis. The potential for scaleup must continue to be guided by the intrinsic depth limitations of this technique, which will proscribe applications subject to severe abrasion or erosion.

References cited in this section

10. B. Torp, B.R. Nielsen, D.M. Ruck, H. Emig, P. Spadtke, and B.H. Wolf, *Rev. Sci. Instruments,* Vol 61, 1990, p 595
15. I. Brown, *J. Vac. Sci. Technol. A,* Vol 11 (No. 4), 1993, p 1480
16. J.R. Treglio, A.J. Perry, and R.J. Stinner, *Surface and Coatings Technology,* Vol 65, 1994, p 184

Diffusion Coatings

Introduction

DIFFUSION COATINGS are deposited either by heating the components to be treated in contact with the powder coating material in an inert atmosphere (solid-state diffusion) or by heating them in an atmosphere of a volatile compound of the coating material (out-of-contact gas-phase deposition, or chemical vapor deposition). Solid-state diffusion methods include pack cementation, which is the most widely employed diffusion coating method and the process described in most detail in this article, and various slurry or powder-paint methods of coating metal parts and assemblies. The most widely

used coatings are those based on aluminum (aluminizing), chromium (chromizing), and silicon (siliconizing). Substrate materials include nickel- and cobalt-base superalloys, steels (including carbon, alloy, and stainless steels), and refractory metals and alloys.

This article is divided into two major Sections. The first Section describes the widespread use of diffusion coatings for elevated-temperature protection of turbine components for aircraft engines or ground- or marine-based gas turbines. The second Section reviews diffusion-coated ferrous alloys.

High-temperature oxidation-resistant diffusion coatings for molybdenum, niobium, tantalum, and tungsten substrates are described in the article "Surface Engineering of Refractory Metals and Alloys" in this Volume. In addition, information on the use of diffusion coatings for wear resistance, for example, coatings based on boron (boronizing) via pack cementation or complex carbides (vanadium carbide, chromium carbide, and niobium carbide) deposited from salt baths, can be found in *Heat Treating,* Volume 4 of the *ASM Handbook;* see the articles "Boriding (Boronizing)" and "Thermoreactive Deposition/Diffusion Process," respectively.

Diffusion Coatings for Gas Turbine Engine Hot Section Parts

G. William Goward, Consultant; Leslie L. Seigle, State University of New York at Stony Brook

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Blades and vanes made from nickel- and cobalt-base superalloys that are used in the hot sections of all gas turbine engines are coated to enhance resistance to hot corrosion. The most widely used coatings are those based on the intermetallic compounds NiAl and CoAl, which are formed by the diffusion interaction of aluminum with surfaces of the nickel and cobalt alloys, respectively. Diffusion chromium coatings are also used to protect against certain forms of molten salt hot corrosion. The majority of these diffusion coatings are manufactured by pack cementation and related "gas phase," or out-of-contact, processes.

The first public descriptions of pack cementation aluminizing were by Van Aller in a U.S. patent filed in 1911 (Ref 1) and in a technical paper by Allison and Hawkins in 1914 (Ref 2)--both from the General Electric Research Laboratories. The process consisted of embedding pieces to be coated in powder mixtures of aluminum, ammonium chloride, and graphite, and heating the assembly at 450 °C (840 °F) for two hours. A few years later, Gilson, of the same laboratory, patented the use of alumina, or aluminum oxide (Al_2O_3), as a substitute for graphite in the mix (Ref 3). The first known use of pack cementation aluminizing of gas turbine parts was for stationary cobalt superalloy vanes in about 1957 (Ref 4). Rotating nickel superalloy turbine blades may have been first aluminized by hot dipping in molten aluminum (Ref 5). Kelley (Ref 6) described his invention of pack cementation chromizing of steels in 1923. Comprehensive reviews of chromide coatings on steels were published in 1951 and 52 (Ref 7, 8). Aluminide coating of chromized steels to further improve high-temperature oxidation resistance was patented in 1953 (Ref 9). The time of first widespread use of chromide coatings on gas turbine parts is obscure but probably occurred in Europe in the early 1960s (Ref 10, 11).

Pack cementation siliconizing of iron and steels with powder mixtures of ferrosilicon, ammonium chloride, and alumina was described in 1954 (Ref 12). Siliconizing of nickel and cobalt superalloys does not produce practically useful coatings because of the formation of low-melting, brittle silicide phases (Ref 13). Minor additions of silicon to aluminide coatings on superalloys do enhance hot corrosion resistance.

Major developments in diffusion coatings for superalloys (and steels) over the last two decades include modifications of aluminide diffusion coatings with chromium (Ref 14), platinum (Ref 15), and to a lesser extent, silicon. The theory of codeposition of combinations of aluminum, chromium, silicon, and the so-called reactive metals (yttrium, rare earths, hafnium, etc.) has been refined and straightforward processes have been developed (Ref 16). Out-of-contact gas-phase coating (chemical vapor deposition, or CVD) has gained in use, not only for coating complex air-cooling passages, but as an overall versatile, environmentally friendly, cost-effective technology (Ref 17, 18, 19). It is estimated that more than 90% of all coated gas-turbine hot-section blades and vanes are coated by pack cementation and related processes.

References cited in this section

1. T. Van Aller, U.S. Patent No. 1,559,974, 1911

2. H.B.C. Allison and L.A. Hawkins, *General Electric Rev.,* Vol 17, 1914, p 947-951
3. E.G. Gilson, U.S. Patent No. 1,091,057, 1914
4. R.P. Seelig and R.P. Stuber,*High Temp.-High Press.,* Vol 10, 1978, p 207-213
5. E.S. Nichols, J.A. Burger, and D.K. Hanink, *Mech. Eng.,* March, 1965, p 52-56
6. F.D. Kelley, *Trans. Amer. Electrochem. Soc.,* Vol 43, 1923, p 351-370
7. R.I. Samuel and M.A. Lockington, *Metal Treatment and Drop Forging,* Vol 18, 1951, p 334-359, 407-414, 440-444, 495-506, and 543-548; Vol 19, 1952, p 27-32, and 81-85
8. R. Drewitt, *Anti-Corros. Methods Mater.,* Vol 16, 1951, p 543-548
9. T. Gibson, U.S. Patent No. 2,809,127, 1957
10. R. Schneider, R. Bauer, and H. Grunling, *Thin Solid Films,* Vol 54, 1978, p 359-367
11. R. Burgel, *Mater. Sci. Tech.,* Vol 2, 1986, p 302-308
12. E. Fitzer, *Arch. Eisenhüttenwes.,* Vol 25, 1954, p 455
13. R. Bauer and H. Grunling, *Thin Solid Films,* Vol 1, 1982, p 3-20
14. K. Godlewski and E. Godlewska, *Oxid. Met.,* Vol 26, 1986, p 125-128
15. G. Lehnardt and H. Meinhardt, *Electrodeposition and Surface Treatment,* Vol 1, 1972, p 189-193
16. R. Bianco and R.A. Rapp, *Metallurgical and Ceramic Coatings,* K.H. Stern, Ed., Chapman and Hall, 1993, Chapter 9
17. J.S. Smith and D.H. Boone, ASME Paper 90-GT-319
18. G. Gauje and R. Morbioli, *High Temperature Protective Coatings,* S.S. Singhal, Ed., The Metallurgical Society of AIME, 1983, p 13-26
19. R.S. Parzuchowski, U.S. Patent 4,132,816, 1979

Principles of Pack Diffusion Coating

Aluminizing. Pack diffusion coating may be considered as a CVD process carried out with the aid of a powder mixture (pack), in or near which the part to be coated (substrate) is immersed or suspended, containing the element or elements to be deposited (source), a halide salt (activator), and an inert diluent such as alumina (filler). When the mixture is heated, the activator reacts to produce an atmosphere of source element(s) halides which diffuse in the pack and transfer the source element(s) to the substrate on which the coating is formed.

Figure 1 presents schematic diagrams of the diffusion zones in a series of packs used for the production of aluminide coatings on nickel- and cobalt-based superalloys, in which the source is aluminum or an aluminum alloy and the activator an ammonium or sodium halide. Upon heating, the activator reacts with aluminum to form H_2(g) or Na(g) and a series of volatile aluminum halides. The nature and partial pressures of the major constituents in the gas phase in equilibrium with aluminum at high activity in the pack, and at lower activity at the surface of the coating, can be calculated when the free energies of formation of the halides and the activity versus composition relationship for aluminum in the source alloy and coating are known. In the presence of a high aluminum activity, no significant amounts of the halides of other metals in the source or superalloy appear in the gas phase, and these metals are, therefore, not transported in packs of this type. Alloying is used simply to control the activity of aluminum in the source in order to obtain a desired concentration of aluminum at the surface of the coating.

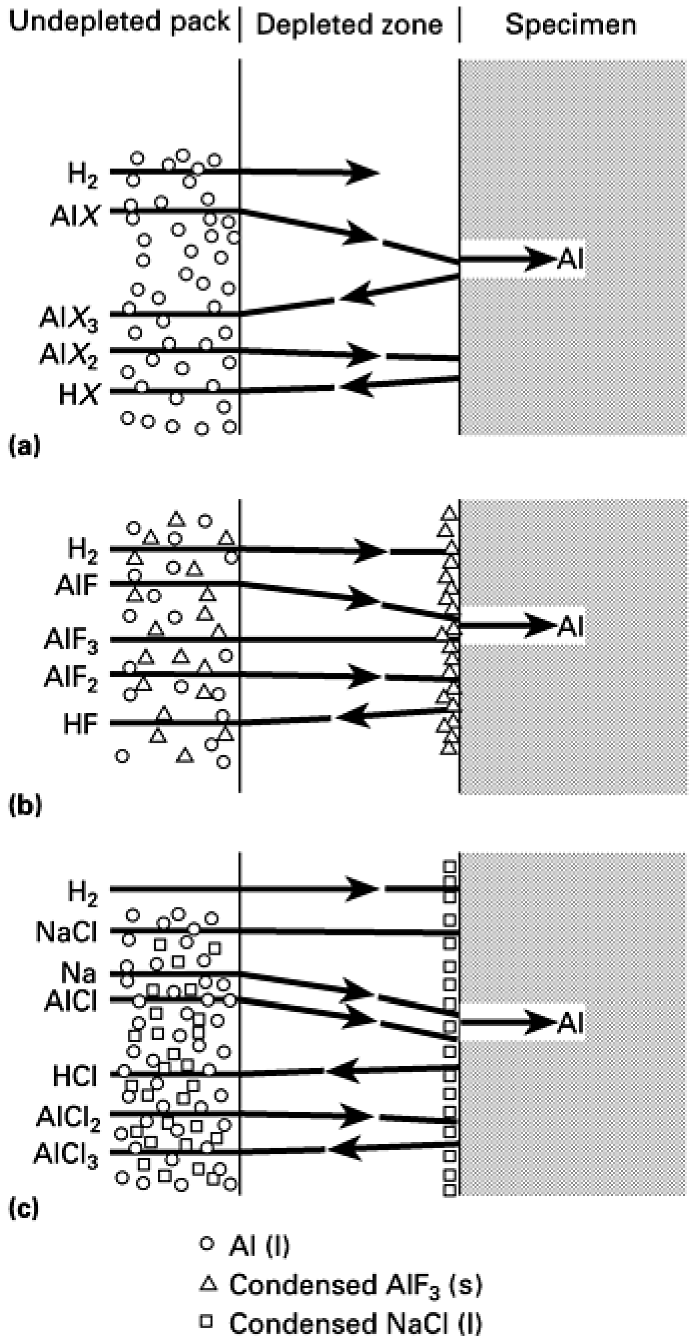

Fig. 1 Schematic diagrams of the fluxes of the major diffusing gaseous species in aluminizing packs activated with (a) NH_4X (X = Cl, Br, or I), (b) NH_4F, and (c) NaCl. Source: Ref 20, 21

Diffusion of the gaseous halides takes place across an aluminum-depleted zone which forms as a result of transport of aluminum into the coating under the action of the partial pressure gradients which exist between the pack and the coating surface (Ref 20, 21). The rate of diffusion of constituent *i* is proportional to:

$$D_i(P_i-P_i') = D_i\Delta P_i$$

where D_i is the interdiffusion coefficient of *i* with the residual gas in the system, and P_i and P_i' the partial pressures of *i* in the bulk pack and at the surface of the coating, respectively. The instantaneous rate of transport of aluminum from the pack to the coating, obtained by summing the contributions from each of the diffusing aluminum halides, can be expressed as:

$$J_{Al} = (\varepsilon/dRT) \sum \alpha_i N_i D_i \Delta P_i$$

where J_{Al} is the rate of transport of aluminum in moles/cm^2 · s; d is the effective diffusion distance in cm; ε is a constant to correct for the porosity of the pack; α_i is a factor to correct for the possible condensation of activator (to be discussed later); N_i is the number of gram atoms of aluminum in the ith species; D_i is diffusion coefficient of constituent i in cm^2/s; P_i is the partial pressure of constituent i in atm; R is the gas constant in cm^3 · atm/mole· deg; and T is temperature in degrees Kelvin, K. For the case of aluminization in a static pack with a high aluminum source, after a short period of time the aluminum concentration at the surface of the coating reaches a constant value, different from that in the source. Under this condition the weight of aluminum W_g (g/cm^2· s) transported to the substrate in t (s) is given by a parabolic expression (Ref 22):

$$W_g^2 = K_g t$$

where

$$K_g = (2\rho\varepsilon M/RT) \sum \alpha_i N_i D_i \Delta P_i$$

in which ρ is the pack aluminum concentration in g/cm^3, and M is the gram-atomic weight of aluminum. The diffusion of aluminum into the coating is also governed by a parabolic expression:

$$W_s^2 = K_s t$$

where K_s is the rate constant for diffusion in the solid, which can be evaluated if diffusion coefficients are known for the phases in the coating. Both K_g and K_s are functions of the surface composition of the coating, and this unknown composition can be determined from the condition that at steady state $K_g = K_s$.

Figure 1(a) shows, in order of increasing partial pressure, the principal diffusing species in a pack activated with NH_4X (X = Cl, Br, or I), and the direction of diffusion of each species. The thermodynamic calculations indicate that ΔP_i is greater for AlX(g) and AlX_3(g) than for the other halides (Table 1). Since, furthermore, the diffusion coefficients of the halides decrease with increasing molecular weight, it can be deduced that in packs activated with ammonium chloride, iodide, or bromide, aluminum is transported mainly by the diffusion of AlX(g) to the coating surface where the reaction:

$$3AlX(g) = 2Al(s) + AlX_3(g)$$

occurs. The Al(s) diffuses to form the coating while AlX_3(g) diffuses back and reacts with Al(l) in the pack to regenerate AlX(g). Moreover, since the value of ΔP_i for AlCl is greater than those for AlBr and AlI, it is expected that ammonium chloride should be a better activator than the bromide or iodide.

Table 1 Values of ΔP_i for the major diffusing gaseous species in variously activated aluminizing packs at 1093 °C (2000 °F)

Activator	ΔP at 1093 °C (2000 °F), atm						
	AlX	**AlX_2**	**AlX_3**	**NaX**	**Na**	**HX**	**H_2**
NH_4Cl	1.27×10^{-1}	1.59×10^{-2}	-0.93×10^{-1}	. . .	. . .	-5.35×10^{-3}	4.41×10^{-2}
NH_4Br	7.66×10^{-3}	. . .	-3.70×10^{-3}	. . .	. . .	-1.93×10^{-5}	1.52×10^{-5}

NH_4I	1.38×10^{-3}	. . .	-3.01×10^{-4}	. . .	. . .	-3.21×10^{-4}	2.21×10^{-5}
NH_4F	1.96×10^{-1}	1.40×10^{-2}	0	. . .	. . .	-3.38×10^{-4}	0.2108
NaF	7.85×10^{-2}	1.94×10^{-3}	-3.15×10^{-3}	0	8.22×10^{-2}	$-1.81 \times 10^{-4,}$	. . .
NaCl	4.34×10^{-3}	2.21×10^{-5}	-0.69×10^{-6}	0	3.74×10^{-3}	-1.51×10^{-4}	. . .
NaBr	1.71×10^{-3}	. . .	6.79×10^{-6}	0	9.95×10^{-4}	. . .	. . .
NaI	4.52×10^{-3}	. . .	4.9×10^{-9}	0	3.53×10^{-3}	-5.12×10^{-5}	. . .

Note: a_{Al} in the pack = 1; a_{Al} at the coating surface = 0.01. Values for NH_4Br, NH_4I, and NaBr activated packs taken from Ref 20.

In packs activated with NH_4F (or AlF_3) (Fig. 1b), AlF_3 appears as a solid at the operating temperature, and its vapor pressure is uniform throughout the pack. This constituent, therefore, does not diffuse in the gas phase. As indicated by Fig. 1(b) and the ΔP_i values in Table 1, aluminum is transported primarily by the diffusion of AlF(g) to the coating surface where deposition takes place by the reaction:

$$3AlF(g) = 2Al(s) + AlF_3(s)$$

The AlF_3(s) which is formed deposits as crystalline solid at the surface, some of which may adhere to the coating. The supply of AlF(g) is maintained by the reverse reaction in the pack.

In packs activated with a sodium halide such as NaCl (Fig. 1c), Na*X*(l) appears as a condensed phase in the pack. Aluminum deposition occurs mainly by the diffusion of Na(g) and Al*X*(g) to the coating surface where a reaction of the type:

$$AlX(g) + Na(g) = Al(s) + NaX(l)$$

occurs with the deposition of Na*X*(l) at the surface. The flux of Al*X*(g) is maintained by the reverse reaction in the pack. Due to the presence of solid or liquid activator, the operating characteristics of packs containing a condensed halide phase differ from those of packs activated with ammonium chloride, bromide, or iodide in the following ways:

- The condensed activator phase serves as a reservoir whose evaporation compensates for leakage of halide vapors out of "semisealed" coating chambers, resulting in more stable pack behavior over time
- The halide partial pressures and, therefore, the rate of aluminum deposition, increase much more rapidly with temperature, since they vary with the vapor pressure of the condensed phase, which increases rapidly with increasing temperature
- Activator as well as aluminum is transported to the coating surface

The expression given for K_g indicates that the instantaneous flux of gaseous halides will increase with an increase in the density (g/cm^3) of aluminum in the pack. The increase would not be directly proportional to ρ, however, since increasing the flux of aluminum would increase the aluminum concentration at the surface of the coating and, therefore, have a complex effect on the aluminum transfer rate as a whole.

Codeposition of Aluminum and Other Elements. For successful codeposition, the thermodynamic equilibrium between the source elements in the pack and halides in the gas phase must permit the attainment of sufficiently high

partial pressures for the halides of all elements desired to be transferred (Ref 16). The partial pressures are functions of the free energies of formation of the halides and activities of the elements in the source alloy. As illustrated by the curves in Fig. 2, the partial pressures of chromium and silicon halides in a pack in which aluminum, chromium, and silicon are present at equal activity are orders of magnitude below those of the aluminum halides, and too low to support the codeposition of an appreciable amount of these metals. An estimate of the general conditions under which codeposition is possible can be obtained by considering the equilibrium constant K for the simple reaction involving a source alloy of two metals A and B and the volatile halides A*X* and B*X:*

$$\mathrm{A}X(\mathrm{g}) + \mathrm{B}(\mathrm{s}) = \mathrm{B}X(\mathrm{g}) + \mathrm{A}(\mathrm{s})$$

where

$$\mathrm{K} = (P_{\mathrm{B}X}/P_{\mathrm{A}X})(a_{\mathrm{A}}/a_{\mathrm{B}})$$

or

$$\mathrm{K} = \exp(-\Delta G^0/RT)$$

and

$$\Delta G^0 = \Delta G_{\mathrm{f,B}X} - \Delta G_{\mathrm{f,A}X}$$

The activity ratio at which $P_{\mathrm{A}X} = P_{\mathrm{B}X}$ is given by:

$$a_{\mathrm{A}}/a_{\mathrm{B}} = \exp\,(-\Delta G^0/RT)$$

If A*X* is more stable than B*X,* the sign of ΔG^0 will be positive and $a_{\mathrm{A}}/a_{\mathrm{B}} < 1$. The activity ratio varies rapidly with ΔG^0. For example, at T = 1300 K, when ΔG^0 = 50,000 J/mole, $a_{\mathrm{A}}/a_{\mathrm{B}} = 9.8 \times 10^{-3}$, and when ΔG^0 = 100,000 J/mole $a_{\mathrm{A}}/a_{\mathrm{B}} = 9.6 \times 10^{-5}$. Conversion of the activity ratio to a composition ratio requires a knowledge of the thermodyamic properties of the source alloy. If this behaves as an ideal solution, the calculations suggest that codeposition is unlikely to occur if the free energies of formation of the source alloy halides (per gram-atom of Cl) differ by more than 50,000 J/mole. The codeposition of chromium with aluminum has been achieved by using chromium-rich source alloys containing 5-10 wt% aluminum (Ref 16, 24, 25). In this case the large negative deviation from ideality of the chromium-aluminum alloys (Ref 26) helps to compensate for the large formation free energy difference between the aluminum and chromium halides.

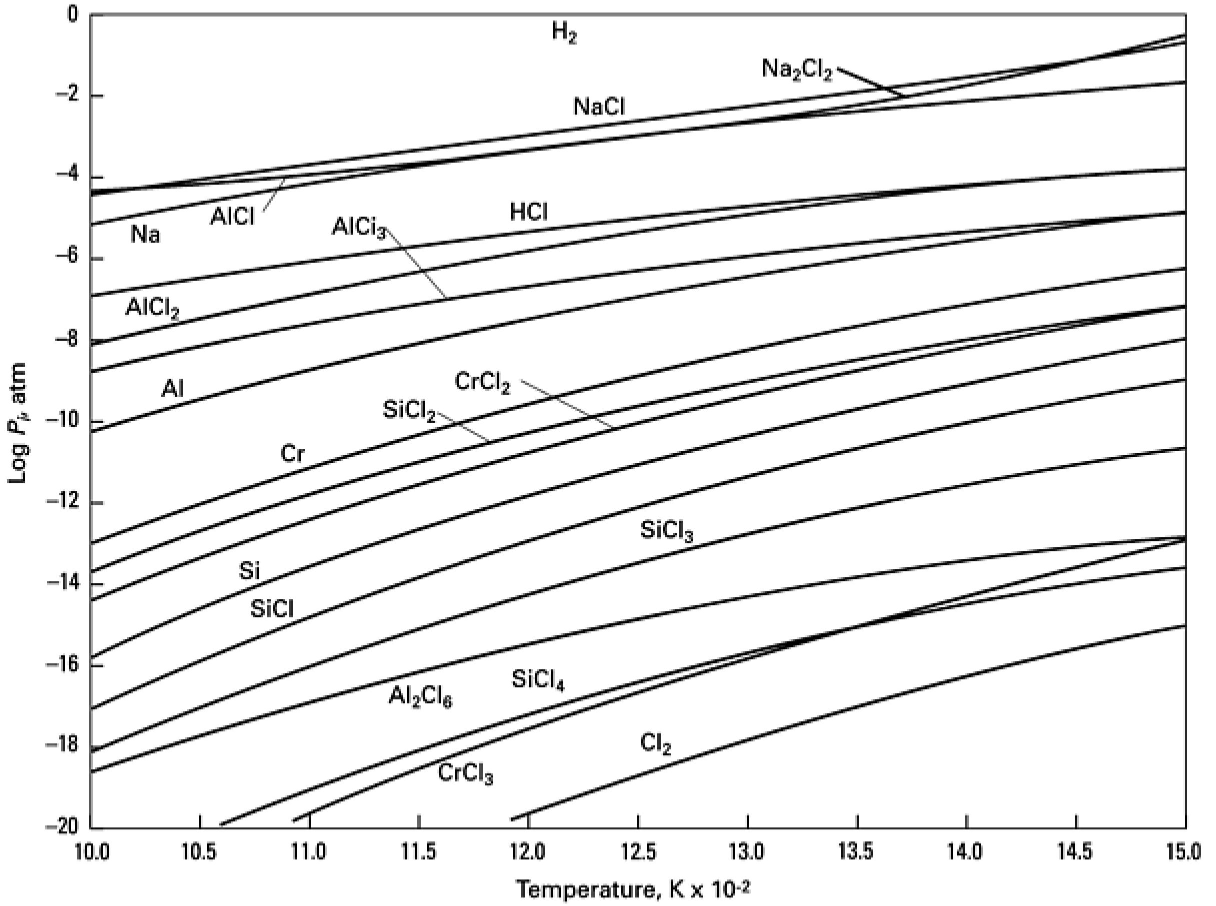

Fig. 2 Equilibrium partial pressures of gaseous species in a NaCl-activated pack containing pure aluminum, chromium, and silicon and a residual atmosphere of H_2. Source: Ref 23, 24

Chromizing. Although many of the same principles apply to chromizing as to aluminizing packs, the fact that chromium halides are less stable than aluminum halides introduces several new factors (Ref 27, 28). In ammonium halide activated chromizing packs, $CrX_2(l)$ appears as a condensed phase. The major constituents in the gas phase in equilibrium with chromium in the pack are $CrX_2(g)$, $CrX_3(g)$, $HX(g)$, and $H_2(g)$. The partial pressure of $HX(g)$ is high enough so that hydrogen reduction according to the reaction:

$$CrX_2(g) + H_2(g) = Cr(s) + 2\ HX(g)$$

at the coating surface is an important mechanism for the deposition of chromium. Since the free energies of formation of FeX_2 and CrX_2 are comparable, if the substrate is an iron-base alloy the exchange reaction

$$CrX_2(g) + Fe(s) = Cr(s) + FeX_2(g)$$

also occurs. The $FeX_2(g)$ diffuses back into the pack where the reverse reaction leads to the deposition of Fe(s) on the particles of the source alloy, thus changing its composition, while the Cr(s) diffuses into the coating. In this case, the weight of the substrate does not change significantly since it loses one atom of iron for every atom of chromium gained. The exchange reaction does not occur to an appreciable extent when nickel- or cobalt-base alloys are chromized, since the halides of these elements are sufficiently less stable than those of chromium so that significant concentrations of these halides do not appear in the gas phase. The replacement of hydrogen with argon as a protective atmosphere, such as would be possible if $CrX_2(s)$ were used as an activator, would significantly change the deposition rate because of elimination of the hydrogen reduction reaction.

Siliconizing. In packs activated with NH_4Cl, the principle constituents in the gas phase in equilibrium with pure Si(s) below 1500 K are $SiHCl_3$(g), $SiCl_4$(g), $SiCl_3$(g), HCl(g), and H_2(g) (Ref 28). Free energy considerations indicate that concentrations of the halides of nickel, cobalt, molybdenum, and tungsten in the gas phase would be very small, and these elements would therefore be immobile in such a pack. Hydrogen reduction of $SiHCl_3$(g) and $SiCl_4$(g) are predicted to be the most probable silicon deposition reactions at the coating surface when the substrate is a nickel- or cobalt-base superalloy, or pure tungsten or molybdenum:

$$SiHCl_3(g) + H_2(g) = Si(s) + 3HCl(g)$$

$$SiCl_4(g) + 2H_2(g) = Si(s) + 4HCl(g)$$

In a pack for the coating of these metals activated with $SiCl_4$(l), in which $SiHCl_3$, HCl, as well as H_2 would be absent, silicon deposition would presumably occur mainly via the disproportionation reaction:

$$2SiCl_2(g) = Si(s) + SiCl_4(g)$$

and, to a smaller extent, by:

$$4SiCl_3(g) = Si(s) + 3SiCl_3(g)$$

Formation free energy values indicate that various amounts of iron, chromium, and titanium chlorides will appear in the gas phase, and these substrate elements will exhibit varying degrees of mobility in a chloride activated siliconizing pack. In this case, exchange reactions such as:

$$SiCl_4(g) + 2M(s) = 2MCl_2(g) + Si(s)$$

and

$$SiCl_2(g) + M(s) = MCl_2(g) + Si(s)$$

may play a significant role in the deposition process. Finally, since for the reaction:

$$3/2SiCl_4(g) + Al_2O_3(s) = 3/2SiO_2(s) + 2AlCl_3(g)$$

where ΔG^0 = -15,400 cal at 1300 K, alumina is evidently not inert in a siliconizing pack, and the use of a different filler such as silica, or silicon dioxide (SiO_2) is advisable.

References cited in this section

16. R. Bianco and R.A. Rapp, *Metallurgical and Ceramic Coatings,* K.H. Stern, Ed., Chapman and Hall, 1993, Chapter 9
20. S. Levine and R.M. Caves, *J. Electrochem. Soc.,* Vol 121, 1974, p 1051-1064
21. B.K. Gupta and L.L. Seigle, *Thin Solid Films,* Vol 73, 1980, p 365-371
22. B.K. Gupta, A.K. Sarkhel, and L.L. Seigle, *Thin Solid Films,* Vol 39, 1976, p 313-320
23. P.N. Walsh, *Chemical Vapor Deposition,* 4th International Conference, The Electrochemical Society, 1973, p 147-168
24. S.C. Kung and R.A. Rapp, *J. Electrochem. Soc.,* Vol 135, 1989, p 89-109
25. R.A. Rapp, D. Wang, and T. Weisert, in *High Temperature Coatings,* M. Khobaib and R. Krutenat, Ed., The Metallurgical Society of AIME, 1983, p 131-141

26. W. Johnson, K. Komarek, and E. Miller, *Trans. Met. Soc. AIME,* Vol 242, 1968, p 1685-1690

27. T.P. Hoar and E.A.G. Croam, *J. Iron Steel Inst.,* Vol 169, 1951, p 101

28. L.L. Seigle, *Surface Engineering,* R. Kossowsky and S.C. Singhal, Ed., Martinus Nijhoff, 1984, p 349-369

Properties of Diffusion Coatings on Superalloys

Coating Formation Mechanisms. Diffusion aluminide coatings on superalloys are classified by microstructure as being of the "inward diffusion" or "outward diffusion" type according to the seminal work of Goward and Boone (Ref 29). The classification was derived from studies of aluminide coating formation on a typical nickel superalloy, Udimet 700, which has a nominal composition of Ni-15Cr-17Co-5Mo-4Al-3.5Ti. It was observed that for pack mixes containing pure aluminum (unit or "high" activity), coatings formed by predominant inward diffusion of aluminum through Ni_2Al_3, and deeper in the coating, through aluminum-rich NiAl (for pure nickel, by inward diffusion through Ni_2Al_3 only). The diffusion rates are abnormally high--practical coating thicknesses can be achieved in a few hours at 760 °C (1400 °F). A typical as-coated microstructure is shown in Fig. 3(a). Upon further heat treatment at, for example, 1080 °C (1975 °F) for four hours, the microstructure shown in Fig. 3(b) is formed--the coating matrix is now NiAl. The single-phase region in the center of the coating is nickel-rich NiAl grown by predominant outward diffusion of nickel from the substrate alloy to react with aluminum from the top layer. The inner layer, or so-called interdiffusion zone, consists of refractory metal (tungsten, molybdenum, tantalum, etc.) carbides and/or complex intermetallic phases in a NiAl and/or Ni_3Al matrix, formed by the removal of nickel from the underlying alloy, thereby converting its Ni-Ni_3Al structure to those phases. Conversely, if the activity of aluminum in the source is reduced by alloying with, for example, nickel or chromium, to a level where nickel-rich NiAl is formed at the surface, the coating, shown in Fig. 3(c), grows by predominant outward diffusion of nickel from the substrate to form NiAl by reaction with aluminum from the source. The lower layer of this coating is formed as previously described. Diffusion rates are relatively low so the coating process must be carried out at higher temperatures--usually greater than 1000 °C (1830 °F). These mechanisms are consistent with those observed by Janssen and Rieck (Ref 30) and later by Shankar and Seigle (Ref 31) during studies of diffusion in the simple nickel-aluminum system. Figure 4 shows the ratios of diffusion rates of nickel and aluminum across the range of stoichiometry of NiAl (Ref 31). At the high aluminum limit of NiAl, diffusion is by predominant motion of aluminum, confirming the earlier postulate of Goward and Boone (Ref 29). A coating with a matrix of NiAl formed by this diffusion mechanism is shown in Fig. 3(d). Upon further heat treatment, this coating will stabilize with a structure similar to that shown in Fig. 3(b).

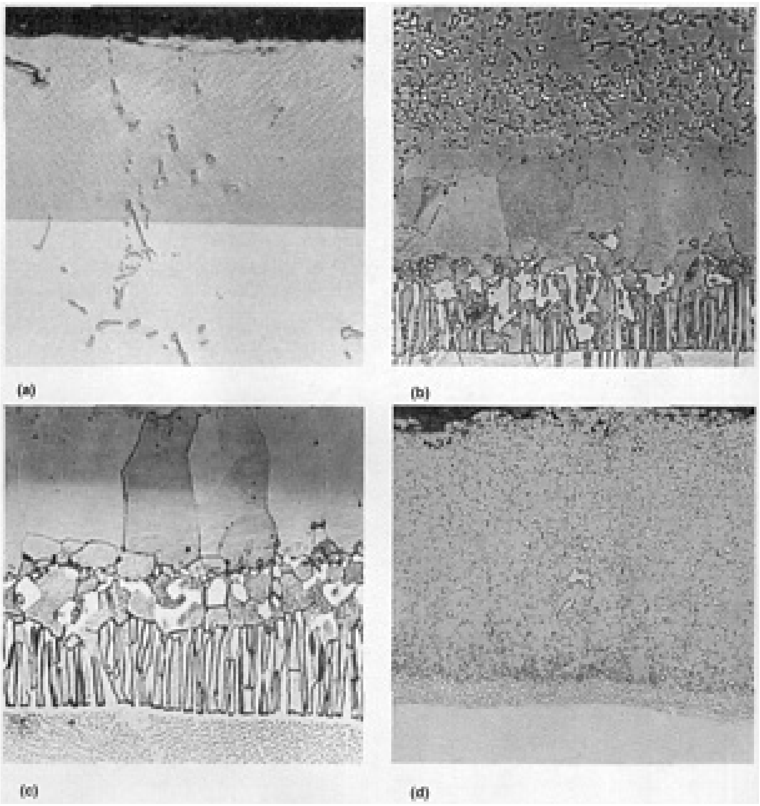

Fig. 3 Archetypical microstructures of aluminide coatings on a nickel superalloy. (a) Inward diffusion based on

Ni_2Al_3 (and aluminum-rich NiAl). (b) Same as (a) but heat treated at 1080 °C (1975 °F). (c) Outward diffusion of nickel in nickel-rich NiAl. (d) Inward diffusion of aluminum in aluminum-rich NiAl. Source: Ref 29

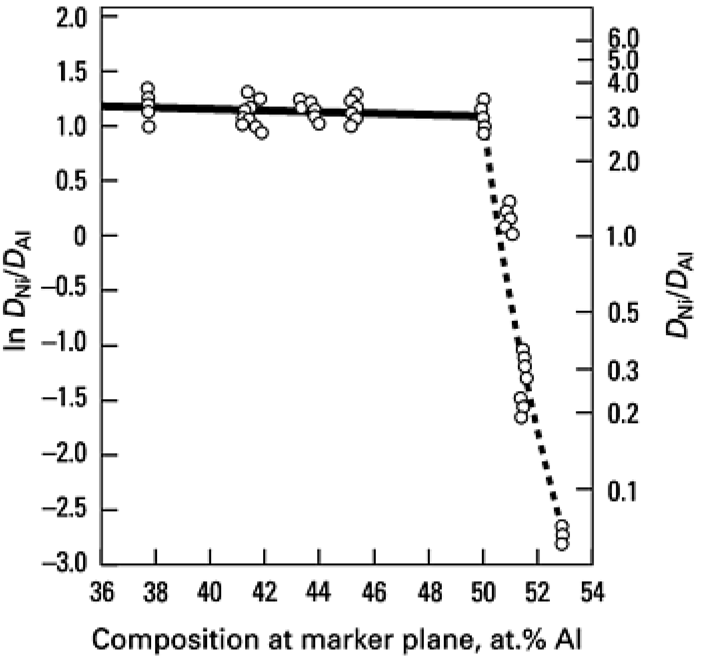

Fig. 4 Ratio of diffusion coefficients of nickel and aluminum as a function of aluminum in NiAl. Source: Ref 31

The above mechanisms apply equally to those coatings formed by out-of-contact or CVD processes, from slurry "slip packs" (Ref 32), and from aluminum alloy powders deposited on superalloys by slurry spraying or by slurry electrophoresis (Ref 33). Coatings applied by spraying (Ref 34, 35) or electrophoretically depositing (Ref 33) pure aluminum or low-melting aluminum alloys, for example, Al-10Si, and then heat treating, form by dissolution of the superalloy into the melt until the melt solidifies, followed by diffusion of aluminum similar to that described above.

All known aluminide-based coatings on nickel superalloys, including those modified by chromium, platinum, and silicon, have one of the archetypical microstructures described above. For pure nickel and nickel alloys containing no aluminum, (or <0.2% Al), the interdiffusion zone does not form. For pure nickel, Kirkendall voids and alumina, from oxygen in the nickel, form at the coating/substrate interface (Ref 29). For nickel alloys containing no aluminum, voids, refractory metal layers, and alumina form at the interface (Ref 29). The adherence of the resulting coatings is compromised and they may not be practically useful. It is anticipated that similar mechanisms apply to the coating of cobalt superalloys. Again, the absence of aluminum in many of these alloys precludes the formation of the interdiffusion zone common to most nickel superalloys. Rather, a refractory metal (tungsten, chromium) carbide forms at the juncture to the base alloy (Ref 40). As described for similar nickel-base alloys, this refractory metal carbide and alumina formed from oxygen in the aluminum-free alloys, can also compromise the adherence of these coatings. Special processing conditions, involving slow coating growth at high temperatures (up to 1095 °C, or 2000 °F) from relatively low aluminum activity sources, can sometimes be used to achieve satisfactory coating adherence. Minor additions of aluminum (1 to 2%) to cobalt superalloys completely obviate these problems--stable interdiffusion zones then form analogous to those on most nickel superalloys (Ref 36).

Diffusion chromide coatings formed on a nickel superalloy by pack cementation and out-of-contact processes are illustrated in Fig. 5. The coating deposited by pack cementation is overlaid with a thin layer of alpha-chromium as shown in Fig. 5(a). Users generally require that this phase be absent. It must then be removed chemically, or alternatively the coating applied by an out-of-contact process to produce the structure shown in Fig. 5(b). These coatings usually then contain chromium to the extent of 20 to 25% at the outer surface. Coating formation, from chromium-alumina-activator (usually ammonium chloride) packs or from out-of-contact sources (powders or chromium granules as described in Ref 18) involves approximately equal rates of interdiffusion of chromium and nickel. Significant depletion of titanium and aluminum from the alloy surface occurs because the sources do not contain these elements. The desired coatings are thus solid solutions of chromium in the remaining nickel-base alloy. Internal oxides of aluminum and titanium can form because the oxygen potential of the sources is normally sufficient to cause internal oxidation. This can be avoided by

adding aluminum to the sources in amounts just below that which would cause aluminizing rather than chromizing (Ref 38).

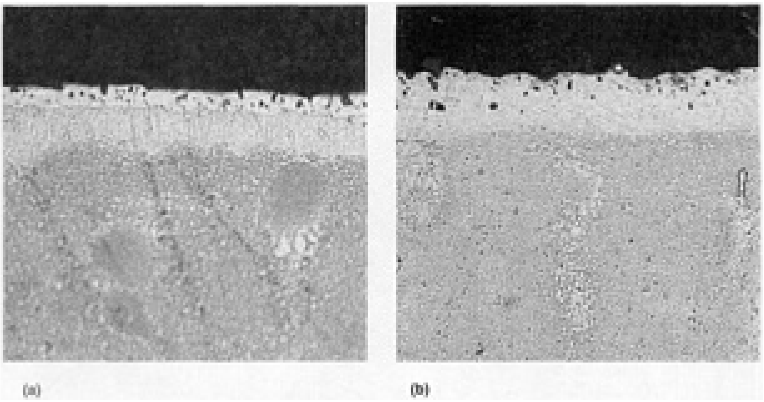

Fig. 5 Chromium diffusion coatings on a nickel superalloy by (a) pack cementation and (b) out-of-contact gas-phase processing. Both at 500×. Source: Ref 37

Rapp and co-workers (Ref 16) have refined the theory of codeposition of aluminum, chromium, silicon, and reactive elements (yttrium and hafnium) by pack cementation and related processes and have demonstrated the benefits derived therefrom. These processes and coatings should find practical applications in the near future.

Coating Protection and Degradation. Simple aluminide coatings resist high-temperature oxidation by the formation of protective layers of alumina and can be used up to about 1150 °C (2100 °F). The coatings degrade by loss of aluminum due to spalling of oxides under thermal cycling conditions. Incorporation of reactive elements, such as yttrium and hafnium, by codeposition during aluminizing (Ref 16) can significantly improve adherence of the protective alumina scales and therefore extend coating life. At temperatures above about 1000 °C (1830 °F) interdiffusion of the coatings with substrates contribute significantly to degradation (Ref 39). Practical coating service lives are limited to operating temperatures of 870 to 980 °C (1600 to 1800 °F) with only short excursions at the highest temperatures.

Chromium modifications, made by diffusion chromizing prior to aluminizing (Ref 14) or by codeposition of aluminum and chromium (Ref 16, 41, 42), have enhanced resistance to various forms of molten-salt hot corrosion. Electroplating with a thin layer of platinum (and possibly rhodium) followed by aluminizing (Ref 15) forms a coating with substantially improved resistance to both oxidation and high-temperature (Type I) molten-salt corrosion. Additions of up to about 5% Si improve both oxidation and hot corrosion resistance (Ref 13). Silicon can be codeposited with aluminum by pack cementation (Ref 16, 43) and related out-of-contact processes. So-called slurry processes wherein a liquid suspension of aluminum and silicon powders is applied to the alloy surface, then dried and fired at elevated temperatures, can also be used to incorporate silicon (Ref 35).

The oxidation and hot corrosion resistance of these coatings are more or less influenced by the composition of substrate alloys. Tantalum and hafnium improve cyclic oxidation and hot corrosion resistance, the latter element by improving the adherence of the protective layer of alumina (Ref 44). Molybdenum and tungsten compromise hot corrosion resistance.

Because of the brittle fracture behavior of NiAl up to temperatures of 650 to 775 °C (1200 to 1400 °F), all aluminide coatings exhibit such fracture below these temperatures while above these limits ductile behavior occurs (Ref 45). This behavior can either compromise or enhance thermal fatigue resistance of substrate alloys depending on such complex factors as the exact nature of the thermal cycle and the structure--equiaxed, directionally solidified, or single crystal--of the alloys (Ref 46). If these effects are limiting, designers may require use of more expensive overlay coatings of the MCrAlY (M = Co and/or Ni) and/or thermal barrier (zirconia) types.

References cited in this section

13. R. Bauer and H. Grunling, *Thin Solid Films,* Vol 1, 1982, p 3-20

14. K. Godlewski and E. Godlewska, *Oxid. Met.,* Vol 26, 1986, p 125-128
15. G. Lehnardt and H. Meinhardt, *Electrodeposition and Surface Treatment,* Vol 1, 1972, p 189-193
16. R. Bianco and R.A. Rapp, *Metallurgical and Ceramic Coatings,* K.H. Stern, Ed., Chapman and Hall, 1993, Chapter 9
18. G. Gauje and R. Morbioli, *High Temperature Protective Coatings,* S.S. Singhal, Ed., The Metallurgical Society of AIME, 1983, p 13-26
29. G.W. Goward and D.H. Boone, *Oxid. Met.,* Vol 3, 1971, p 475-495
30. M.M.P. Janssen and G.D. Rieck, *Trans. Met. Soc. AIME,* Vol 239, 1967, p 1372-1385
31. S. Shankar and L.L. Seigle, *Met. Trans. A,* Vol 9A, 1978, p 1468-1476
32. J.D. Gadd, F.J. Najedlik, and L.D. Graham, *Electrochem. Tech.,* Vol 6, 1968, p 307-315
33. M.J. Barber, N.D. McMurray, and T. Pacala, Final Report, Air Force Contract F33615-78-C-5102, 1983
34. G.H. Howe, U.S. Patent No. 1,655,269, 1925
35. A.D. Joseph, U.S. Patent No. 3,102,044, 1963
36. G.W. Goward and S. Shankar, U.S. Patent 4,837,389, 1989
37. G.W. Goward and L.W. Cannon, *Trans. ASME,* Vol 110, 1988, p 150-154
38. H.W. Brill-Edwards, U.S. Patent No. 3,694,255, 1970
39. J.L. Smialek and C.E. Lowell, NASA TM X-68274, 1974
40. C. Duret and R. Pichoir, *Coatings for High Temperature Applications,* E. Lang, Ed., Applied Science Publishers, 1983, p 33-78
41. Rolls Royce Ltd., French Patent 1,511,698, 1969
42. G.H. Marijnissen, *High Temperature Protective Coatings,* S.S. Singhal, Ed., TMS-AIME, 1983, p 27-35
43. E.V. Clark *et al.,* U.S. Patent 3,779,719, 1973
44. P. Aldred, SAE Paper 751049, National Aerospace Engineering and Manufacturing Meeting, Los Angeles, CA, 1975
45. G.W. Goward, *J. Met.,* Vol 22, 1970, p 31-39
46. J.W. Holmes and F.A. McClintock, *Met. Trans. A,* Vol 21A, 1990, p 1209-1222

Manufacturing Technology

A flow path for a typical production-scale pack cementation process is shown in Fig. 6. Practical manufacturing aspects of the various steps of the process are described below.

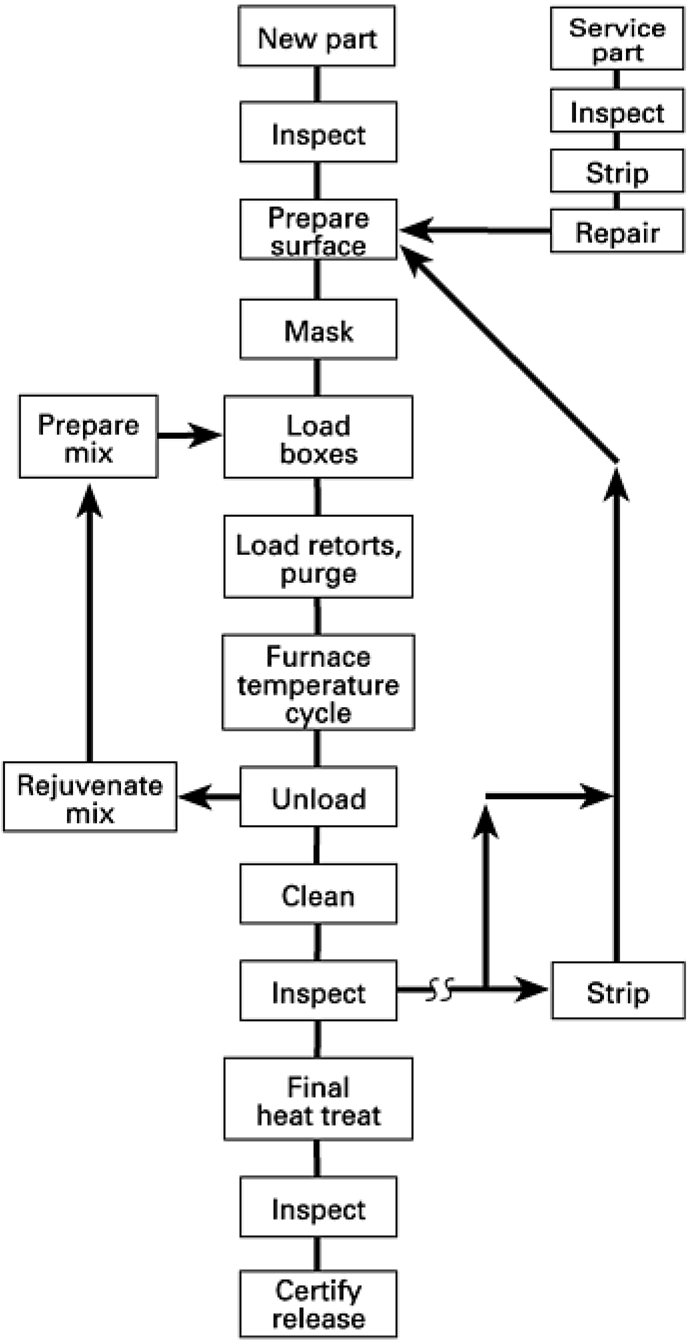

Fig. 6 Flow diagram for typical pack cementation processes. Source: Ref 37

Inspection. Visual and flow inspection of cooled airfoils before coating affords the last opportunity to determine if all surfaces are suitable for the intended use. Oxidized surfaces and the remains of investment casting core and shell materials can interfere with coating deposition and compromise useful service lives.

Surface Preparation. Surface preparation to remove superficial oxides is usually accomplished by grit blasting with intermediate sized alumina grit. Grit blasting with silicon carbide is avoided because any entrapped grit forms low-melting eutectic phases with superalloys. Vibratory finishing is used where a surface finish is specified to achieve aerodynamic design intent. Removal of oily residues from machining by vapor degreasing or low temperature burnout may be required.

Masking to prevent coating on critical mechanical contact surfaces, such as blade roots, may be required. This can be accomplished with mechanical, oxide barrier, or chemically reactive masks. Complete exclusion of coating by mechanical masks is difficult for processes with high throwing power, a property common to those run at higher temperatures, for

example, >870 °C (1600 °F). Chemically reactive masks containing elemental or alloy powders which react with the coating species to prevent coating deposition on the surface are more effective at higher processing temperatures. Coating before machining, to obviate expensive masking requirements, is strongly recommended.

Pack Mix (Source) Preparation. Preparation of pack mixes requires the use of large-scale powder handling equipment designed for effective mixing, storage, and dispensing. Examples of mix (source) compositions are given in Table 2. Closed handling systems are now required for health and safety reasons. The possibility of explosive burning of metal powders must be excluded. In general, various chemical engineering technologies are applicable.

Table 2 Examples of pack mixes/sources and processing parameters for various coatings on nickel and cobalt superalloys

Coating type	Source composition	Processing parameters
Pack aluminizing, inward diffusion in Ni_2Al_3 in nickel alloys[(a)]	5-20% Al (Al-10Si), 0.5-3% NH_4Cl, balance Al_2O_3 powder	1 to 4 h at 650 to 680 °C (1200 to 1255 °F) in air, argon, H_2; heat treat 4 to 6 h at 1095 °C (2000 °F) in argon
Pack aluminizing, inward diffusion in NiAl in nickel alloys[(b)]	44% Al, 56% Cr NH_4Cl balance Al_2O_3 powder	5 to 10 h at 1040 °C (1900 °F) in vacuum (argon, H_2)
Pack aluminizing, outward diffusion in NiAl in nickel alloys[(c)]	2-3% Al, 20% Cr, 0.25% NH_4HF_2, balance Al_2O_3 powder	25 h at 1040 °C (1900 °F) in argon
Pack aluminizing of cobalt alloys[(d)]	8% Al, 22% Cr 1% NH_4F, balance Al_2O_3 powder	4 to 20 h at 980 to 1150 °C (1800 to 2100 °F) in argon
Gas-phase aluminizing, outward diffusion in NiAl in nickel alloys[(e)]	10% Co_2Al_5, 2.5% NaCl, 2.5% $AlCl_3$, balance Al_2O_3 powder	3 h at 1095 °C (2000 °F) in argon
Gas-phase aluminizing, outward diffusion in NiAl in nickel alloys[(f)]	30% Al-70% Cr alloy granules, NH_4F	4 h at 1150 °C (2100 °F) in argon
Pack or gas-phase chromizing of nickel alloys[(g)]	15% Cr, 4% Ni, 1% Al, 10.25% NH_4Br or NH_4Cl, balance Al_2O_3 powder	3 h at 1040 °C (1900 °F) in argon

(a) U.S. Patent 3,544,348.

(b) U.S. Patent 3,625,750.

(c) U.S. Patent 3,716,398.

(d) U.S. Patent 3,257,230.

(e) U.S. Patent 4,132,816.

(f) Ref 18.

(g) U.S. Patent 3,801,353

Loading Boxes and Retorts. Loading of parts, which consists of embedding parts in coating powder mixtures in controlled positions in coating boxes ("boats"), is labor intensive and environmentally unfriendly. Automation with robotics is theoretically possible but no such systems are known to be in use.

Furnace Temperature Cycle and Heat Treatments. Furnaces with specified temperature capability and uniformity and associated inert gas delivery systems are the most costly components of coating plants. For most processes, coating boxes are loaded into retorts constructed of high-temperature alloys, for example, Inconel 600 or 601, and are capable of being sealed (sand, glass, or water-cooled seals) to exclude air. Retorts for gas-fired or electrically fired pit furnaces can be as large as 1.2 m (4.0 ft) in diameter and 2.4 m (8.0 ft) tall. A supply of inert gas, argon or hydrogen is required to purge retorts free of air and moisture, and to maintain an inert environment during the coating cycle.

A coating cycle includes bringing the retort and contents to temperature, holding at temperature for several hours, and then cooling to ambient temperature while maintaining the inert gas environment. Coating temperatures range from 650 °C (1200 °F) for low-temperature inward diffusion aluminizing to as high as 1150 °C (2100 °F) for outward-diffusion aluminizing of nickel superalloys. Processing times range from 4 to 24, h respectively. Some examples of time-temperature cycles are given in Table 2. Temperature uniformity within the retort load during the holding period is usually required to be within 14 °C (25 °F) of nominal. Off-gases from the process, carried by the inert gas flow, contain environmentally harmful chemicals such as aluminum chloride, hydrogen chloride, aluminum fluoride, hydrogen fluoride, and chromium chloride. These must be captured by scrubbing and filtering before the inert gas is vented to the atmosphere, and then disposed of in accord with applicable environmental regulations.

Unloading the retorts and boxes, separating the parts from powders and masking devices, and cleaning the parts, including thorough water washing, are currently labor intensive. Blades and vanes may require further heat treatment to cause proper development of the coating and/or to obtain optimum mechanical properties of the substrate alloy. Such treatments require inert or vacuum environments with the same rigid temperature controls as the coating thermal cycle.

Source Rejuvenation. It is common practice to rejuvenate powder mixes by additions of coating elements and alloys, and activators. Chemical analysis of the used mixes facilitates control of critical constituents. For simple systems historical data can sometimes be applied empirically for these purposes. Disposal of used mixes is quite costly under current environmental regulations. Recovery and recycling of expensive metals is being practiced with increasing frequency.

Quality Control. The most widely accepted quality control practice requires coating of representative samples with each processing cycle and destructively evaluating these to determine accordance with user specifications for thickness (in the range of 25 to 100 μm, or 1 to 4 mils for most applications), and microstructure. Quantitative analysis by x-ray fluorescense or electron microprobe for elemental composition, for example, aluminum, chromium, and platinum content, may also be required. Complete coating coverage can be confirmed by contact thermocouple measurement or by heat tinting aluminized nickel alloys in air at 621 °C (1150 °F) for one hour--coated areas exhibit a gold color and uncoated areas a dark blue color. Procedures for nondestructive coating thickness measurements are available (Ref 47), but are not widely used for control of new coating production. There is increasing interest in measuring coating thickness and aluminum content to judge the remaining life of coatings on used parts (Ref 48).

If inspection reveals faulty coatings, parts may be overcoated using appropriate time-temperature cycles. In extreme cases the coatings are stripped in acid solutions, for example, nitric or hydrochloric acid for aluminide coatings, and subjected to another full coating cycle. This is to be avoided because aluminide coatings are formed by consumption of the nickel component of the alloy and removal of the coating can result in significant reduction in critical part dimensions. Increasingly, statistical process control is being used to avoid these problems.

Out-of-Contact Processes. When aluminizing and/or chromizing are to be accomplished by out-of-contact CVD processes, all preparation steps are as described previously. For simple static aluminizing or chromizing, parts may be

surrounded by suitable source material in the form of granules contained in baskets in a variety of coating box designs. A typical example is shown schematically in Fig. 7. Activator chemicals are simply sprinkled into the boxes which are then covered, placed in retorts, purged with inert gas and subjected to the usual time-temperature cycles. If coating of blade and vane cooling passages is required, a flow of the inert gas is used to carry the coating species through the passages (Ref 19). Alternatively, pressure can be lowered (Ref 49) or cycled (Ref 50) to accomplish internal passage coating. For so-called CVD processes, the coating species may be generated by passing reactive gases, based on hydrogen chloride or hydrogen fluoride in a carrier gas over the source material in a separate reactor with the gas stream directed into the main coating chamber to coat external or internal surfaces or both (Ref 17). In any case, all other items shown in Fig. 6 still apply. More detailed information on CVD processing can be found in the article "Chemical Vapor Deposition of Nonsemiconductor Materials" in this Volume.

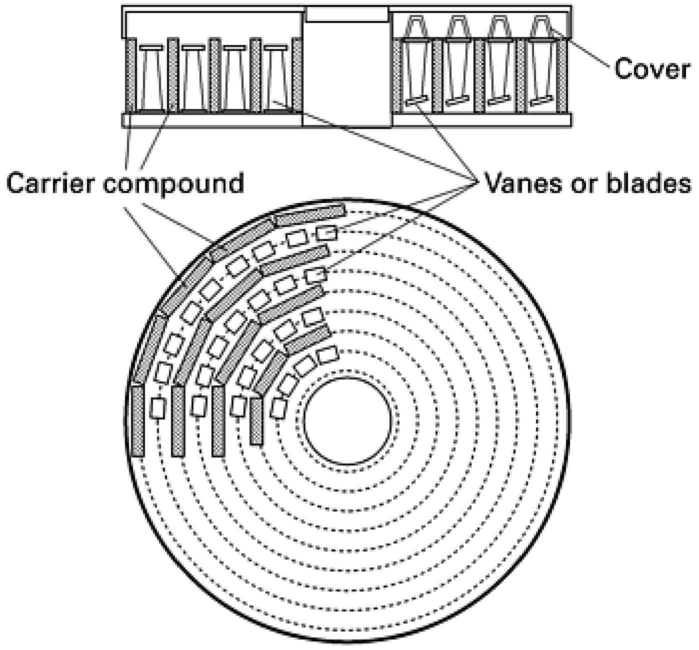

Fig. 7 Schematic of a coating chamber for an out-of-contact aluminizing process. Source: Ref 18

Repair. It is frequently possible to repair blades and vanes that have been in service for some time. To accomplish this, the first coating, now depleted during service, is removed by acid stripping. Parts are then repaired as appropriate, by welding, and/or brazing and re-machining (Ref 51). Suitable coatings are then re-applied as shown in Fig. 6.

References cited in this section

17. J.S. Smith and D.H. Boone, ASME Paper 90-GT-319
18. G. Gauje and R. Morbioli, *High Temperature Protective Coatings,* S.S. Singhal, Ed., The Metallurgical Society of AIME, 1983, p 13-26
19. R.S. Parzuchowski, U.S. Patent 4,132,816, 1979
37. G.W. Goward and L.W. Cannon, *Trans. ASME,* Vol 110, 1988, p 150-154
47. O.H. Kriege and D.H. Boone, *Mater. Eval.,* Vol 32, 1973, p 38-44
48. C.H. Wells *et al., Proceedings of Steam and Combustion Turbine Blading Workshop,* Electric Power Research Institute, Jan 27-31, 1992
49. L. Vandenbulke, G. Leprince, and B. Nciri, *Mater. Sci. Eng.,* Vol A21, 1989, p 379-386
50. J.E. Restall and M.I. Wood, *Mater. Sci. Tech.,* Vol 2, 1986, p 225-231
51. K.C. Antony and G.W. Goward, *Superalloys 1988,* D.N. Duhl *et al.,* Ed., The Metallurgical Society of AIME, 1988, p 745-754

Practical Applications

For aircraft gas turbine blades fabricated from moderately-corrosion resistant nickel alloys (those containing 12 to 15% Cr), simple aluminide coatings of the inward and outward diffusion types provide adequate protection for many contemporary engines. When alloys are more corrosion prone (those containing 7 to 10% Cr), current practice is to modify aluminide coatings by chromizing prior to aluminizing. Aluminizing should be by inward diffusion of aluminum to locate the higher chromium concentration in the outer layer of the coating (Ref 14). For more severe Type I hot corrosion resulting from exposure of engines to salt spray from marine environments, modification of aluminide coatings with silicon (or better, by platinum) can prove to be the more cost effective solution.

If more expensive structure modifications of nickel superalloys, such as single crystals, are used to full strength-temperature capabilities to enhance fuel efficiency, contemporary diffusion coatings may not meet design objectives for oxidation and/or thermal fatigue service lives of the turbine. For these conditions use of the more expensive MCrAlY overlay and/or ceramic (zirconia-based) thermal barrier coatings may be in order.

Ground-Based and Marine Gas Turbines. Achieving cost effective hot corrosion protection for ground- or marine-based gas turbines is a more complex problem because of wide variations in local environments with respect to air contaminants (salts, sulfur oxides, and other industrial pollutants) and fuel constituents (salts, sulfur, vanadium, etc.). Burgel (Ref 11) identified chromizing as one of the best solutions in ground-based engines subjected to severe Type II hot corrosion in the metal temperature range of 740 °C (1365 °F)--this in comparison to silicide, platinum-aluminide, and some MCrAlY type coatings. Chromide coatings are, however, not satisfactory above 800 °C (1470 °F). Platinum aluminides provide moderate protection at somewhat higher temperatures but may not be sufficiently resistant to lower temperature Type II hot corrosion. Similar considerations appear to apply for marine environments (Ref 52).

The trend for most ground-based gas turbines is toward the use of various modifications of MCrAlY type coatings, particularly those with higher chromium and perhaps silicon additions (Ref 53, 54). For the very latest machines operating at the higher temperatures for improved fuel efficiency, these coatings may be overaluminized (Ref 55, 56) and internal cooling passages simultaneously aluminized to resist increasingly severe oxidation conditions.

References cited in this section

11. R. Burgel, *Mater. Sci. Tech.,* Vol 2, 1986, p 302-308
14. K. Godlewski and E. Godlewska, *Oxid. Met.,* Vol 26, 1986, p 125-128
52. J.F.V. Harry, *Mater. Sci. Tech.,* Vol 2, 1986, p 295-301
53. W.F. Schilling, *NATO Advanced Workshop on Coatings for Heat Engines,* I. Kvernes, Ed., Aquafreda di Maratea, Italy, 1984
54. M. Fishman, U.S. Patent 4,774,149, 1988
55. J.R. Rairden III, U.S. Patent 3,874,901, 1975
56. J.L. Walker and J.R. Ross, U.S. Patent 3,873,347, 1975

Future Development

Future development activity for pack cementation and related coatings, primarily for use in aircraft engines, will focus on more efficient automated and environmentally friendly manufacturing technology. In addition, means to incorporate additions of beneficial elements, such as hafnium and other oxygen-active elements, by codeposition with aluminum, should become practically available in the near future (Ref 16).

Pack Cementation Aluminizing of Steels

L. Keith Bennett and George T. Bayer, Alon Processing, Inc.

The pack cementation aluminizing process is used to improve the performance of steels in high-temperature corrosive environments. The complex aluminide intermetallic coatings formed during the process exhibit superior resistance to

oxidation, carburization, and sulfidation (Ref 57). Table 3 provides a partial listing of commercial applications for the pack aluminizing process. Typical applications include carbon steel heat exchanger tubes used in sulfuric acid plants, low-alloy steel pipes and fittings used in petroleum refinery heaters, type 304 stainless steel vessels used in flue gas desulfurization systems, and HK or HP cast tubing for ethylene pyrolysis units.

Table 3 Partial list of commercial applications of pack cementation aluminizing

Industry	**Component**	**Typical materials aluminized**
Hydrocarbon processing	Refinery heater tubes	$2\frac{1}{4}$% Cr-1% Mo steel
	Ethylene pyrolysis furnace tubes	Incoloy 802
	Hydrodesulfurizer furnace tubes	$2\frac{1}{4}$% Cr-1% Mo steel
	Delayed coker furnace tubes	9% Cr-1% Mo steel
	Catalyst reactor screens	347 stainless steel
	Catalyst reactor grating	Carbon steel
Sulfuric acid	Gas-to-gas heat exchanger tubes	Carbon steel
Industrial furnace components	Aluminum plant furnace parts	Carbon steel
	Heat treating pots	Carbon steel
	Structural members	High-nickel alloy steel
	Thermowells	Carbon and stainless steels
Steam power and cogeneration	Waterwall tubes	$2\frac{1}{4}$% Cr-1% Mo steel
	Fluidized bed combustor tubes	$2\frac{1}{4}$% Cr-1% Mo steel
	Waste heat boiler tubes	Carbon steel
	Economizer and air preheater tubes	$2\frac{1}{4}$% Cr-1% Mo steel

	Superheater tubes	$2\frac{1}{4}$% Cr-1% Mo steel
Aerospace[a]	Turbine blades	Nickel-base superalloy
	Turbine vanes	Nickel-base superalloy
Flue gas scrubbers	NO_x/SO_x removal units	304 stainless steel
Chemical processing	Reactor vessels and tubing	304/316 stainless steel
Cement	Cooler grates	Stainless steel, HP, HK

(a) Aerospace applications are described in the Section "Diffusion Coatings for Gas Turbine Engine Hot Section Parts" of this article.

Reference cited in this section

57. R.B. Setterlund and G.R. Prescott, Corrosion Characteristics of Iron-Aluminum and Iron-Chromium-Aluminum Alloys in High Temperature Petroleum Applications, *Corrosion,* Vol 17 (No. 6), June 1961, p 277t-282t

Generalized Reaction Agents and Products

As described in the previous Section of this article which dealt with diffusion coatings for turbine blades and vanes, the pack cementation aluminizing coating process is performed in a pack consisting of the following mixture:

- Aluminum--in the form of a pure metal powder or alloy powder
- Filler--a ceramic powder phase, to prevent sintering of the mix during high-temperature processing. Usually aluminum oxide is used
- Activator--a volatile halide, usually an ammonium or sodium halide, to act as a chemical transfer medium for the aluminum

The precleaned steel parts to be pack aluminized are placed in a retort, or reactor vessel, with the pack mixture. Using ammonium halide ($NH_4X; X$ = F,Cl,Br,I) as the activator, the following sequence of high-temperature reactions occurs when aluminum is deposited on the surfaces of an iron-base alloy:

- Decomposition of NH_4X

$$NH_4X(s) = NH_3(g) + HX(g)$$

- Formation of volatile aluminum halides

$$6HX(g) + 2Al(pack) = 2AlX_3(g) + 3H_2(g)$$

$$AlX_3(g) + 2Al(pack) = 3AlX(g)$$

- Deposition of aluminum onto steel (substrate) surface

$$2AlX(g) + 3Fe(substrate) = 2AlFe(alloy) + FeX_2(g) \text{ (displacement reaction)}$$

$$3FeX_2(g) + 5Al(pack) = 3AlFe(alloy) + 2AlX_3(g) \text{ (displacement reaction)}$$

$$3AlX(g) + 2Fe(substrate) = AlX_3(g) + 2AlFe(alloy) \text{ (disproportionation reaction)}$$

$$2AlX(g) + 2Fe(substrate) = 2AlFe(alloy) + X_2(g) \text{ (decomposition reaction)}$$

$$2AlX(g) + H_2(g) + 2Fe(substrate) = 2AlFe(alloy) + 2HX(g) \text{ (reduction reaction)}$$

-

It is probable that deposition occurs principally by the disproportionation reaction, with replacement of Al*X* by the reaction $AlX_3(g) + 2Al(pack) = 3AlX(g)$. Rates of deposition are controlled by partial pressure gradients of reaction species between the source material and the coating surface.

Photomicrographs of the structure, including the diffusion zones, of pack aluminized low-carbon steel and type 304 stainless steel are shown in Fig. 8 (Ref 58). Comprehensive metallographic, x-ray, and electron microprobe analysis of the aluminum diffusion zone in stainless steels indicate an aluminum-rich surface (26-34 wt% Al) after undergoing this pack aluminizing process (Ref 59).

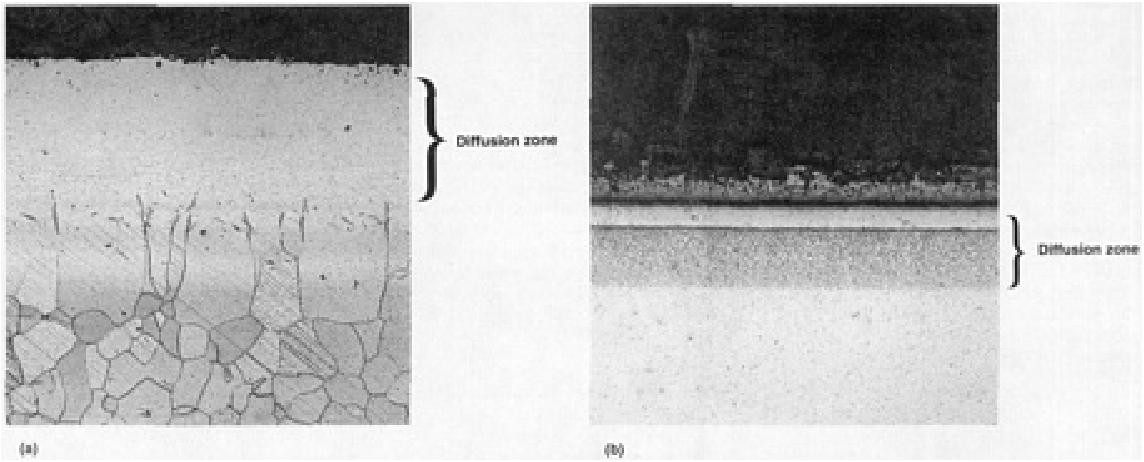

Fig. 8 Photomicrographs showing the structure of pack aluminized (a) low-carbon steel and (b) type 304 stainless steel. Courtesy of Alon Processing, Inc.

References cited in this section

58. "Alonized Steels for High-Temperature Corrosion Resistance," Alon Processing, Inc., Tarentum, PA, 1990
59. L.L. Oden, M.P. Krug, and R.A. McCune, "Analysis of Vapor-Aluminum-Diffused Stainless Steels," U.S. Bureau of Mines, Report of Investigations 8629, 1982

Processing Procedures

Cleaning. Prior to processing of parts, all surfaces should be cleaned to be free of oil, grease, mill scale, crayon, weld slag or spatter, and other foreign materials. A typical cleaning procedure might involve acid pickling to remove mill scale, removal of oil and/or grease by vapor degreasing, as well as abrasive or grit blasting. Grit blasting should be done using aluminum oxide abrasives (60 to 320 mesh, depending on surface finish) at 400 to 550 kPa (60 to 80 psi) from a 75 to 150 mm (3 to 6 in.) standoff. Residual grit should be blown off with a clean source of compressed air. From this point on until packing, parts should be handled with clean cotton gloves to prevent contamination.

Powder Blending. Depending on the material being processed and the desired aluminum activity of the pack, the aluminum pack cementation powder mix contains the following typical range:

- Aluminum (pure metal or ferroalloy): 4% to 25%
- Inert filler (Al_2O_3): 70% to 95%
- Halide activator: 0.5% to 4%

The two types of pack cycles are known as high activity and low activity (see the discussion on "Principles of Pack Diffusion Coating" in the previous Section of this article on "Diffusion Coatings for Gas Turbine Engine Hot Section Parts"). A high-activity pack contains a relatively high fraction of pure aluminum (Table 2) as the source material, a halide activator, and an inert diluent, usually alumina; the process is performed at lower temperatures (650 to 815 °C, or 1200 to 1500 °F). This type of pack generally requires a subsequent high-temperature heat treatment under an inert atmosphere in order to complete diffusion and obtain the required surface aluminum content and diffusion depth. A low-activity pack contains a lower fraction of aluminum, usually in the form of an alloy with iron or chromium, and is performed at higher temperatures (815 to 1150 °C, or 1500 to 2100 °F) with no subsequent heat treatment.

Packing. Retorts can be constructed from a variety of alloys ranging from plain carbon steel to nickel-base superalloys, depending upon desired service life and acceptable costs. Retorts should be fabricated to best accommodate the job being processed. The parts to be coated in the retort should be completely covered with pack mix and should not be allowed to touch each other or the walls of the retort. Prior to sealing the retort, it is advised to make sure that the pack mix is well settled. Low-temperature (high-activity) packs can be run in air, but with high-temperature (low-activity) packs, a protective blanket of hydrogen or inert argon gas is required. For obvious reasons, the use of argon is preferable for safety considerations. High-temperature retorts must be constructed with provisions for gas input/removal kept in mind.

Coating Cycle. Depending on the base material to be pack aluminized, processing temperatures can range from 650 to 1150 °C (1200 to 2100 °F), as measured from a thermocouple inside the retort. At specific process temperatures, a maximum of ±14 °C (±25 °F) must be maintained. Process cycle times can range from 3 to ≥40 h, depending on process temperature and base material to be processed. Transport of aluminum as aluminum chloride through the pack and solid state diffusion of aluminum through the base material is more influenced by process temperature than process time. Although higher process temperatures generally increase surface aluminum content and overall diffusion depth, in some cases the higher processing temperatures can have undesirable effects on the mechanical properties of the base material. In these cases, parts are processed at lower temperatures for longer periods of time.

Finishing. Retorts should be cooled to below 95 °C (200 °F) before opening. Parts should be removed and cleaned by brushing or by a light wet or dry abrasive blast. Certain alloys require controlled cooling cycles to maintain mechanical properties.

Classification of Materials

Pack compositions, process temperatures and process times depend on the type of base material to be aluminized. Materials fall into one of the following general classifications:

- Class I: carbon and low-alloy steels and copper
- Class II: ferritic and martensitic stainless steels and austenitic stainless steels with less than 20% Ni
- Class III: austenitic stainless steels with 21-40% Ni and iron-base superalloys

- Class IV: nickel-and cobalt-base superalloys

As a general rule, overall aluminum diffusion is slower as the nickel, chromium, and cobalt contents increase. Therefore, higher temperatures and longer process times are required to produce greater aluminum diffusion thicknesses as the base material goes from Class I to Class IV. (The Class IV materials are covered in the Section "Diffusion Coatings for Gas Turbine Engine Hot Section Parts" of this article.)

Quality Control

Process quality is monitored by testing of coupons or test pieces which are run in the retort with the production materials during the process cycle. These test pieces are used to determine quality and depth of aluminum diffusion, and should be of the same or similar base material as the production parts. These pieces should be located in the hottest and coldest sections of the furnace loads. These locations should be determined prior to actual processing of parts through furnace surveys.

After the processing has been completed, the test pieces are removed from the retort and examined according to ASTM C 664-87, "Standard Test Methods for Thickness of Diffusion Coating." There are two procedures for measuring the thickness of diffusion coatings. Method A is the determination of the dimensional-change thickness, defined as the difference in the part before and after coating. This method employs a micrometer. Method B is the determination of total coating thickness, defined as the distance between the observably unaffected substrate and the exterior surface of the coating. This method employs standard metallographic specimen preparation equipment for mounting, polishing, and etching as well as a metallographic or optical microscope for observation of the diffusion layer at 100× and 500×.

Quality control reporting should include the maximum, minimum, and average coating thickness (in mils) of the individual measurements made on a specific part of the specimen surface. If Method B is used, a photomicrograph showing the bounds of a typical area of the coating is recommended. Depending on base materials and processing conditions, thicknesses from 1 to ≥40 mils (25 to 1000 μm) can be produced.

Additional mechanical testing may also be appropriate for processed materials which may undergo mechanical property changes due to the temperatures encountered in the process cycle. This testing could include hardness/microhardness measurements, as well as tensile testing to determine yield strength, ultimate tensile strength, and percent elongation.

Properties of Pack Aluminized Steels

Oxidation Resistance. The action of pack aluminized steels under heat is similar to that of unprocessed stainless steels. Stainless steels owe their oxidation resistance to the formation of a thin chromium-rich oxide (Cr_2O_3) film which protects the underlying steel. A similar reaction occurs with aluminized steels, which form an even more protective oxide. Al_2O_3, from the aluminum in the coating. This oxide grows at a lower rate than Cr_2O_3 and does not exhibit volatility in the presence of oxygen above about 927 °C (1700 °F) as does Cr_2O_3. While a type 304 stainless steel scales excessively at temperatures of ≥870 °C (≥1600 °F) in an oxidizing environment, a pack aluminized carbon steel exhibits only slight discoloration of the surface under these conditions. Figure 9 compares aluminized carbon steel with bare carbon steel, 5% Cr steel, 12% Cr steel, and 18Cr-8Ni steel with respect to the temperature at which scaling is less than 10 mg/cm^2 for oxidation in air. High-strength, highly alloyed stainless steels are also frequently aluminized to improve their oxidation resistance in elevated-temperature applications.

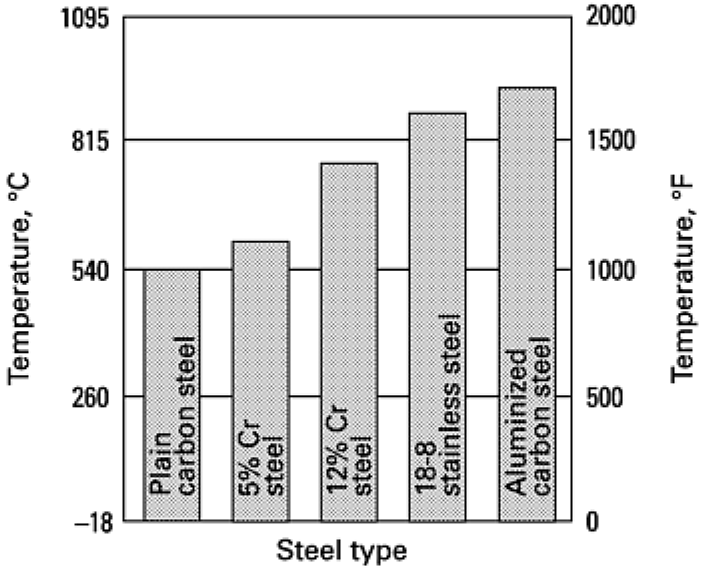

Fig. 9 Oxidation of steels in air at the temperature at which scaling is less than 10 mg/cm^2. Source: Ref 60

Sulfidation Resistance. Pack aluminized steels have remarkable resistance to the corrosive attack of gases such as hydrogen sulfide (H_2S), sulfur dioxide (SO_2), and sulfur trioxide (SO_3) as well as many other sulfur-bearing atmospheres at temperatures exceeding 230 °C (450 °F). The diffusion zone typically contains a minimum of 20% Al while the alloy surface is about 50 at.% Al and is far more resistant to high-temperature sulfide corrosion than stainless steels containing as much as 28% Cr. The maximum temperature at which these materials can be used in sulfur-bearing environments is limited by the high-temperature mechanical properties of the base steel. Figure 10 provides experimental data on the relative corrosion rates of bare and aluminized 9Cr-1Mo steel in H_2S environments.

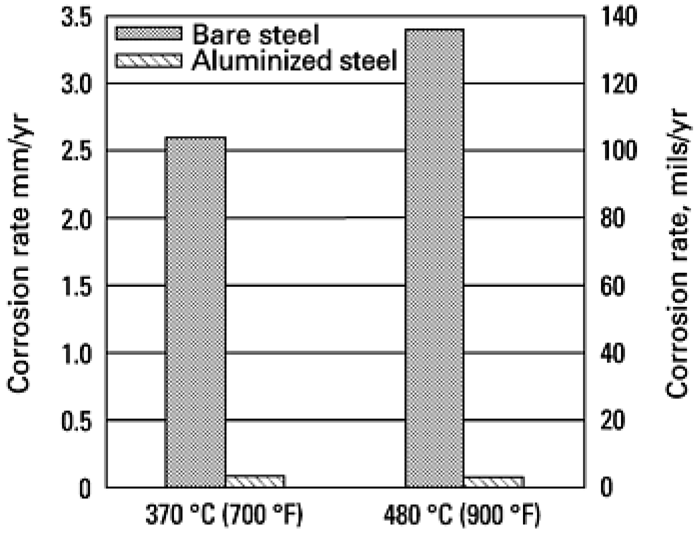

Fig. 10 Relative corrosion rates of 9Cr-1 Mo alloy steel in 5 mol% H_2S at 3550 kPa (515 psi) for 300 h. Source: Ref 61

Carburization Resistance. When exposed at high temperatures to carbon-rich atmospheres, both stainless and alloy steels will carburize, become extremely brittle, and lose their heat- and corrosion-resistance properties. In certain environments, metal dusting associated with carburization will rapidly destroy the steel. Pack aluminized steels, however, suffer negligible deterioration from either carburization or metal dusting in high-temperature, carbon-rich atmospheres,

thus greatly lengthening the service life of the steels in these environments. Figure 11 compares the carburization resistance of bare and pack aluminized austenitic stainless steels.

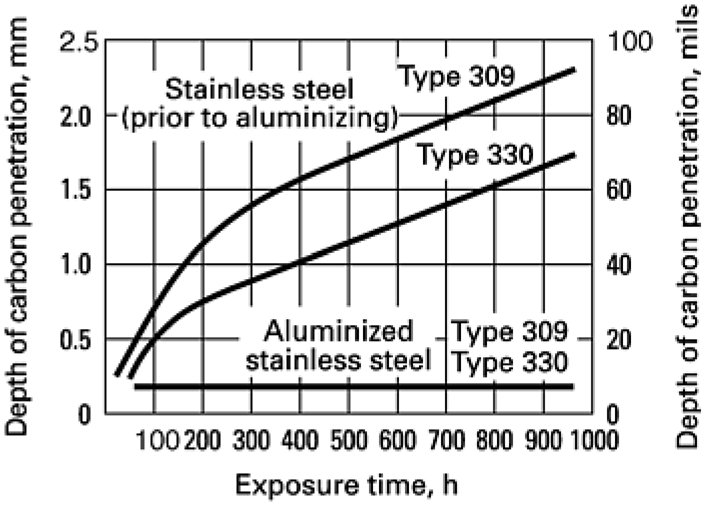

Fig. 11 Carburization resistance of bare and aluminized stainless steels at 925 °C (1700 °F). Source: Ref 62

References cited in this section

60. W. Beck, "Comparison of Carbon Steel, Alonized Type 304 For Use as Dummy Slabs in Reheat Furnace Operation," Alon Processing, Inc., Tarentum, PA
61. T. Perng, "A Fundamental Study of the Noxso NO_x/SO_2 Flue Gas Treatment," Noxso, 1984
62. "Alonized Steels for High-Temperature Corrosion Resistance," Alon Processing, Inc., Tarentum, PA, 1990

Pulsed-Laser Deposition

James S. Horwitz, Naval Research Laboratory

Introduction

PULSED-LASER DEPOSITION (PLD) is a physical vapor deposition (PVD) technique that has gained popularity for the growth of high-quality multicomponent oxide thin films (Ref 1, 2, 3). Conceptually, PLD is an extremely simple PVD technique. The output of a short laser pulse (10 to 30 ns) is focused onto a solid target. The laser rapidly raises the surface temperature of a small portion of the target well beyond the vaporization temperature. A plume of evaporated material is ejected from the target and is collected on a nearby substrate. The congruent non-equilibrium evaporation of multicomponent materials and the transfer of the target composition to the deposited film make available high-quality thin films of materials that could not be deposited by other PVD techniques.

Much of the current research on PLD is due to the success realized with high-temperature superconductor (HTS) materials. In 1986 (Ref 4), the discovery of ceramic superconductors was soon followed by an intense search for a PVD technique that could be used to cast these materials in thin film form. Ceramic superconductors are generally complex multicomponent oxides containing three or more metals (e.g., $YBa_2Cu_3O_7$, or YBCO) with anisotropic electrical properties. PLD was among the techniques surveyed for possible application in the fabrication of thin-film superconductors at the time that bulk superconductors were being developed. Even though PLD was far from the advanced level of other film growth techniques, it was demonstrated that high-quality superconducting films could be reproducibly deposited by PLD. As a result, the technique became an integral component in the development of thin film applications of HTS materials.

Prior to 1987, there were very few research efforts in the area of PLD. This is despite the fact that literature references as early as 1965 (Ref 5) cite the capability of a short-pulse, high-peak power laser to "flash evaporate" a multicomponent target and transfer the composition of that target to a nearby substrate. PLD did not achieve widespread popularity at the time of its discovery, partly because the lasers required were not commercially available and the duty cycles (≤ 1 Hz) at which research laser systems operated were not suitable thin film production. At the time of its discovery, laser flash evaporation was not perceived to have any clear advantage over conventional evaporation techniques.

Between 1964 and 1987, research on the production of high-powered lasers was accompanied by studies of the interaction of the radiation field with solids, primarily to determine the origin of optical damage (Ref 6). These studies included an analysis of the vapor created by lasers focused to ablation energy densities. Film growth studies included the deposition of complex materials (ReB_{22}) (Ref 7), reactive deposition (Ref 8) (i.e., oxidizing ambients and enhanced gas-phase reaction due to high kinetic energies of evaporated material) (Ref 9), and the growth of high-quality II-VI semiconductor superlattices (Ref 10, 11, 12). However, research in these areas was still not sufficient to distinguish PLD as a new and important coating technology. The rapid development of the technique since 1987 is a combination of a materials need that could not be adequately met by conventional film growth techniques and the commercial availability of high-powered excimer lasers. Had high-temperature superconductivity been discovered in simpler, binary systems, PLD may have remained the interest of a relatively small research community. However, many of these new materials contain four or five elements, and the systems have extremely complex phase diagrams. These systems were the driving force in the development of this new technique.

The general attributes of PLD for thin film growth are summarized in Table 1. In addition to congruent evaporation and stoichiometric vapor transport, the high instantaneous growth rates lead to low impurity incorporation from the background. Although the pulsed lasers used generally have high peak powers, average power is low, and therefore the target remains thermally stable. PLD is a simple technique and therefore leads to reproducible deposition conditions. However, the technique is new, and it is difficult to predict optimum growth conditions. For most materials, it is still a trial-and-error process to determine optimum deposition conditions.

Table 1 Attributes of PLD

Attribute	Effect on film
Positive	
Congruent evaporation	Stoichiometric deposition
Large range of deposition pressures	Control of vapor energy; control of volatile components
High instantaneous deposition rate	Low impurity incorporation
Low average power	Target remains thermally stable
Simple equipment	Reproducible properties
Negative	
Relatively new technique	Difficult to predict film properties
Line of sight	Difficult to coat nonplanar objects

High instantaneous evaporation rate	Particulates

PLD research now covers a wide variety of conducting and insulating metal oxide thin films (e.g., ceramic superconductors, ferroelectrics, and ferrites) as well as nonoxide materials (e.g., semiconductors, metals, nitrides, and diamond-like carbon) (Ref 13). The areas of application range from electronics to biology, tribology, and optics. The list of materials successfully deposited as high-quality thin films is continuously growing. In spite of its success, the technique remains primarily a laboratory research tool, providing high-quality thin films and multilayers of complex materials for materials research and the development of new devices and applications based on these materials. This review describes the PLD technique and the components required for a simple system, examines the properties of the depositing vapor and how it is affected by the deposition parameters, and cites examples of classes of materials for which the technique offers a unique advantage over more conventional processes.

References

1. *MRS Bull.,* Vol 27, 1992
2. Laser Ablation in Material Processing: Fundamentals and Applications, *Mat. Res. Soc. Proc.,* Vol 285, 1992
3. *Laser Ablation: Mechanisms and Applications,* J.C. Miller and R.F. Haglund, Jr., Ed., Springer Verlag, 1991
4. J.G. Bednorz and K.A. Muller, *Z. Phys. B,* Vol 64, 1986, p 189
5. H.M. Smith and F.A. Turner, *Appl. Optics,* Vol 4, 1965, p 147
6. J.F. Ready, *Effects of High Power Radiation,* Academic Press, 1971
7. J. Desserre and J.F. Eloy, *Thin Solid Films,* Vol 29, 1975, p 29
8. H. Osterreicher, H. Bittner, and B. Kothari, *J. Solid State Comm.,* Vol 26, 1978, p 97
9. S.P. Tang, B.G. Wicke, and J. Friichtenicht, *J. Chem. Phys.,* Vol 68, 1978, p 5471
10. N.P. Ong, J.K. Moyle, J. Bajaj, and J.T. Cheung, *J. Vac. Sci. Tech.,* Vol A5, 1987, p 3079
11. J.T. Cheung and J. Madden, *J. Vac. Soc. Technol.,* Vol B5, 1987, p 705
12. J.T. Cheung, E-H. Cirlin, and N. Otsuka, *Appl. Phys. Lett.,* Vol 53, 1988, p 310
13. D.B. Chrisey and G.K. Hubler, *Pulsed Laser Deposition of Thin Films,* Wiley, 1994

General Description

In PVD of multicomponent thin films, the preparation of a stoichiometric vapor is often difficult to achieve. When single-element sources are used, the arrival rate of each individual component must be calibrated and inter-regulated. In PLD, the composition of the vapor is the same as that of the target. Starting with the correct composition of the vapor greatly facilitates the growth of a desired phase in the depositing film. In addition, the absence of filaments or charged particles allows films to be grown by PLD in the presence of reactive gases. These gases can promote the growth of the desired thin film material through gas-phase reactions with the evaporated target material and gas-surface reactions with the growing film.

The pulsed laser ablation of materials can be viewed as taking place in several stages (Ref 6). The laser deposits energy into the target. Absorption of the radiation by the target material leads to surface heating and defect formation. The energy absorbed per unit volume depends on the optical penetration depth, the thermal diffusivity, and the rate at which the energy is deposited (Ref 14, 15, 16). The rate at which the energy is deposited is determined by the laser pulse width. The rise in surface temperature can be calculated from the ratio of the rate at which energy is deposited into the material to the rate at which the heat is conducted away. Typically, the laser is focused to a small spot (e.g., a few square millimeters) to minimize the volume of material being heated and to achieve surface temperatures that are greater than the melting temperature. If the optical penetration depth is small compared to the thermal diffusion length, surface heating is confined to the thermal diffusion length, and the change in temperature can be calculated from the energy absorbed, the volume of material irradiated, and the heat capacity. If the optical penetration depth is long, the rise in temperature is at a maximum at the target surface but decays exponentially as a function of depth below the surface (Ref 14, 15, 16).

Surface heating is followed by melting and evaporation. For most materials, there is a threshold laser fluence for the macroscopic removal of material from the surface (Ref 17). The high temperatures generated at the surface cause the emission of many species from the target, including ions and electrons generated by thermionic emission as well as atoms and molecules. Continued interaction of the laser pulse with the evaporated material causes the vapor to be ionized via nonresonant multiphoton processes, creating a plasma above the target. As the density of electrons increases, the laser radiation is absorbed preferentially in the plasma by inverse bremsstrahlung scattering (Ref 6). The absorption further heats the plasma and at the same time screens the laser pulse from further interaction with the target.

The high-pressure, high-temperature plasma expands rapidly into the vacuum. The dynamic behavior of the expansion has been compared to a supersonic or free-jet expansion (Ref 18, 19). In a free-jet expansion, the random motion of gas-phase particles in a high-pressure plasma is converted to a directed mass flow by expanding through a pinhole into a low-pressure region. Free-jet expansions are characterized by narrow, energetic velocity distribution about a center of mass velocity (Ref 20). A similar phenomenon is observed in PLD. A small high-pressure region is created at the target surface and then expands into the relatively low pressure of the vacuum system. The laser-generated plasma is a complex mixture of neutral and charged particles, each with different kinetic energies. Average neutral energies of ≈ 10 eV are observed (compared to thermal evaporation particle energies of ≈ 0.1 eV). Charged particle kinetic energies of as much as 10 to 100 times the neutral particle energies are also observed. The fraction of ionized material in the plasma is difficult to measure. Estimates vary between 1 and 10% (Ref 21).

The high energy content of the depositing vapor is believed to be one of the reasons for the success of PLD over other PVD techniques. The added energy can benefit film quality in several ways. First, gas-phase reactivity increases with atom kinetic energy. Enhanced oxidation cross sections are reported for laser-evaporated materials (Ref 22). For some materials, a correlation has been reported between the maximum concentration of metal oxides formed in the gas phase and optimum film properties (Ref 21, 29). Secondly, PLD films can typically be grown at a reduced substrate temperature in comparison to other PVD techniques. Substrates are usually heated to provide the arriving vapor with enough surface mobility for the atoms to build up on the surface in thermodynamically stable sites. Adding the energy to the vapor, as is done in PLD, means the substrate temperature can be lowered. This is desirable in cases in which the vapor can undergo a chemical reaction and the substrate or volatile components can be lost from either the film or the substrate.

Under optimized conditions, oriented thin films can be prepared by PLD in situ, minimizing the production of impurity phases, grain boundaries, and random orientations that might be formed during a postdeposition anneal. Although average film deposition rates for PLD are comparable to those in many other PVD techniques, the pulsed arrival of the vapor at the substrate results in instantaneous deposition rates of ≈ 1000 to 10,000 Å/s. The instantaneous deposition rate minimizes the incorporation of background impurities into the depositing films, further improving the film quality.

Plume Diagnostics. A number of diagnostics have been used to characterize the laser-generated plasma (Ref 23): optical emission (Ref 24, 25, 26), absorption (Ref 27), laser-induced fluorescence (Ref 28, 29), resonance-enhanced multiphoton ionization (Ref 30), mass spectrometry (Ref 31, 32, 33 , 34), and ion probes (Ref 35). These diagnostics are being used to address several mechanistic issues relevant to film growth (Ref 23):

- The role of thermal versus nonthermal evaporation
- The extent to which the laser radiation interacts with the evaporated material
- The effect of the laser-generated plasma on the target
- The expansion mechanism responsible for the high initial particle energy
- The fraction of ionized material from the target surface out to the substrate surface
- The importance of clusters
- The role of the ambient in scattering, diffusion, shock front formation, and gas phase chemistry

The answers to these questions will come not from a single technique, but from a combination of the information provided by each of the diagnostics (Ref 23).

In the laser-generated plasma, the distribution of particles and the particle energy depend on the material, laser wavelength, laser fluence, and ambient composition and pressure. The characteristics are both temporally and spatially dependent. Presumably, this is the reason that optimized deposition conditions vary from system to system. An ideal vapor arrives at the substrate surface compositionally correct and with a kinetic energy that is high enough to allow

adequate surface mobility, but not so high as to introduce defects or sputter the depositing vapor. The goal of these studies is to make a direct correlation between the vapor phase properties and the film properties.

Among the plasma diagnostics mentioned above, optical techniques have dominated the research efforts. These techniques are noninvasive and can be performed at the pressures under which films are deposited. Optical techniques have been used to identify the dominant components of the plume as being atomic and small molecular species. Dispersed emission spectra have been measured as a function of distance above the target from the vacuum ultraviolet through the visible (Ref 23, 24, 25, 26). Close to the target a continuum in the emission spectrum is observed, indicative of bremsstrahlung emission and a high density of free electrons. Several centimeters above the target, emission spectra are more characteristic of the isolated atomic species. The presence of electronically excited atoms and molecules at this distance is due to collisional, not optical, excitation. Secondary electrons generated from background gas ionization recombine with highly charged particles to form electronically excited species.

The dispersed spectra have been used to estimate the plasma temperature, which varies from 5,000 to 15,000 K (Ref 26, 36). Particle velocities (v) have been modeled using Maxwell-Boltzmann distributions $f(v) \sim \exp(-mv^2/2kT)$ and shifted distributions about a common center of mass $f(v) \sim \exp(-m(v-v_{cm})^2/2kT)$ (Ref 30). The shifted Maxwell-Boltzmann arises as a result of a Knudsen layer formed at the target surface (Ref 37, 38). Peak velocities are reported as $\sim 10^5$ to 10^6 cm/s (Ref 21). Optical techniques have also monitored the formation of gas-phase species from the reaction of the ambient with the ablated material. In these studies, maximum gas phase production has been correlated with optimum film growth pressures. For example, in YBCO, the concentrations of YO and CuO are at a maximum at the optimum deposition pressure for high-quality films (Ref 21, 29).

Optical imaging techniques have also been used to detect the presence of a shock front (region where the plume and background gas pressure are the same) (Ref 39, 40, 41). The position of the shock front depends on the plasma temperature and pressure and the total system pressure. In vacuum, the shock front is relatively far from the target surface (several times the target substrate distance in typical deposition systems). As the ambient pressure is increased, the shock front moves in toward the target. The position of the shock front relative to the substrate is important for optimizing the properties of the deposited film.

References cited in this section

6. J.F. Ready, *Effects of High Power Radiation,* Academic Press, 1971
14. K.L. Saenger, *Processing of Advanced Materials,* Vol 3, 1993, p 63
15. J.T. Cheung and H. Sankur, *CRC Crit. Rev. Solid State Mat. Sci.,* Vol 15, 1988, p 63
16. D.L. Lin, X. Li, Z.D. Liu, and T.F. George, *J. Appl. Phys.,* Vol 72, 1992, p 4227
17. A. Inam, X.D. Wu, T. Venkatesan, S.B. Ogale, C.C. Chang, and D. Dijkkamp, *Appl. Phys. Lett.,* Vol 51, 1987, p 1112
18. H.S. Kwok, D.T. Shaw, Q.Y. Ying, J.P. Zheng, S. Witanachchi, E. Petrou, and H.S. Kim, *Proc. SPIE,* Vol 1187, 1989, p 161
19. N.H. Cheung, Q.Y. Ying, J.P. Zhang, and H.S. Kwok, *J. Appl. Phys.,* Vol 69, 1991, p 6349
20. J.B. Anderson and J.B. Fenn, *The Physics of Fluids,* Vol 8, 1965, p 780
21. N.S. Nogar, R.C. Dye, R.C. Estler, S.R. Foltyn, R.E. Muenchausen, and X.D. Wu, in *Laser Ablation: Mechanisms and Applications,* J.C. Miller and R.F. Haglund, Jr., Ed., Springer Verlag, 1991, p 3
22. A. Gupta, *J. Appl. Phys.,* Vol 73, 1993, p 7877
23. D.B. Geohegan, in *Pulsed Laser Deposition of Thin Films,* D.B. Chrisey and G.K. Hubler, Ed., Wiley, 1994, p 115
24. W.A. Weimer, *Appl. Phys. Lett.,* Vol 52, 1988, p 2171
25. C. Girault, D. Damini, J. Aubreton, and A. Catherinot, *Appl. Phys. Lett.,* Vol 55, 1989, p 182
26. G. Mehlman, D.B. Chrisey, P.G. Burkhalter, J.S. Horwitz, and D.A. Newman, *J. Appl. Phys.,* Vol 74, 1993, p 53
27. D.B. Geohegan and D.N. Mashburn, *Appl. Phys. Lett.,* Vol 55, 1989, p 2345
28. L. Lynds, B.R. Weinberger, B.M. Potrepka, G.G. Peterson, and M.P. Lindsay, *Physica C,* Vol 159, 1989, p

29. C.E. Otis and R.W. Dreyfus, *Phys. Rev. Lett.,* Vol 67, 1991, p 2102
30. R.C. Estler and N.S. Nogar, *J. Appl. Phys.,* Vol 69, 1991, p 1654
31. L. Wiedeman and H. Helvajian, *J. Appl. Phys.,* Vol 70, 1991, p 4513
32. C.H. Chen, T.M. Murphy, and R.C. Phillips, *Appl. Phys. Lett.,* Vol 57, 1990, p 937
33. C.H. Becker and J.B. Pallix, *J. Appl. Phys.,* Vol 64, 1988, p 5152
34. H. Dupendant, J.P. Gavigan, D. Givord, A. Lienaard, J.P. Rebouillat, and Y. Souche, *Appl. Surf. Sci.,* Vol 43, 1989, p 369
35. D.B. Geohegan, in *Laser Ablation: Mechanisms and Applications,* J.C. Miller and R.F. Haglund, Jr., Springer Verlag, 1991, p 28
36. R. Tambay, R. Singh, and R. Thareja, *J. Appl. Phys.,* Vol 72, 1992, p 1197
37. R. Kelly and R. Dreyfus, *Surface Science,* Vol 198, 1988, p 236
38. R. Kelly, *J. Chem. Phys.,* Vol 92, 1990, p 236
39. R.A. Lindley, R.M. Gilenbach, and C.H. Ching, *Appl. Phys. Lett.,* Vol 63, 1993, p 888
40. D.B. Geohegan, in *Pulsed Laser Deposition of Thin Films,* D.B. Chrisey and G.K. Hubler, Ed., Wiley, 1994, p 115
41. P.E. Dyer, A. Issa, and P.H. Key, *Appl. Phys. Lett.,* Vol 57, 1990, p 186

Equipment

Vacuum System. Figure 1 is a schematic of a PLD system. The laser radiation is focused onto a rotating target at an angle of ~45°. The substrate is mounted at 90° with respect to the target normal. Typically, the target and substrate are separated by ~5 cm, but distances as large as 12 cm have been reported (Ref 42). The vacuum system requirements vary depending on the material. Generally, oxide films are deposited in an oxygen ambient at pressures <1 torr and do not require systems with ultrahigh vacuum base pressures. Gas flow rates of 10 standard cm^3/min at the desired deposition pressure can be achieved by gating the pump with the total system pressure controlled by a solenoid-activated leak valve that is controlled by a pressure transducer. At a minimum the vacuum chamber requires a pumping port, a gas inlet and pressure monitoring, a window transparent at the laser wavelength, and a viewport.

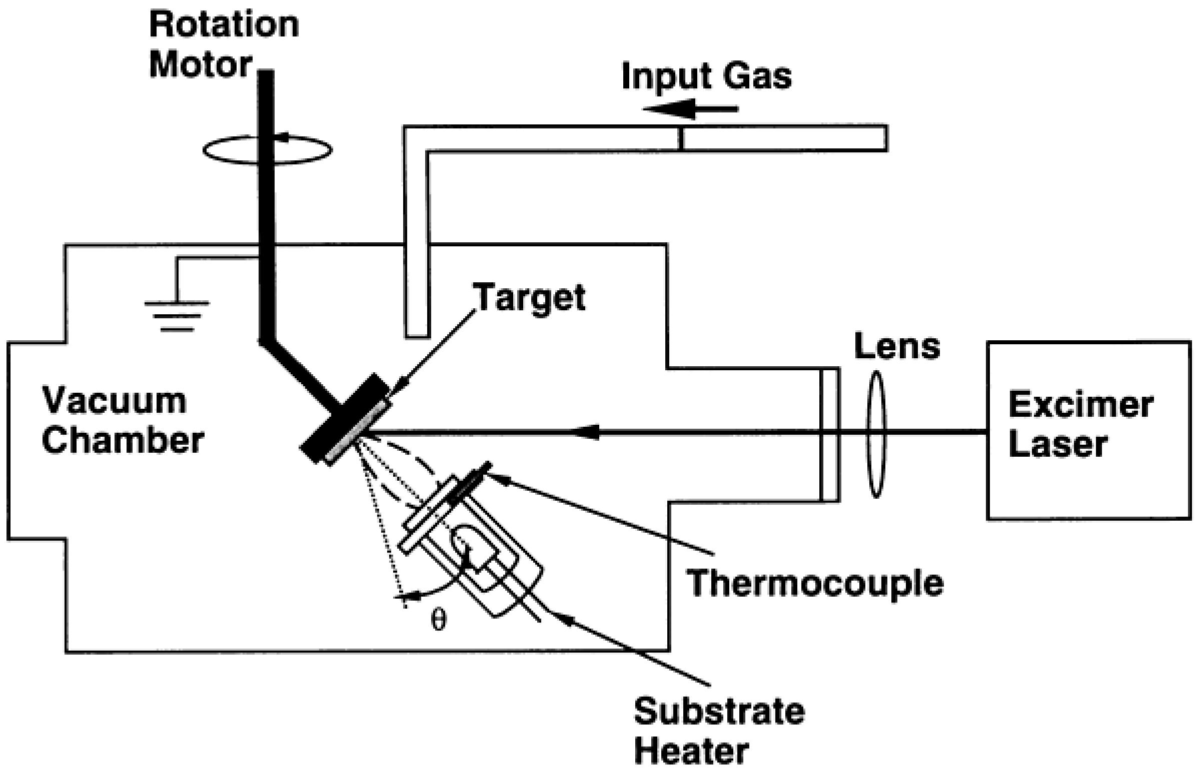

Fig. 1 Schematic diagram of a typical pulsed laser deposition system

Laser. The laser system and focusing optics are located outside the chamber. The focal length needs to be matched to the chamber size so that the required energy densities can be achieved at the target surface. Many different laser wavelengths have been successfully used. The excimer is the most commonly used laser because of its high peak power (> 40 MW) in the ultraviolet and ease of operation. In an excimer laser, the lasing medium is a rare gas/halogen mixture. A summary of rare gas mixtures and the output laser wavelengths is presented in Table 2. KrF (248 nm) is probably the most common excimer used for thin film deposition due to its stability and high peak power. In addition to excimer lasers, other gas laser systems (CO_2) and solid state laser systems (Nd:YAG) have been used to deposit thin films. The output wavelengths of these lasers can vary from 0.2 to 10 μm. Film quality as a function of laser wavelength has been compared (Ref 43), and it is generally accepted that film quality is significantly better for ultraviolet (UV) lasers (200 to 300 nm) than for infrared (IR) lasers (1 to 10 μm). This is due to a decreasing penetration depth of the laser radiation into the bulk material as the wavelength is reduced. The shallower penetration depth results in more energy being deposited per unit volume for comparable UV and IR pulse energies. As a result, UV lasers produce higher surface temperatures and more efficient evaporation of the solid target. IR lasers are often associated with thin films having rough surface morphologies, as a result of the incomplete vaporization of the target and the ejection of micron-size particles. Attenuation of the radiation by oxygen (in addition to the photochemical production of ozone) limits the use of laser wavelengths below 200 nm.

Table 2 Excimer laser wavelengths

Wavelength, nm	Rare gas/halogen mixture
157	F_2
293	Ar-F_2
222	Kr-Cl_2
248	Kr-F_2
308	Xe-Cl_2
351	Xe-F_2

An individual laser pulse transfers a large amount of material from the target to the substrate (~10^{16} atoms per pulse), resulting in average deposition rates of ~1 Å/laser pulse (deposition rates are a strong function of the target composition and phase and the deposition conditions). To achieve a coating thickness on the order of 1.0 μm requires 5000 to 20,000 laser pulses. Commercial excimer systems operate at repetition rates as high as 150 Hz, and high-quality films 0.5 μm thick have been deposited at average growth rates as high as 150 Å/s.

Substrate Heater. For many materials, it is desirable to deposit at elevated substrate temperatures. Two problems are often encountered when trying to achieve uniform substrate temperatures $\leq$900 °C in oxidizing environments. First, the heating element must be inert to the ambient. Second, the typical deposition conditions (10^{-6} to 1 torr) do not allow for efficient gas-phase heat conduction from the radiating element to the substrate. Projection lamps serve as efficient heating elements because the filament is encapsulated in a quartz envelope. The lamps can be used to heat a small steel block to temperatures that approach the softening temperature of the quartz. The substrate is mounted onto the steel heater block. Transfer of the heat from the steel block to the substrate is usually done through a conductive bonding agent such as silver paint. This type of heater can be used for small substrates (up to ~1 in. diameter) and temperatures up to ~950 °C.

Alternatively, substrates can be heated using a pseudo-blackbody heater (Ref 42). Here the substrate is encased in a well-shielded heater with only a small opening for the depositing vapor. The substrate is not required to be in intimate thermal contact with the heater block because the temperature everywhere inside the blackbody is the same. Substrate heaters of this type have been successfully developed for the deposition of large-area films (>1 in. diameter). Rotation of the substrate inside the blackbody heater improves the temperature uniformity.

Target Manipulation. The target must be continuously manipulated to avoid having the laser strike the same spot on the target with successive shots. This is done exclusively by rotating the target during deposition. This minimizes problems associated with erosion at the target surface. Commercial systems are available that hold up to six rotating targets, 1 in. in diameter, that can be selected under computer control to be positioned in front of the laser focus. With this type of system, multilayer structures can easily be formed.

Laser Beam Rastering. Target rotation ensures uniform erosion. The laser beam can also be rastered across the target. In addition to minimizing problems associated with erosion, rastering of the laser beams increases the area of a substrate that can be coated. In PLD, the plume of evaporated material is highly forward-directed. If the position of the laser beam remains fixed in space, the plume of evaporated material is directed at a relatively small area on the substrate. For most deposition systems, a stationary laser beam produces a uniform coating over 1 cm^2. In its simplest form, the laser beam is moved by a motorized mirror mount across the target. The substrate and target are mounted so that their centers are on axis. The plume of evaporated material is swept across the substrate. The main limitation to this geometry is that the coated area is determined by the size of the target. Off-axis geometries have also been demonstrated (Ref 44). Offsetting the target center from the substrate center allows the same aerial coverage with a target that is only half the size of the substrate. Another scale-up technique is to raster the substrate in two dimensions while holding the laser position fixed on the target (Ref 45). This scheme has the advantage of not requiring large-area targets but suffers from the complications of having to move the heating elements.

Research efforts continue on the scale-up of PLD to large areas, although it is not yet clear what technological application will be the first to implement large-scale PLD in an industrial environment. Both ferroelectric and HTS thin films have been deposited over large areas as demonstrations. Uniform coatings have been successfully demonstrated on planar surfaces up to 5 in. in diameter. However, there is still a great deal of work to be done on the device structures based on these materials, and the demands for large-area coatings is relatively small. The versatility of the technique is simply not yet great enough to generate industrial acceptance.

Deposition Parameters. Typical deposition conditions are:

- *Laser wavelength:* 193 nm to 1.06 μm
- *Laser spot size:* 3-5 mm^2
- *Laser pulse energy:* 100-500 mJ
- *Laser pulse width:* 10-30 ns
- *Laser fluence:* 1-5 J/cm^2
- *Laser repetition rate:* 5-100 Hz
- *Substrate temperature:* Room temperature to 950 °C
- *Ambient pressure:* 10^{-6} to 1 torr

References cited in this section

42. J.A. Greer, *J. Vac. Sci. Tech.,* Vol A10, 1992, p 1821
43. G. Koren, A. Gupta, P.J. Baseman, M.I. Lutwyche, and R.B. Laibowitz, *Appl. Phys. Lett.,* Vol 55, 1989, p 2450
44. S.R. Foltyn, R.E. Muenchausen, R.C. Dye, X.D. Wu, L. Luo, D.W. Cooke, and R.C. Taber, *Appl. Phys. Lett.,* Vol 59, 1991, p 1374
45. M.F. Davis, J. Wosik, K. Forster, S.C. Deshmukh, H.R. Rampersad, S. Shah, P. Siemsen, J.C. Wolfe, and D.J. Economou, *J. Appl. Phys.,* Vol 69, 1991, p 7182

Deposition Characteristics

Angular Distribution. In general, the angular distribution of material from the laser-generated plasma is sharply peaked with respect to the target normal, with some tilting of the distribution toward the incident laser beam. Early studies on the PLD of multicomponent films indicated that the spatial distribution of deposited material was also accompanied by a spatial variation in film composition. In thermal evaporation, a small effusive source is described as having a $\cos(\theta)$ distribution (θ is the angle at which the material is ejected from the target relative to the surface normal of the target; see Fig. 1). This results in a $\cos^4(\theta)$ thickness distribution of the film on the substrate. In a purely effusive source, there are no collisions from the evaporation region to the substrate surface. In PLD, a large number of collisions take place in the high-pressure plasma and are responsible for the forward peaking. It is difficult to generalize on the exact functional dependence of the angular distribution of material because it is sensitive to a number of the deposition parameters (e.g., laser wavelength, fluence, spot size and geometry, target-substrate distance, and background gas pressure). As an example, in vacuum the angular distributions, as determined from film thickness, for single and multicomponent materials have yielded values of x ($\cos^x(\theta)$) ranging from 2.3 to 30 (Ref 46).

The angular distribution of ejected material is also sensitive to the shape of the laser spot on the target. The rectangular shape of excimer laser beams typically results in a rectangular focused spot on the target. In some systems, it has been observed experimentally that the deposited film has a rectangular image, with the long and short axis of the film reversed from the image on the target. The rotation of the image is an indication that plume expansion proceeds fastest along the shorter axis (i.e., there are fewer collisions and the particles can achieve greater velocities).

Effects of Added Gas. The addition of a background gas has a strong effect on the angular distribution of the evaporated material. Where direct comparison measurements have been made, the distribution has been less sharply peaked at an elevated pressure. Measurements on multicomponent oxides (e.g., YBCO) are complicated by gas-phase chemistry. For example, a comparison study has shown a reduction from $\cos^{23}(\theta)$ to $\cos^{17}(\theta)$ associated with a change from vacuum to 100 mtorr of oxygen (Ref 46).

The angular distribution changes nonlinearly with the added gas pressure. For elemental systems such as copper (Ref 47) or platinum (Ref 48), the initial addition of either argon (for copper) or oxygen (for platinum) leads to a forward focusing effect; that is, ejection of material occurs at smaller angles. Forward focusing is manifest as a narrowing of the angular distribution function (increasing x) and an increase in the average film deposition rate. This behavior reaches a maximum effect at low pressures (~1 to 50 mtorr). Above this pressure, scattering dominates and the average deposition rate decreases as material is scattered over larger angles.

References cited in this section

46. K.L. Saenger, *Pulsed Laser Deposition of Thin Films,* D.B. Chrisey and G.K. Hubler, Ed., Wiley, 1994, p 199
47. J.C. Kools, *J. Appl. Phys.,* Vol 74, 1993, p 1
48. R.E. Leuchtner, D.B. Chrisey, J.S. Horwitz, and K.S. Grabowski, *Surf. and Coatings Tech.,* Vol 51, 1992, p 476

Particulates

One of the most often cited drawbacks to PLD is the rough surface morphology of the deposited films. The observed surface roughness can originate from a variety of mechanisms. For the same deposition conditions (i.e., laser parameters), the particulate density (number of particles/$cm^2 \cdot Å$ of film) varies significantly from material to material (Ref 49). No one model is able to predict the size and distribution of the particulates. One of the main causes of surface roughness is the ejection of micron-size particles from the target. These particles can be problematic for electronic materials, especially those involving multilayers of conductors and insulators, as well as optical materials in which particles can serve as scattering centers. There are at least three mechanisms associated with formation of surface particulates: subsurface boiling (Ref 50), shock wave recoil (Ref 51), and exfoliation (Ref 52). Subsurface boiling occurs when the required heat transfer time is less than the evaporation time. The subsurface reaches a molten temperature before the surface layer has evaporated. The effect of subsurface boiling can be minimized by reducing the laser power, which also reduces the deposition rate. Above the target surface, a shock wave is formed at the boundary of the high-pressure region and the vacuum. Recoil pressure from the shock wave into the target can also result in the ejection of micron-size particles. These particles can be reduced by reducing laser power. Continuous heating and cooling of the laser target leads not only to erosion but also to modification of the target surface. Micron-size cones that point back at the direction of the incident

laser beam are observed on the surface of ceramic targets and can be broken off by the shock of the laser. The presence of these structures can be minimized by mechanical polishing of the target surface.

Mechanical Filters. Although the presence of particulates seems to be an inherent property of the PLD process, careful control of deposition parameters can minimize their density. Additional particulate reduction can be achieved mechanically through the use of a particle filter (Ref 53). A velocity filter operates on the principle that particle size can be correlated with particle velocity. A shutter can be used to allow fast-moving (10^6 cm/s) atomic vapor to pass while blocking the slower-moving (10^3 cm/s) particulates (Ref 34). In practice, a rotating chopper (3000 to 10,000 rpm) can be synchronized to the firing of the laser. Mechanical filters are effective at reducing the aerial density of particulates regardless of the mechanism of origin.

Off-Axis PLD. The most common PLD geometry has the substrate facing the target, separated by a few centimeters. This is designed to maximize the film deposition rate. Recently, there have been a few reports of off-axis PLD. Non-normal geometries have been successfully used in the PLD of YBCO thin films, and two geometries have been reported. Mounting the substrate surface so that it is parallel to the target normal is essentially equivalent to an off-axis sputtering geometry (Ref 54). The majority of the ejected vapor (in addition to the particulates) travels across the substrate surface, without depositing. Although the deposition rate is decreased, there is substantial discrimination of the larger particulates in the depositing thin film. Additionally, substrates have been mounted facing away from the target surface (Ref 55). Films are deposited in high background pressures of reactive gases. Preferential slowing of the atomic vapor over the particulates allows deposition of smooth films and a substantial reduction in the average deposition rate. The required thermalization of the evaporated material and the absence of energetic ions in the depositing vapor does not seem to affect the properties of YBCO films.

References cited in this section

34. H. Dupendant, J.P. Gavigan, D. Givord, A. Lienaard, J.P. Rebouillat, and Y. Souche, *Appl. Surf. Sci.,* Vol 43, 1989, p 369
49. J.A. Greer and J.Van Hook, *SPIE Proceedings,* No. 1377, 1990
50. J.F. Ready, *Appl. Phys. Lett.,* Vol 3, 1963, p 11
51. R. Kelly et al., *Nuclear Inst. and Methods in Physics Research,* Vol B9, 1985, p 329
52. J.T. Cheung, in *Pulsed Laser Deposition of Thin Films,* D.B. Chrisey and G.K. Hubler, Ed., Wiley, 1994, p 1
53. T. Venkatesan, X.D. Wu, R.E. Muenchausen, and A. Pique, *MRS Bull.,* Vol 27, 1991, p 54
54. B. Holzapfel, B. Roas, L. Schultz, P. Bauer, and G. Saemann-Ischenko, *Appl. Phys. Lett.,* Vol 61, 1992, p 3178
55. R.J. Kennedy, *Thin Solid Films,* Vol 214, 1992, p 223

Materials

PLD is currently being used to deposit thin films for a wide range of technological applications. These films vary from epitaxial superlattices of electronic materials to polycrystalline bioceramics. Several recent review articles have attempted to catalog research efforts to date (Ref 15, 56, 57), indexing films by composition, phase, and the laser used to deposit the film. It would appear that the vast majority of research published to date on PLD has been directed at multicomponent oxides. The technique offers a clear advantage when the material contains more than two elements. The ceramic superconductors have provided the complex materials needed to accelerate research in PLD.

High-Temperature Superconductors. More research has been devoted to PLD of superconductors than to PLD of any other class of materials. There are two classes of oxide superconductors:

- *Cuprates:* Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O, La-Sr-Cu-O, Nd-Ce-Cu-O, Tl-Ba-Ca-Cu-O
- *Noncuprates:* Ba-K-Bi-O, Ba-Pb-K-Bi-O

YBCO was the first of these materials to exhibit superconductivity above liquid nitrogen temperatures (Ref 58). Although other materials have since exhibited higher critical temperatures, YBCO still remains one of the more promising materials for applications because it is relatively easy to obtain in single-phase form. Crystallographically, the YBCO unit cell is based on a cubic perovskite structure. The superconductor is a triple layer of the cubic unit cell, with the corners of the perovskite either CuO_4 or CuO_5. The electrical properties of YBCO are highly aniostropic. Phase pure, polycrystalline materials have low critical currents (10^3 to 10^4 A/cm^2) because of the poor electrical conductivity of the randomly oriented grains. Epitaxial or even textured thin films (with the *c*-axis normal to the substrate surface) provide alignment of the conduction planes and high critical currents on the order of 10^6 A/cm^2. Current technological applications of YBCO thin films are divided into two classes: active components (based on Josephson junctions) and passive components (e.g., microwave wave guides) (Ref 59).

Currently, smooth YBCO films can be deposited by a large variety of PVD techniques (Ref 60), including single-source techniques such as sputtering as well as multisource techniques such as molecular beam epitaxy and chemical vapor deposition. In spite of the equivalent film properties of these techniques, PLD remains one of the preferred deposition techniques because of its minimal vacuum system requirements, high average deposition rate, and ease of optimization (see Table 1). However, most applications for superconductors require integration of the superconducting thin film with insulating thin films. The superconductor-insulator interface should be sharp, with the insulating material latticed matched to the superconductor. The deposition technique needs to be versatile to switch between the superconductor and the insulating material.

The first generation of passive microwave electronics based on HTS thin films were fabricated from patterned superconducting thin films deposited onto one side of low-dielectric substrates. MgO and $LaAlO_3$ substrates have been used in the majority of these applications. Advanced microwave devices will be fabricated from trilayer films: superconductor/dielectric/superconductor. In these multilayer structures, the dielectric films (2000 Å to 10 μm thick) must have a low dielectric constant, low loss tangent, and high resistivity, and they must provide a lattice-matched surface for the growth of the top superconducting thin films. Several dielectric films have been successfully deposited in trilayer structures by PLD. Insulating materials include $LaAlO_3$ (Ref 61), $NdGaO_3$ (Ref 62), and $PrGaO_3$ (Ref 63). The deposition of these multilayers can be achieved easily in situ simply by moving the laser beam from the superconducting target to the insulating target.

Barrier layers are also important for the application of HTS materials. Low-dielectric substrates, such as Al_2O_3, and semiconducting substrates, such as silicon or GaAs, react at the elevated deposition temperatures required for HTS thin films, leading to a degradation in the superconducting thin film properties. Barrier layers such as Y-ZrO_2 (Ref 64), $CoSi_2$ (Ref 65), CeO_2 (Ref 66), and $SrTiO_3$ (Ref 67, 68) eliminate substrate film interdiffusion and provide lattice-matched surfaces for superconducting thin film growth. Perhaps the most challenging barrier is that required for a Josephson junction. These barriers (deposited between two superconducting layers) must be on the order of the coherence length for the superconductor (for YBCO, ~10 to 30 Å). The nonsuperconducting praseodymium analog of YBCO is one of the candidate materials for this application (Ref 69, 70). For the application of high-temperature superconductors, PLD has been demonstrated to be capable of integrating many different materials into a multilayer structure.

Ferroelectrics are a class of high-dielectric materials that may also be piezoelectric and pyroelectric. These materials are suitable for a wide variety of thin film electronic applications, including displays, sensors, nonvolatile random access memories, optical switches, modulators, surface acoustic waves, and radio frequency electronics. Although the properties of ferroelectric materials have been known for some time, thin film applications are not very common due to a lack of availability of high-quality thin films. The rate of research into PLD of ferroelectrics is rapidly approaching the rate of research into PLD of HTS materials (Ref 71).

Many ferroelectrics have crystal structures that are based on a modified perovskite, similar to the ceramic superconductors, and as such have benefited from research in the area of PLD. Ferroelectric properties arise as a consequence of a nonsymmetric crystal lattice structure and the ability of that structure to be polarized in an applied electric field. Both the field-induced and spontaneous (or naturally occurring) polarization can be reversed by an applied field of the opposite polarity. A ferroelectric material will retain that polarization, even after the field is removed. Ferroelectric materials are characterized by a phase-transition temperature (Curie temperature). Below the Curie temperature is the ferroelectric phase. Above the Curie temperature is the nonferroelectric (polarizable but with no retained polarization) paraelectric phase.

Many of the electronic applications for ferroelectric thin films require integration with semiconductor electronics. Low processing temperatures are a desirable feature of the film processing technique. Ferroelectric thin films that have been deposited by PLD are:

- *Perovskites:* $PbTiO_3$, $BaTiO_3$, $PbZr_xTi_{(1-x)}O_3$
- *Nonperovskites:* $KTa_{(1-x)}Nb_xO_3$, $Bi_4Ti_3O_{12}$, $LiNbO_3$

Many of these materials contain volatile components such as lead (Ref 72), potassium (Ref 73), or lithium (Ref 74). These elements present unique problems for obtaining crystalline thin films. The crystallization temperatures (500 to 700 °C) can lead to changes in the film composition because of evaporation of the more volatile components. In spite of large differences between component vapor pressures, high-quality ferroelectric films have been successfully deposited by PLD.

In PLD, stoichiometric evaporation and transfer of the target material does not guarantee a stoichiometric thin film. That is to say, the surface temperatures required to ensure adequate surface mobility may give rise to nonstoichiometric films because of evaporation. One simple solution to this problem has been to overcompensate in the target for volatile species that may be lost from the film (i.e., add excess PbO to the target to minimize the loss of lead from the film) (Ref 75). The technique may work in some cases but is undesirable, because the compensating factors may change depending on the conditions.

It has been observed that in several systems the PLD deposition conditions can be adjusted to compensate for the loss of volatile components at elevated substrate temperatures. It appears that in these systems, higher ambient pressures ($\geq$300 mtorr) minimize the loss of these components. This is probably the result of several factors. Higher gas pressures lead to a reduction in the kinetic energy of the arriving vapor (increasing the sticking coefficient). Higher pressures favor increased oxidation, either in the gas phase or as a result of gas-surface collisions. In the case of lead, it is believed that PbO has a lower equilibrium vapor pressure than lead and is therefore retained at elevated oxygen deposition pressures.

As with HTS materials, single-layer ferroelectric films by themselves are not easily incorporated into a device. The ferroelectric properties of interest arise as a result of electric field effects and as such have presented a unique challenge for their implementation. Electrodes are required that are noninteracting under film growth conditions and that do not degrade the ferroelectric film behavior under repeated cycling. Although noble metals such as platinum or gold are commonly used, the interface between the metal and the ferroelectric film causes the ferroelectric to degrade in time. Oxide conductors such as YBCO (Ref 76), $(La,Sr)CoO_3$ (Ref 77), and $(Sr,Ca)RuO_3$ (Ref 78) are ideally suited for ferroelectric integration. These oxide conductors are lattice-matched perovskites. Multilayer structures have been successfully deposited by PLD that have demonstrated superior characteristics over noble metal structures.

References cited in this section

15. J.T. Cheung and H. Sankur, *CRC Crit. Rev. Solid State Mat. Sci.,* Vol 15, 1988, p 63
56. K.L. Saenger, *Processing of Advance Materials,* Vol 3, 1991, p 1
57. F. Beech and I. Boyd, *Photochemical Processing of Electronic Materials,* I. Boyd and R. Jackman, Ed., Academic Press, 1992, p 389
58. M.K. Wu, J.R. Ashburn, C.T. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Y.Q. Wang, and C.W. Chu, *Phys. Rev. Lett.,* Vol 58, 1987, p 908
59. D.B. Chrisey and A. Inam, *MRS Bull.,* Vol 27,1992, p 37
60. L. Correra, Ed., *High T_cSuperconducting Films,* Elsevier, 1992
61. J.M. Pond, K.R. Carroll, J.S. Horwitz, D.B. Chrisey, M.S. Osofsky, and V.C. Cestone, *Appl. Phys. Lett.,* Vol 59, 1991, p 3033
62. Y. Boikov, G. Brorsson, T. Claeson, and Z.G. Ivanov, *Appl. Phys. Lett.,* Vol 59, 1991, p 2606
63. G. Brorsson, P.A. Nilsson, E. Olsson, S.Z. Wang, T. Claeson, and M. Löfgren, *Appl. Phys. Lett.,* Vol 61, 1992, p 486
64. S.P. Ogale, R.P. Vispute, and R.R. Rao, *Appl. Phys. Lett.,* Vol 57, 1990, p 1805

65. A. Kumar and J. Narayan, *Appl. Phys. Lett.,* Vol 59, 1991, p 1985
66. L. Luo, X.D. Wu, R.C. Dye, R.E. Muenchausen, S.R. Foltyn, Y. Coulter, C.J. Maggiore, and T. Inoue, *Appl. Phys. Lett.,* Vol 59, 1991, p 2043
67. J.T. Cheung, I. Gergis, M. James, and R.E. DeWames, *Appl. Phys. Lett.,* Vol 60, 1992, p 3180
68. J.J. Kingston, F.C. Wellstood, P. Lerch, A. Miklich, and J. Clarke, *Appl. Phys. Lett.,* Vol 56, 1990, p 189
69. C.T. Rogers, A. Inam, M.S. Hedge, B. Dutta, X.D. Wu, and T. Venkatesan, *Appl. Phys. Lett.,* Vol 55, 1989, p 2033
70. S.J. Pennycook, M. Chisholm, D.E. Jesson, D.P. Norton, D.H. Lowndes, R. Fenstra, R. Kerchner, and J.O. Thomson, *Phys. Rev. Lett.,* Vol 67, 1991, p 765
71. R.E. Lenchton and K.S. Grabowski, in *Pulsed Laser Deposition of Thin Films,* D.B. Chrisey and G.K. Hubler, Ed., Wiley,1994, p 473
72. J.S. Horwitz, K.S. Grabowski, D.B. Chriwey, and R.E. Leuchtner, *Appl. Phys. Lett.,* Vol 59, 1991, p 1565
73. S. Yilmaz, T. Venkatesan, and R. Gerhard-Multhaput, *Appl. Phys. Lett.,* Vol 58, 1991, p 2479
74. Y. Shibata, K. Kaya, K. Akashi, M. Kanai, T. Kawai, and S. Kawai, *Appl. Phys. Lett.,* Vol 61, 1992, p 1000
75. G.A. Petersen and J.R. McNeil, *Thin Solid Films,* Vol 220, 1992, p 87
76. R. Ramesh, A. Inam, B. Wilkens, W.K. Chan, T. Sands, J.M. Tarascon, D.K. Fork, T.H. Geballe, J. Evans, and J. Bullington, *Appl. Phys. Lett.,* Vol 59, 1991, p 1782
77. J.T. Cheung, P.E.D. Morgan, D.H. Lowndes, X.-Y. Zheng, and J. Breen, *Appl. Phys. Lett.,* Vol 62, 1993, p 2045
78. C.B. Eom, R.J. Cava, R.M. Fleming, J.M. Phillips, R.B. Van Dover, J.H. Marshall, J.W.P. Hsu, J.J. Krajewski, and W.F. Peck, Jr., *Science,* Vol 258, 1992, p 1766

Film Thickness Measurements Using Optical Techniques

Harland G. Tompkins, Motorola, Inc.

Introduction

MEASURING THE THICKNESS of thin films can be accomplished in many ways, but this article will focus on the optical method of single-wavelength ellipsometry (SWE) and two multiple-wavelength methods of reflectometry and spectroscopic ellipsometry (SE). Single-wavelength ellipsometry and reflectometry are relatively inexpensive methods that excel when a single film on a substrate is to be measured. Single-wavelength ellipsometry is particularly effective for films a few nanometers thick to a few hundred nanometers thick, and reflectometry is particularly effective for films thicker than a few hundred nanometers. Spectroscopic ellipsometry is a more expensive and more complex method that can be readily used with multiple films.

In this article, the general capabilities and principles of ellipsometry and reflectometry are discussed in terms of nondestructive methods for measuring the thickness of thin films. The film thicknesses to be considered will be from a few. nanometers to a few micrometers. Emphasis is placed on the methods that are available commercially rather than methods that require more specialized development.

In their rudimentary form, the initial expenses for purchasing the equipment for SWE and reflectometry are roughly the same. Although SE has been used in research laboratories for over a decade, it has only been used regularly in industry since the early 1990s. The initial cost of SE in its rudimentary form is three or five times that of the other two techniques. Very few users in industry purchase these techniques in their rudimentary form, however, and the additional options can often double or triple the cost.

This article does not discuss methods such as optical microscopy of cross-sectioned samples or the shift of interference fringes at a purposely fabricated step. The thickness of a thin evaporated metal on a microscope slide can be determined by measuring the fraction of transmitted light, after suitable calibration. This requires a special substrate, however; it is not an in-line technique and will not be considered here.

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General Background

A basic requirement for using optical methods for determining the thickness of a film is that the light must be able to reach the bottom of the film and interact with the underlying layer. Transparent materials such as most oxides qualify throughout the above-mentioned thickness range up to a few micrometers. Many semiconductors are nearly transparent and also easily qualify. Metals, however, must be very thin for these optical methods to be applicable.

The intensity change upon reflection for very thin films is quite small. On the other hand, the phase shift differences are significant. For this reason, ellipsometry is one of the most powerful techniques for very thin films. Other traditional thickness measuring techniques such as stylus profilometry and interferometry are ineffective for films thinner than 50 nm. Electrical phenomena. such as eddy currents are sometimes used for thickness measurements of metal films. These techniques require significantly greater calibration efforts, however, and always depend on assumptions wit regard to microstructure.

Ellipsometry and reflectometry basically involve the measurement of changes in phase shift or intensity, respectively, as light reflects from material. Optical properties and film thicknesses of the samples are then calculated based on a chosen model. Regression software is able to determine the thicknesses that give the best fit to within a few angstroms. In many cases, the regression software also gives a "goodness-of-fit" parameter. The "goodness-of-fit" parameter provides a test of the model describing the sample. If the value is outside the acceptable range, then another model may be required. In any event, thickness is not determined directly; the assumption of a model allows calculation of the ellipsometry or reflectometry parameters and subsequent. comparison of calculated values and measured values. Differences between the

results of an analysis and reality are more often due to an oversimplified model than to limitations in the capability of the measuring instrument.

Basic Theory

For general information on electromagnetic waves and optics, the reader should refer to textbooks (Ref 1, 2, 3, 4, 5) and reference books (Ref 6) on the subjects. Some of the salient features that are directly applicable to reflectometry and ellipsometry (Ref 7, 8) are reviewed here.

The electromagnetic wave is a transverse wave consisting of both an electric field vector and a magnetic field vector that are mutually perpendicular and perpendicular to the propagation direction of the wave. The wave can be specified with either the magnetic field vector or the electric field vector. For simplicity, the electric vector only is considered. The light wave can be represented mathematically as a sine wave with amplitude *A*. Waves transport energy, and the amount of energy per second that flows across a unit area perpendicular to the direction of travel is called the *intensity* of the wave and will be denoted as *I*. The intensity, or energy density (Ref 7), is proportional to the square of the amplitude.

Reflection. For a single film on a substrate (Fig. 1), reflections rather than transmission, are the primary concern. As shown in Fig. 1, some of the light is reflected and some passes into the material at the air-to-solid interface. At the second interface, again, some is reflected and some is transmitted. The various rays that leave the material from the top surface combine to make the outgoing wave. For reflectometry, the ratio of the intensity of the outgoing wave to the intensity of the incoming wave is measured. Reflectometry measurements are often made at normal (perpendicular) incidence. The various rays give constructive or destructive interference, depending on the wavelength of the light, the thickness of the film, and the optical properties of the various materials. For the reflectometry technique, one measures the reflected intensity versus the wavelength of light to deduce the film thickness.

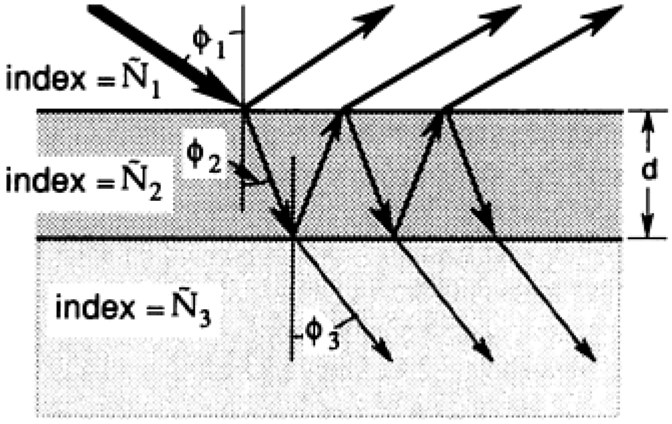

Fig. 1 Schematic of light reflected and transmitted at film interfaces. The outgoing beam is a combination of all of the rays emerging from film from the top interface. Each material is characterized by the index of refraction N_1. The thickness of the film is *d*. Source: Ref 8

For ellipsometry, the measured parameter is the ratio of the wave amplitude parallel to the plane of incidence versus the wave amplitude perpendicular to the plane of incidence. The reflection process also causes a phase shift between these two waves, and this phase shift is measured during ellipsometry. The amplitude ratios and phase shifts are functions of the wavelength, thickness, optical properties of the various materials, and angle of incidence.

Polarized Light. Most light sources emit unpolarized light, or light with electric-field components oriented in all possible directions perpendicular to the direction of travel. If all the photons in a light beam have the electric field oriented in one direction, the light is referred to as *polarized light* or, more completely, *linearly polarized light.* Some light sources emit polarized light. In addition, one can obtain polarized light by passing the light beam through an optical element or by causing the beam to make a reflection under some specific conditions.

Figure 2(a) illustrates two light beams with the same frequency moving along the same path, one polarized in the vertical plane and the other polarized perpendicular to the vertical plane. In this case, the maxima of the two beams coincide (i.e.,

the phase is the same). These two beams can be combined to give a resultant light beam that is also linearly polarized. The key point here is that *when two linearly polarized waves with the same wavelength (or frequency) are combined in phase, the resultant wave is linearly polarized and lies in a plane*.

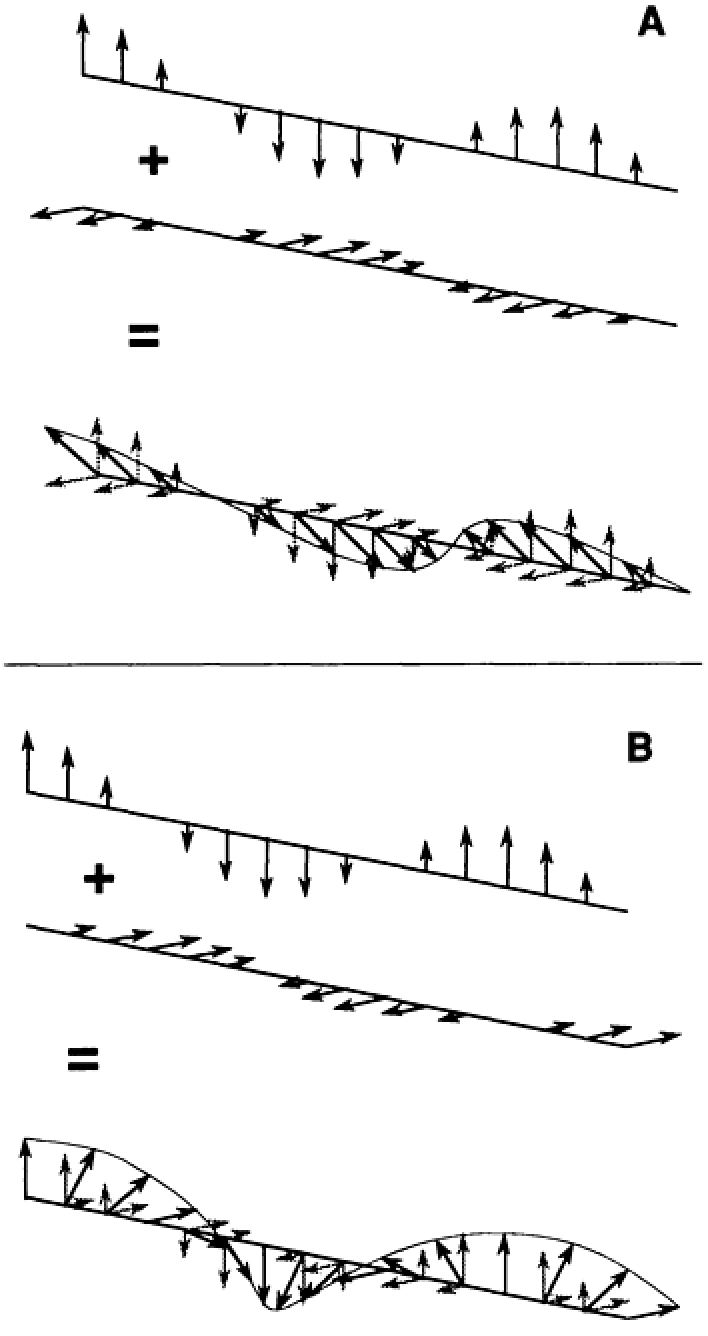

Fig. 2 Linear and elliptical polarization. (a) If two linearly polarized light beams that are in phase are combined, the resultant light beam is linearly polarized. (b) If two linearly polarized light beams that are out of phase are combined, the resultant light beam is elliptically polarized. In this particular example, they are out of phase by 90°. Because the amplitudes are equal, the resultant beam is circularly polarized. Source: Ref 8

Figure 2(b) shows two beams where the maxima do not coincide, but are out of phase. When these two waves are combined, the tips of the arrows do not move back and forth in a plane as in the previous example. This is, in general, elliptically polarized light. The key point is that *when two linearly polarized waves with the same wavelength (or frequency) are combined out of phase, the resultant wave is elliptically polarized or spiraling in three-dimensional space*.

In ellipsometry the important fact is that when linearly polarized light makes a reflection on a metal surface, there is a shift in the phases of both the components (parallel and perpendicular to the plane of incidence). For non-normal incidence, the shift is, in general, not the same for both components, and hence the resultant light will be elliptically polarized. The induced amount of elliptical polarization depends on various factors including the optical properties of the substrate as well as the thickness and optical properties of overlying films. From this concept of elliptical polarization, the term *ellipsometry* takes its name for the measurement of induced ellipticity.

The Complex Index of Refraction. When light passes from one medium (e.g., ordinary room air) into another medium that is not totally transparent (Fig. 1), several phenomena occur at the interface. Some of the light is reflected back and does not enter the second medium, while an unreflected component enters the second medium. The unreflected component will be considered first.

The parameter used to describe the interaction of light with the material is the complex index of refraction, *N*, which is a combination of a real part and an imaginary part and is given as

$$N = n - jk \qquad \textbf{(Eq 1)}$$

where *n* is also called the *index of refraction* (sometimes leading to confusion), *k* is called the *extinction coefficient,* and j is the imaginary number $\sqrt{-1}$.

For a dielectric material such as glass, none of the light is absorbed and $k = 0$. In this case, only *n* is being considered. Both *n* and *k* are functions of the wavelength. It is not uncommon for a material to have $k = 0$ for a range of wavelengths and $k \neq 0$ for another wavelength range.

The index of refraction *n* is defined to be:

$$n = c/v \qquad \textbf{(Eq 2)}$$

where *c* and *v* are the velocities of light in free space and in the material, respectively.

The extinction coefficient *k* is a measure of how rapidly the light is absorbed as a function of depth in the material. A transparent material such as glass has an extinction coefficient of zero. Metals typically have values ranging from $k = 2$ to about $k = 6$.

Dispersion. It should be noted that *n* and *k* are not simple constants for a given medium, but are in fact functions of the wavelength, λ. This is the reason that white light entering a prism emerges with the various colors separated.

The term *dispersion* is used to describe the way in which the optical constants change with wavelength. Figure 3 shows how *n* and *k* vary for a metal such as nickel and for a dielectric such as silicon nitride (Ref 9). The index of refraction *n*, for both materials, is near 2 for the entire range of wavelength. From an optical point of view, the quantity that differentiates these two materials is not *n*, but *k*. In a material with $k \neq 0$, the intensity of light *I* decreases as a function of distance into the material. The functional form is:

$$I/I_0 = \exp(-\alpha z)$$

where *z* is the distance into the material and α is the absorption coefficient (related to the extinction coefficient, *k*). Because the intensity continuously decreases, the concept of how far the light goes into the material has no meaning. Instead, to illustrate penetration, the distance *z* is used where the quantity αz is equal to unity and $I/I_0 = \exp(-1) \approx 0.37$.

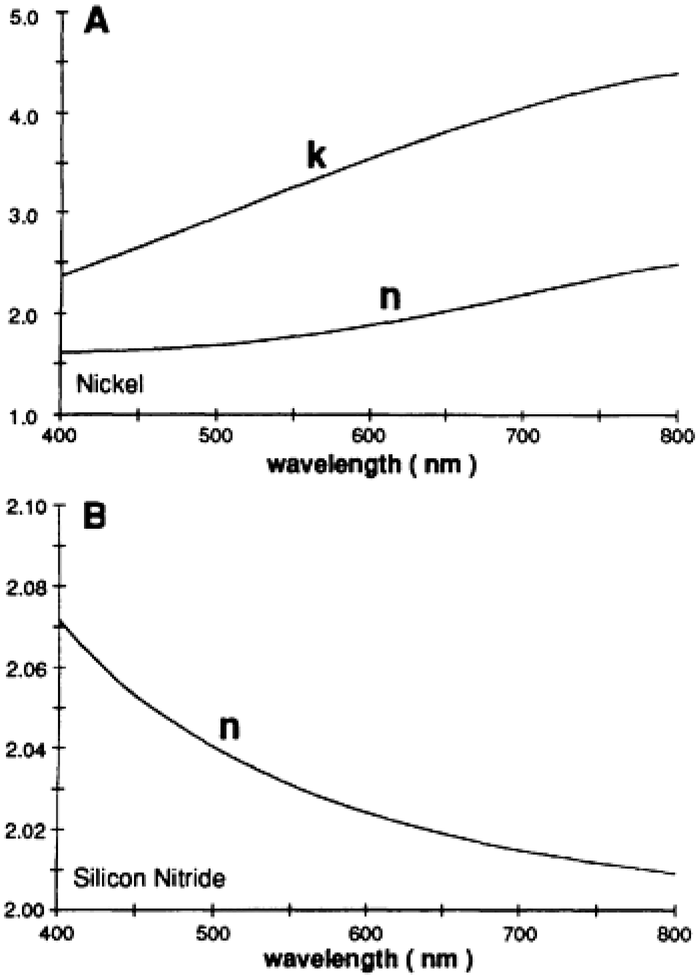

Fig. 3 Optical constants for (a) nickel and (b) silicon nitride. The value of *k* for silicon nitride is zero in the wavelength range shown. Source: Ref 9

Nickel has a value of *k* that is greater than 2 for the entire range. The thickness where the intensity drops to 37% is about 13 nm. For thicknesses three times this value, or about 40 nm, the material is essentially opaque. For silicon nitride, the value of *k* is zero for the entire range. This material is transparent.

References cited in this section

1. F.A. Jenkins and H.E. White, *Fundamentals of Optics,* 3rd ed., McGraw-Hill, 1957
2. J. Morgan, *Geometrical and Physical Optics,* McGraw-Hill, 1953
3. F.W. Sears, *Optics,* Addison-Wesley, 1958
4. M.V. Klein, *Optics,* John Wiley, 1970
5. G.S. Monk, *Light,* Dover, 1963
6. M. Born and E. Wolf, *Principles of Optics,* 4th ed., Pergamon Press, 1969
7. R.M.A. Azzam and N.M. Bashara, *Ellipsometry and Polarized Light,* North Holland Publishing Co., 1977
8. H.G. Tompkins, *A User's Guide to Ellipsometry,* Academic Press, 1993
9. E.D. Palik, Ed., *Handbook of Optical Constants of Solids,* Academic Press, 1985; E.D. Palik, Ed., *Handbook of Optical Constants of Solids II,* Academic Press, 1991

Single-Wavelength Ellipsometry (SWE)

Ellipsometry was first practiced by Paul Drude (Ref 10) just prior to 1890. The name *ellipsometry* was introduced by A. Rothen (Ref 11) in 1945. Clearly, this is not a recently developed technique. Ellipsometry uses monochromatic light, optical elements that change the polarization state of the light, some sort of detector, and some calculation facilities. Although rudimentary forms of these requirements have been present throughout this century, the development of the photomultiplier, the laser, and the desktop computer have greatly enhanced the use of this technique to the point that it is now routinely used as a metrology tool in semiconductor wafer manufacturing.

Instrumentation. Figure 4 shows the basic requirements for SWE. The figure shows the arrangement of a manual null ellipsometer. The source generates monochromatic light, and the polarizer passes only light that is polarized in a particular direction. The quarter-wave plate (QWP) then converts the light to elliptically polarized light. If the polarizer and QWP are positioned correctly, the ellipticity is reversed by the reflection, giving linearly polarized light. The analyzer nulls out the light so that the intensity at the detector is zero. The optical elements used for the polarizer and analyzer are both polarizers. The terminology describes function, in that it is the function of the element called *polarizer* to cause the light to be polarized, and it is the function of the *analyzer* to determine the polarization state of the light.

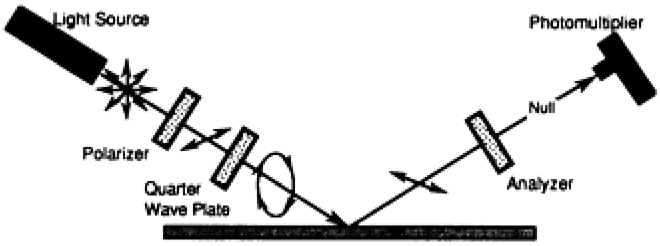

Fig. 4 Schematic of manual null ellipsometer. The quarter-wave plate is fixed at either ± 45° and the polarizer and analyzer are rotated to find the null. The positions of the polarizer and analyzer are then used to calculate the ellipsometric parameters *Del* and *Psi.* Source: Ref 8

Operation of this instrument requires iterative adjustment of the polarizer and the analyzer until the null positions are located. The angular position of the polarizer and analyzer are then used to calculate the ellipsometric parameters, *Del* and *Psi. Del* is the reflection-induced phase shift between the waves that are perpendicular and parallel to the plane of incidence, and *tan* (*Psi*) is the amplitude attenuation ratio of the parallel wave to the perpendicular wave.

Although the manual null instrument illustrates the concepts reasonably well, most commercial instruments are rotating-element instruments. In some cases, the polarizer and analyzer are rotated by the instrument, under microprocessor control, until null is found. In other cases, only the analyzer is rotated, and *Del* and *Psi* are calculated from photometric measurements, rather than null positions.

Analysis of Films. Regardless of whether the measurement is made with a manual null instrument, a rotating-element null instrument, or a rotating-element photometric instrument, the parameters that an ellipsometer measures are *Del* and *Psi.* For a film-free surface (a substrate), *Del* and *Psi* can be converted to the values of the optical constants for the substrate material, $N = n - jk$. The value of *Del* for a substrate will be between zero and 180° and the value of *Psi* will be between zero and 45°. In Fig. 5, the film-free value of *Del*/*Psi* for silicon is about 178°/10.5°. If a dielectric film (i.e., $k = 0$) with index $N = 1.46$ is added, the location of the *Del*/*Psi* joint begins to change on the *Del*/*Psi* domain. When the film thickness is 20 nm, the *Del*/*Psi* location is about 129.9°/13.7°. As the thickness increases, the *Del*/*Psi* trajectory is traced out until the value of thickness reaches the period thickness. At this thickness, the *Del*/*Psi* point has returned to the film-free location. For added thicknesses, the *Del*/*Psi* point simply retraces the trajectory. For the particular example given in the figure, the period thickness is 283.2 nm.

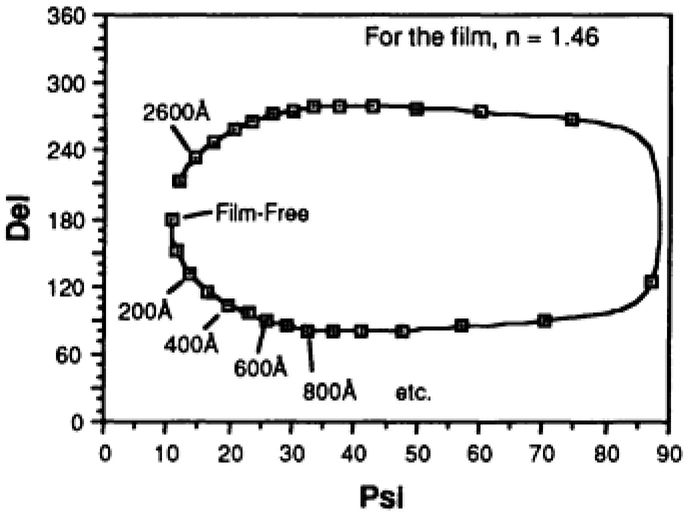

Fig. 5 The *Del/Psi* trajectory for silicon dioxide on silicon with angle of incidence of 70° and wavelength of 632.8 nm. Source: Ref 8

The physics and mathematics for converting ellipsometric measurements to optical constants and film thicknesses are beyond the scope of this article. The reader should refer to books by Azzam and Bashara (Ref 7) and Tompkins (Ref 8) for details. The important point to remember is that the technique relies on differences in phase shift and reflectance for the two directions of polarization, and on changes in these differences as a function of film thickness.

The trajectory that is traced out depends on the index of refraction of the film. Figure 6 shows the first part of trajectories for films on silicon, with *n* values 1.46, 1.6, 1.8, and 2.0. If an unknown film were measured and the resulting values of *Del*/*Psi* were 70.0°/28.9°, it could be determined by inspection from Fig. 6 that the *Del*/*Psi* point falls on the *n* = 1.8 trajectory, and the position on this trajectory indicates that the thickness is 60 nm. Although the calculations to plot these trajectories can be made (Ref 8), normally the microprocessor in the ellipsometer makes the calculations and provides the values of *n* and thickness. This has led to the common misconception that ellipsometers measure the index of refraction and thickness. In fact, ellipsometers measure *Del*and *Psi*, and the values of *n* and thickness are calculated based on a model. The model is implicitly chosen when the program on the microprocessor is chosen (e.g., single film or substrate).

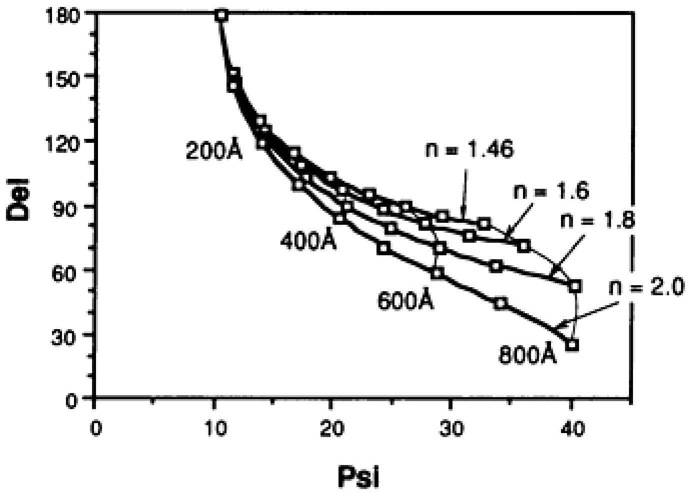

Fig. 6 The *Del/Psi* trajectories for films with several different indices of refraction on single crystal silicon substrates. The first 80 nm is shown. Source: Ref 8

Because of the periodicity, the resulting thickness value is not unique. A *Del*/*Psi* point of 129.9°/13.7° could represent a film 20 nm thick, 283.2 + 20 nm thick, 2 × 283.2 + 20 nm thick, and so on. In many cases, other processing information can be used to deal with this matter. The deposition or film formation rate can often be used to estimate the film thickness to well within one period thickness. For a totally unknown film, however, other methods must be used. The period thickness depends on the index of refraction of the film, the angle of incidence, and the wavelength of light being used. By using another wavelength of light or another angle of incidence, the question of period can often be resolved. If unknown film stacks are routinely encountered, spectroscopic ellipsometry might be a more appropriate technique.

For non-dielectric films, the *Del*/*Psi* trajectory does not close on itself. An example is shown in Fig. 7. Conceptually, with no film present, the *Del*/*Psi* point represents the substrate. When there is a thick film of an opaque material present, the *Del*/*Psi* point will represent a substrate of the film material. The *Del*/*Psi* trajectory during film growth is simply the movement of the *Del*/*Psi* point between the location for the original substrate to the location for a substrate of the film material. In Fig. 7 the growth of a tungsten film on silicon is shown. As long as the film is thin enough that light reaches the silicon substrate, ellipsometry can be used for film thickness measurements. For tungsten, the method could be used for films up to about 20 nm thick. Beyond that, the points are too close together for the method to be useful.

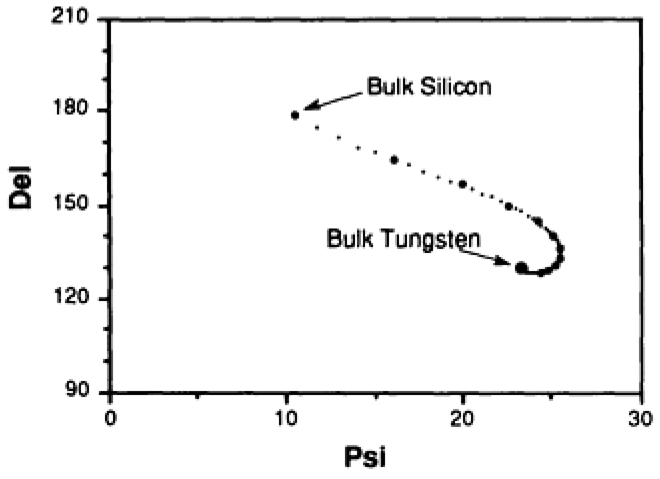

Fig. 7 The *Del*/*Psi* trajectory when a film of tungsten is deposited onto silicon. The small dots are at 1 nm intervals. The large dots are at 5 nm intervals from zero thickness. Source: Ref 8

Areas of Applicability. Ellipsometers can measure *Del*/*Psi* to a few hundredths of a degree. A change in film thickness (with n = 2.0) of 0.1 nm represents about 0.25° in *Del.* This technique therefore can be used to measure monolayer changes. This is a particularly powerful technique in the thickness range from about 1 nm to a few hundred nanometers. When the thickness is greater than several period thicknesses, other techniques such as reflectometry may be more appropriate for thickness measurements. Even in this case, however, ellipsometry may be used to provide index of refraction information for the reflectometry instrument.

When multiple films are present, information about the top film can be determined if information is available for all of the underlying films. In metrology situations, this is often the case, but for totally unknown films, other methods normally must be used.

References cited in this section

7. R.M.A. Azzam and N.M. Bashara, *Ellipsometry and Polarized Light,* North Holland Publishing Co., 1977

8. H.G. Tompkins, *A User's Guide to Ellipsometry,* Academic Press, 1993

10. P. Drude, *Wied. Ann.,* Vol 36, 1889, p 532, 865; Vol 39, 1890, p 31

11. A. Rothen, *Rev. Sci. Instruments,* Vol 16, 1945, p 26

Reflectometry

Reflectometry is normally done at normal incidence and is simply the measure of the ratio of the intensity of the reflected light to the intensity of the incident light (Ref 12). This is usually done at various wavelengths over the visible, ultraviolet, and/or infrared region. Figure 8 shows the schematic setup of a typical instrument used for this measurement. Measurements are often made on patterned wafers, hence it is necessary to have an image detector for proper positioning of the sample. The diffraction grating separates the light into its various wavelengths. As this is rotated, the photometric detector is used to measure the reflectance spectrum.

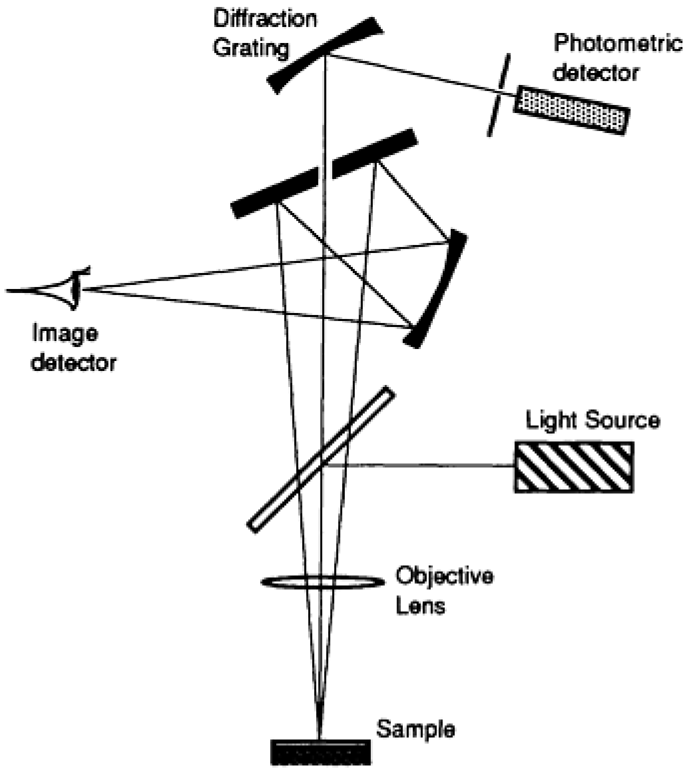

Fig. 8 Schematic of reflectance instrument

Rudimentary instruments scan between about 400 and 800 nm and contain the software to determine film thickness for several specific film/substrate materials (with the optical constants included in the software). More advanced instruments allow the introduction of other values for the indices of refraction and give plots of the calculated spectrum versus the measured spectrum. Other advanced features include regression analysis of thicknesses and optical constants for multiple films and extended wavelength ranges.

Spectral Interpretation. The equipment is basically an interferometer that scans wavelength for a fixed interference path rather than scanning distance at a fixed wavelength. The technique relies on interference between light reflected from the film and light reflected from substrate surfaces. Figure 9 shows a generic reflectance spectrum. When the wavelength/film thickness ratio is large, no interference occurs. As the wavelength/film thickness ratio decreases, the first order minimum is approached. Here, light reflecting from the lower interface destructively interferes with light reflecting from the upper interface and gives a minimum in intensity. As the wavelength/film thickness ratio decreases further, constructive interference causes the first order maximum to be reached. Further decreases in the wavelength/film thickness ratio cause the intensity to pass successively through various minima and maxima. Figure 9 can be described as a generic reflectance spectrum that shows interference phenomena but does not include the influence of dispersion of the index of refraction of either the film or the substrate. What is shown is a rather wide range in wavelength/film thickness. In an actual measurement, only a part of the entire spectrum would be observed because the wavelength range of available instruments is limited.

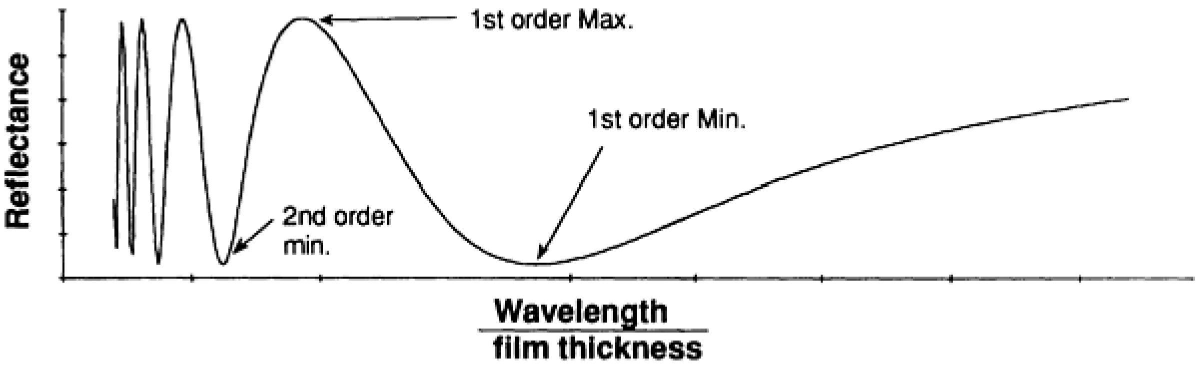

Fig. 9 Generic interferogram plotting reflectance vs. the wavelength/film thickness ratio. Optical constant dispersion is ignored. Note that for a finite wavelength range, a given instrument will not measure the entire interferogram

Moving from the generic to the specific, Fig. 10 shows calculated reflectance spectra for a Si_3N_4 film on a nickel substrate. In Fig. 10(a) the film thickness is 2 μm and in Fig. 10(b) the film thickness is 0.2 μm. Note that there are many maxima and minima in the spectrum from the thicker film. Some instruments simply determine where the maxima and minima occur and use this information for calculating the film thickness. When there are insufficient numbers of maxima and minima for this method (e.g., as in Fig. 10b), curve fitting is used to determine the film thickness. In some instruments, curve fitting is used for all thicknesses. In still other instruments, the reflectances at predetermined wavelengths are used in a lookup table. When the film thickness is below a few tens of nanometers, the curve shapes are insignificantly different from each other, and spectral reflectometry is insufficient for film thickness measurements.

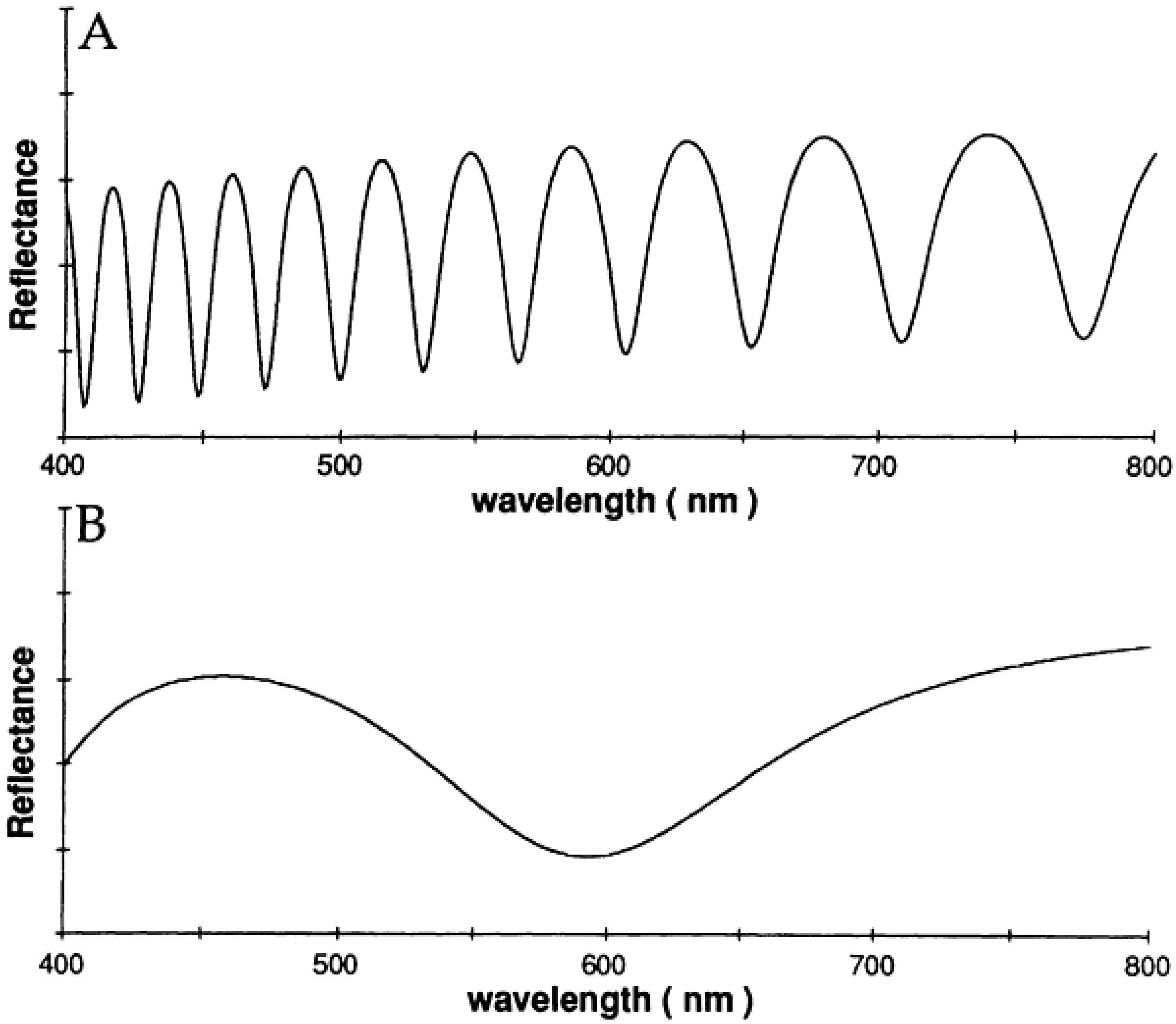

Fig. 10 Interferogram for Si_3N_4 on nickel. (a) The film thickness is 2 μm. Note that there are many maxima and minima in the wavelength range. (b) The film thickness is 0.2 μm. Note that there are only one maximum and one minimum in the wavelength range.

Applicability. The uncertainty due to periodicity found in SWE is not present in reflectometry. The method works best when the optical constants of both the film and the substrate are known and the only quantity to be determined is the film thickness. It is particularly appropriate for films thicker than several hundred nanometers. Some of the latest models make it possible to determine material constants for materials not preprogrammed into the software.

Reference cited in this section

12. Mark Keefer, Prometrix Corp., private communication

Spectroscopic Ellipsometry

Contrasted to SWE and Reflectometry. Both SWE and reflectometry excel when the sample of interest is a single film on a substrate. For samples with two layers on a substrate, both SWE and reflectometry can be used if many of the optical parameters are known, with only a few to be determined. These are special cases, however. Spectroscopic ellipsometry, on the other hand, is designed specifically to be used with multiple layers (Ref 13).

The function of the SE instrument, like that of the SWE instrument, is to measure the ellipsometric parameters. The primary difference is that for SE, the measurements must be made at many wavelengths. Because a QWP used in SWE is specific to a given wavelength, it cannot conveniently be used for SE. In addition, the light source gives out radiation with

all of the wavelengths of interest, and they are sampled one at a time by using a monochromator. Because many measurements must be made for a single spectrum, the photometric method is used rather than the null method, because it is faster. For rotating-element instruments without QWPs, the quantities measured are *tan*(ψ) and *cos*(Δ) rather than ψ and Δ as in SWE.

Multilayer Example. As an example of the use of SE, Fig. 11 shows the SIMOX structure (Ref 14, 15, 16, 17, 18). This structure is fabricated by implanting oxygen into silicon and then annealing the structure at temperatures above 1200 °C (2200 °F). The anneal helps segregate the implanted oxygen into a well-defined oxide layer and reduces defectivity in the layers. The top silicon retains its crystallinity due to elevated sample temperatures during the implant. One side effect is the formation of the silicon nodules shown near the bottom of the oxide. Any oxide formed on the top silicon layer during the anneal is removed as a final processing step. The usual native oxide then forms upon exposure to the atmosphere.

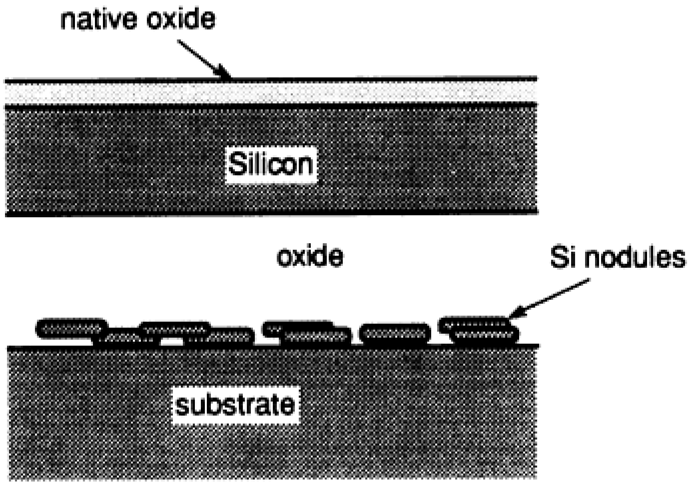

Fig. 11 Film structure formed by implanting silicon with oxygen (SIMOX structure) and then annealing at a temperature greater than 1200 °C (2200 °F)

Analysis with SE consists of measuring the parameters *tan*(ψ) and *cos*(Δ) for the wavelengths of interest and then determining the thicknesses and optical constants of all the layers by regression analysis. In many cases, the optical constants are known and preprogrammed into the analysis software. Figure 12 shows the SE spectra along with the best regression fit when the nodule layer is ignored and the sample is modeled as silicon wafer/oxide/silicon/native oxide.

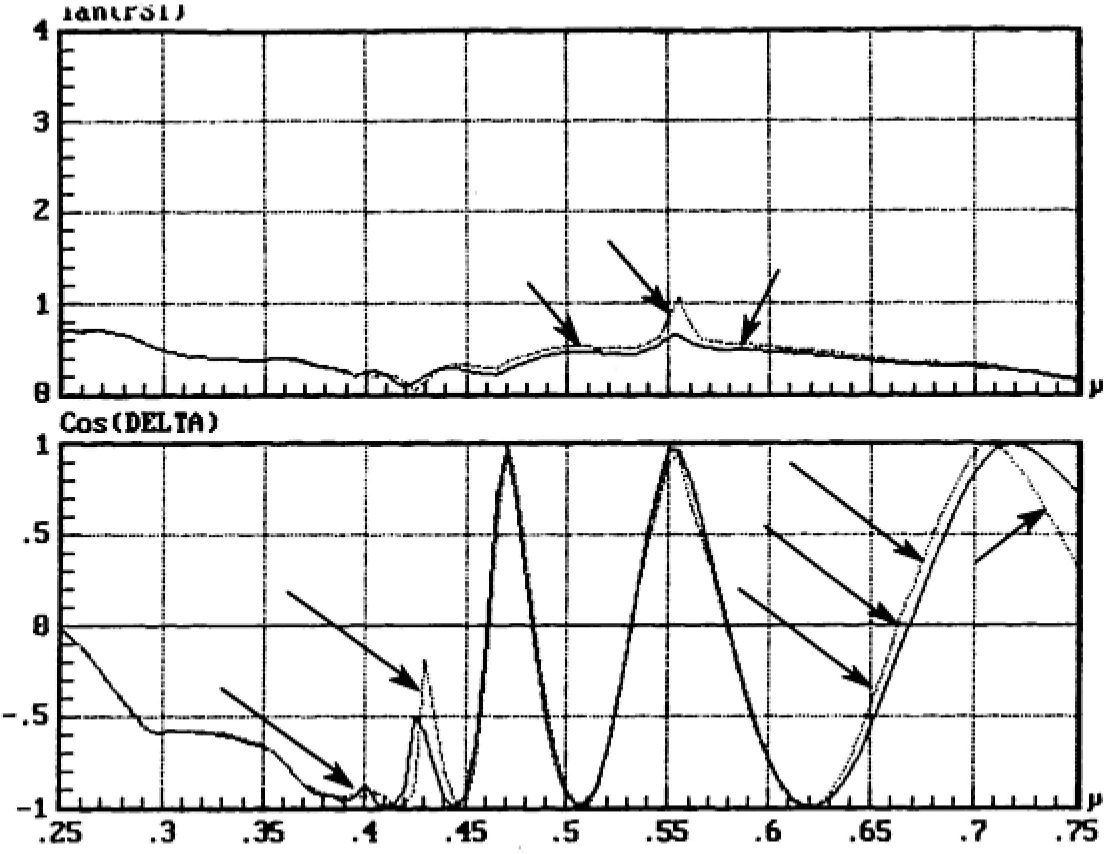

Fig. 12 The measured spectroscopic values for a SIMOX sample along with the calculated values using a model that ignores the silicon nodules. The arrows indicate regions of serious lack of fit.

For this fit, the thicknesses are 360.1, 211.2, and 1.8 nm for the oxide, silicon, and native oxide, respectively. Although the regression analysis curve matches the measured curve in many places, there are several locations where the misfit is noticeable, and these are indicated by arrows.

To improve the fit, the oxide can be modeled as two layers. The top layer is simply the oxide, and the bottom layer (to deal with the nodules) is a mixture of oxide and silicon. The concentration of the silicon in the mixture is one of the quantities to be determined, along with the thicknesses of the various layers. Figure 13 shows the regression fit best for this model, showing that the fit has been improved. Goodness of fit is measured by comparing the calculated curve to the measured curve and is significantly better for the curve shown in Fig. 13 than in Fig. 12. The thicknesses of the layers with this model are 32.9, 325.2, 210.9, and 1.8 nm for the mixture, oxide, silicon, and native oxide, respectively. The concentration of the silicon in the bottom oxide layer is 46%.

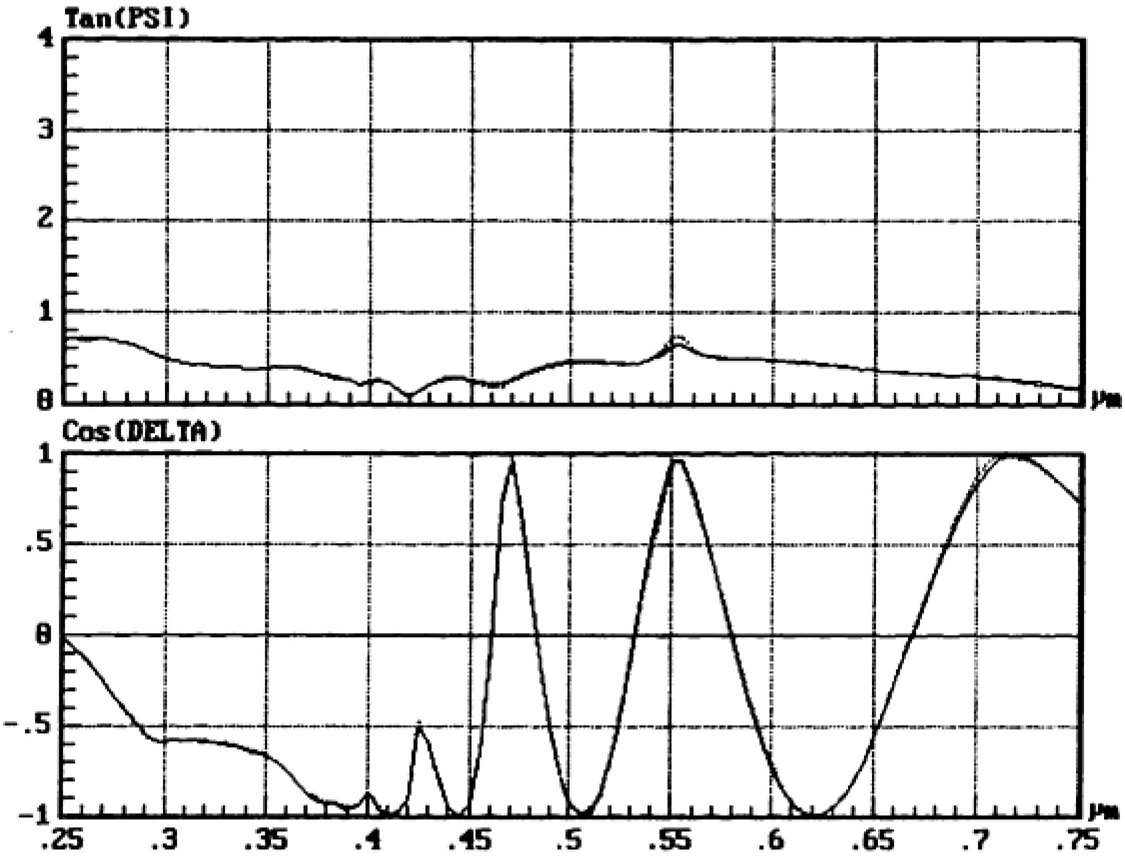

Fig. 13 The measured spectroscopic values for a SIMOX sample along with the calculated values using a model that includes a layer of a "mixture" consisting of oxide and silicon

Applicability. Spectroscopic ellipsometry can be used to measure layers in thicknesses ranging from a few nanometers to a few micrometers. The optical constants of many materials make them opaque in part of the spectral region and transparent in other parts of the spectrum. This feature can be used to advantage to distinguish between top layers and underlying layers. The most important feature of SE is that multilayers can readily be measured.

References cited in this section

13. W. Henderson, SOPRA, Inc. and John Woollam, J.A. Woollam Co., private communication
14. J. Vanhellemont, H.E. Maes, and A. DeVeirman, *J. Appl. Phys.,* Vol 65, 1989, p 4454
15. C. Pickering, S. Sharma, A.G. Morpeth, J.M. Keen, and A.M. Hodge, *Proc. 4th International Symposium on SOI Technology and Devices,* Vol 90-6, D. Schnidt, Ed., The Electrochemical Society, 1990, p 175
16. P.H. Chang and B.Y. Mao, *Appl. Phys. Lett.,* Vol 50, 1987, p 152
17. F. Ferrieu, D.P. Vu, C. D'Anterroches, J.C. Oberlin, S. Maillet, and J.J. Grob, *J. Appl. Phys.,* Vol 62, 1987, p 3458
18. S. Lynch, G.M. Crean, R. Greef, and J. Stoemonos, *Appl. Surface Sci.,* Vol 63, 1993, p 40

Corrosion Testing of Coatings

Hermann A. Jehn and Andreas Zielonka, Research Institute for Precious Metals and Metals Chemistry

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Introduction

CORROSION, according to the *ASM Materials Engineering Dictionary*, is "the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties." Because corrosion is related to the material and its environment, it occurs under an immense variety of conditions. The environment includes not only the gas atmospheres or liquid media in their actual composition surrounding the piece, but also temperature and its changes and specific conditions of flow. This means that corrosion is a materials behavior in a specific environment.

Increasingly, corrosion resistance must be provided even by decorative coatings and those used for wear resistance. Numerous corrosion protection techniques have been developed (e.g., conversion coatings, organic coatings, and metallic thin and thick films). These techniques introduce a new system property, the coating-substrate behavior. The major requirements for good corrosion protection are high corrosion resistance of the coating material, a pore-free structure, and good adhesion. Additionally, production costs play an important role in the selection of a coating-substrate for a given problem.

This article discusses the testing and typical corrosion behavior of coating-substrate systems in aqueous solutions and humid aggressive atmospheres. There is a short review of the fundamentals of corrosion, followed by discussion of specific system behavior, electrochemical and laboratory accelerated tests, and simulated service tests. Finally, the article gives examples of types of corrosion damage and guidelines for improving corrosion resistance by coatings. A more detailed description of general corrosion phenomena, corrosion testing and evaluation, corrosion protection, corrosion of specific alloy systems, and corrosion in specific industries and environments is given in *Corrosion*, Volume 13 of the *ASM Handbook* (Ref 1), as well as in other review books and articles (Ref 2, 3, 4, 5). The behavior of nitride hard coatings deposited by physical vapor deposition or chemical vapor deposition is summarized in Ref 6.

References

1. *Corrosion,* Vol 13, *ASM Handbook,* ASM International, 1987
2. *Corrosion and Metal Finishing,* John Wiley & Sons, 1987
3. J.O.M Bockris and A.K.N. Reddy, *Modern Electrochemistry,* Plenum Press, 1970
4. W.H. Ailor, Ed., *Handbook on Corrosion Testing and Evaluation,* John Wiley & Sons, 1971
5. F. Walsh, G. Ottewill, and D. Barker, Corrosion and Protection of Metals, Part I: The Origin and Rate of Corrosion and Part II: Types of Corrosion and Protection Methods, *Trans. Inst. Metal Finish.,* Vol 71 (No. 3), 1993, p 113, 117
6. H.A. Jehn, I. Pfeifer-Schäller, and M.E. Baumgärtner, Korrosion von Hartstoffschichten, Teil 3: Elektrochemische Korrosionsuntersuchungen an Dekorativen Hartstoffschichten, *Galvanotechnik,* Vol 84 (No. 12), 1993, p 4059-4064

Fundamentals of Corrosion of Coating-Substrate Systems

Corrosion Processes. Corrosion is based on the reaction of a metallic material or layer with its environment. The metal atoms of a component change from the metallic state into an oxidized state. The products may be dissolved species or solid corrosion products. The driving force of this process is the tendency of the system to lower its free energy.

Corrosion in aqueous media is a surface reaction that takes place as an electrochemical process. In terms of electrochemistry, the metal and the corrosive medium are the electrode and the electrolyte, respectively. The electrolyte is conductive due to the presence of dissolved cations and anions. Hence, the corrosion reaction is a closed electrical circuit in which the current is based on the electrical conductivity of the metal on one hand, and on the ionic conductivity of the electrolyte on the other hand. Corrosion results from a direct electrical contact between the metal and the electrolyte. In the case of the formation of a nonconducting, pinhole-free surface layer (e.g., aluminum oxide on aluminum), no corrosion current is possible.

This type of corrosion involves at least two or more separate electrochemical reactions that take place simultaneously. The transfer of a metal atom into a metal forms free electrons, which leads to the reduction of the corresponding oxidant. The deciding factor governing the corrosion reaction is the electrochemical equilibrium between the metallic surface and the aqueous corrosive medium in contact with it. This equilibrium is influenced by which materials are in contact and the activity of the reacting species.

In the case of a very low metal ion concentration in the electrolyte, the corrosion current is anodic to its major part (i.e., the metal is corroded by its dissolution in the electrolyte). Under closed-system conditions, the current exists only as long as the system has not reached its equilibrium state. In the dynamic equilibrium the sum of the anodic and cathodic currents becomes zero (i.e., the rate of metal dissolution equals the rate of metal deposition), and no loss of mass can be observed any longer by microscopy. In practice, the equilibrium state is normally never reached, so corrosion proceeds continuously.

The standard electrochemical potential of metals is defined as the potential in the equilibrium state. The measurement of the electrode potential is only possible relative to that of a second electrode, so all potentials are related to the potential of a standard hydrogen electrode, which is by definition set to zero as reference. Standard potentials can be listed for all metals and for specific electrochemical reactions. Table 1 shows the standard potentials of selected metals. Additionally, potentials are listed for these metals under different conditions. As can be seen, the order of the different metals changes. For corrosion processes, such tables indicate which metal of a pair in contact is more noble or less noble. Factors influencing the actual potential values are temperature, concentration of the electrolyte, and alloy composition of the metal.

Table 1 Electrochemical potential of selected metals under three different conditions

Metal	**Potential, mV**
Versus standard hydrogen electrode	
Gold	+1360
Silver	+800
Copper	+350
Hydrogen	0
Tin	-140
Nickel	-230
Iron	-440
Chromium	-560
Zinc	-760
Aluminum	-1670
In artificial seawater [(a)]	
Gold	+243

Silver	+149
Nickel	+46
Copper	+10
Chromium	-290
Iron	-450
Aluminum	-670
Zinc	-800
In water [(b)]	
Gold	+306
Silver	+194
Copper	+140
Nickel	+118
Aluminum	-169
Chromium	-249
Tin	-275
Iron	-400
Zinc	-790

(a) pH 7.5, 1 bar (DIN 50907).

(b) pH 6, 1 bar

In practice, where different metals are present as alloy components or in coating-substrate systems, the different electrochemical reactions take place simultaneously, resulting in a mixed or galvanic couple potential. The corrosion behavior of a specific system is determined by the relation of the respective metals in contact. Furthermore,

environmental conditions such as pH value, temperature, concentration of the electrolyte, and the hydrodynamic conditions at the electrode affect the actual behavior (Ref 1, 2, 3, 4).

Corrosion of Coating-Substrate Systems. In principle, the corrosion behavior of a coated part (i.e., a coating-substrate system) is determined by the corrosion resistance of the coating material in the respective medium. However, this holds only for absolutely dense coatings that completely separate the aqueous corrosive medium from the underlying substrate material. In practice, coatings and thin films show pores, pinholes, and other defects after their deposition, or they may be damaged by scratches or other wear mechanisms. Both types of defects allow the corrosive medium to contact the substrate material or the interlayers and underlayers.

Depending on the materials combination, the coating material is either *more* noble or *less* noble than the substrate material. The behavior of the two adjacent layers and the interlayers can be characterized in the same way. The relative corrosion behavior depends on the corrosion medium and the specific conditions. Their order can vary markedly, as shown in Table 1.

The electrochemical reactions are schematically illustrated in Fig. 1. In the case of a more noble coating (Fig. 1a), the corrosion medium reaches the substrate material, and a galvanic cell is formed between the anodic substrate material and the cathodic coating material. This results in strong local corrosion of the substrate. The anodic metal ion current density is rather high because of its very small surface area, whereas the cathodic H^+ discharging or oxygen reduction takes place over the entire coating surface. This explains why defects can be so detrimental. If a system cannot be deposited without defects, a fine and homogeneous distribution of them reduces local corrosion. This explains why the well-known microcrack network is used in electrolytic chromium plating.

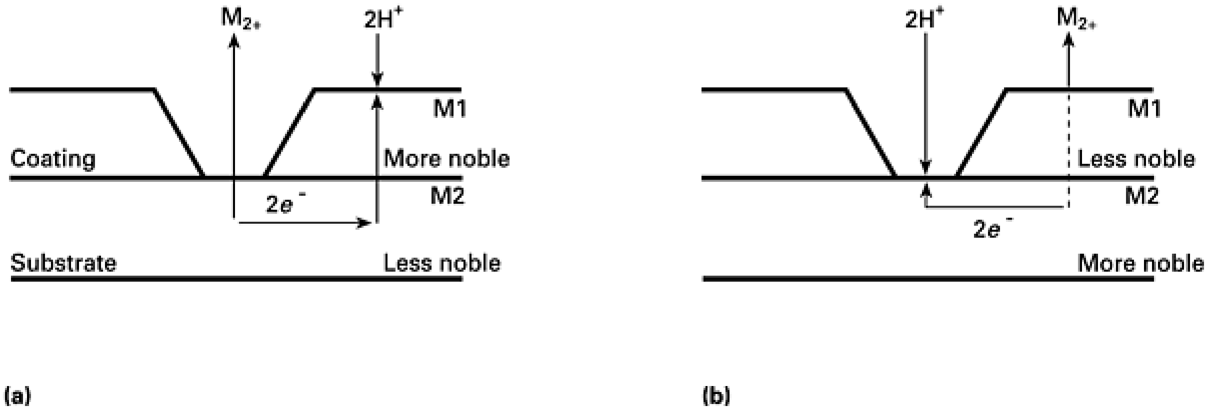

Fig. 1 Schematic illustration of corrosion of coating substrate systems in the presence of pores. M, metal. (a) More noble coating on less noble substrate (galvanic corrosion). Increased corrosion of substrate material, small anodic area, large cathodic area. (b) Less noble coating on more noble substrate (anodic corrosion). Cathodic protection of substrate material, coating material dissolved, large anodic area, small cathodic area

In the case of a less noble coating material (Fig. 1b), anodic protection of the substrate is observed. The anodically polarized coating is uniformly dissolved, and in general the relatively small cathodic area yields a low rate of corrosion.

Figure 2 schematically illustrates some typical examples of corroded coating-substrate systems, demonstrating the system effects in the corrosion performance of a part.

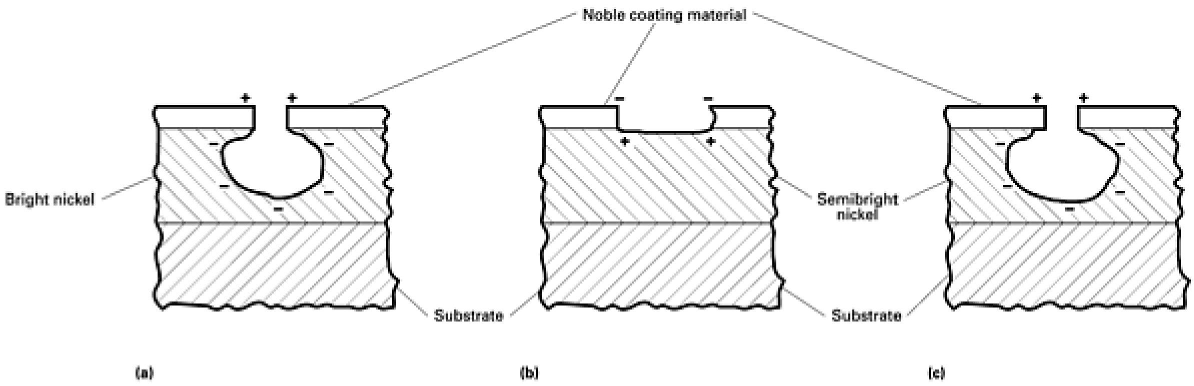

Fig. 2 Corrosion of coating-substrate systems showing the different behaviors with respect to system and electrolyte. Solution 1, Cl^-. Solution 2, SO_4^{2-}. (a) Solutions 1 and 2. (b) Solution 1. (c) Solution 2

As a consequence of these two types of coating-substrate corrosion behavior, two methods for improving corrosion resistance are applied in practice:

- *A more noble coating* protects the less noble substrate. The coating should have high corrosion resistance and be highly defect-free; otherwise, severe local galvanic corrosion can degrade the material. Examples are copper, nickel, and chromium plating.
- *A less noble coating* is deposited as sacrificial protection material. Corrosion protection is virtually guaranteed as long as coating material is present. Examples are zinc and cadmium coatings.

References cited in this section

1. *Corrosion,* Vol 13, *ASM Handbook,* ASM International, 1987
2. *Corrosion and Metal Finishing,* John Wiley & Sons, 1987
3. J.O.M Bockris and A.K.N. Reddy, *Modern Electrochemistry,* Plenum Press, 1970
4. W.H. Ailor, Ed., *Handbook on Corrosion Testing and Evaluation,* John Wiley & Sons, 1971

Electrochemical Corrosion Tests

Because corrosion of metals is an electrochemical process, electrochemical measurements are especially suited to it. As described above, the corrosion reaction occurs between the cathodic and anodic parts of a corroding system, resulting in an electric current in the metal and an ionic current in the electrolyte at the metal-electrolyte interface. The amount of current produced is a measure of the oxidation or reduction reaction, so it provides information about the rate of the corrosion process.

In principle, electrochemical methods of corrosion measurements can be divided as follows:

Without external electrical source

- Current measurements
- Potential measurements

With external electrical source

- Polarization measurements

- Tafel extrapolation
- Polarization resistance measurements
- Impedance measurements

In the first type, different electrical parameters can be present. In the latter type, only system-adjusted values are measured (Ref 1, 2, 7, 8, 9). All measurements are performed in different electrochemical cells (Fig. 3). The following paragraphs describe these techniques in more detail.

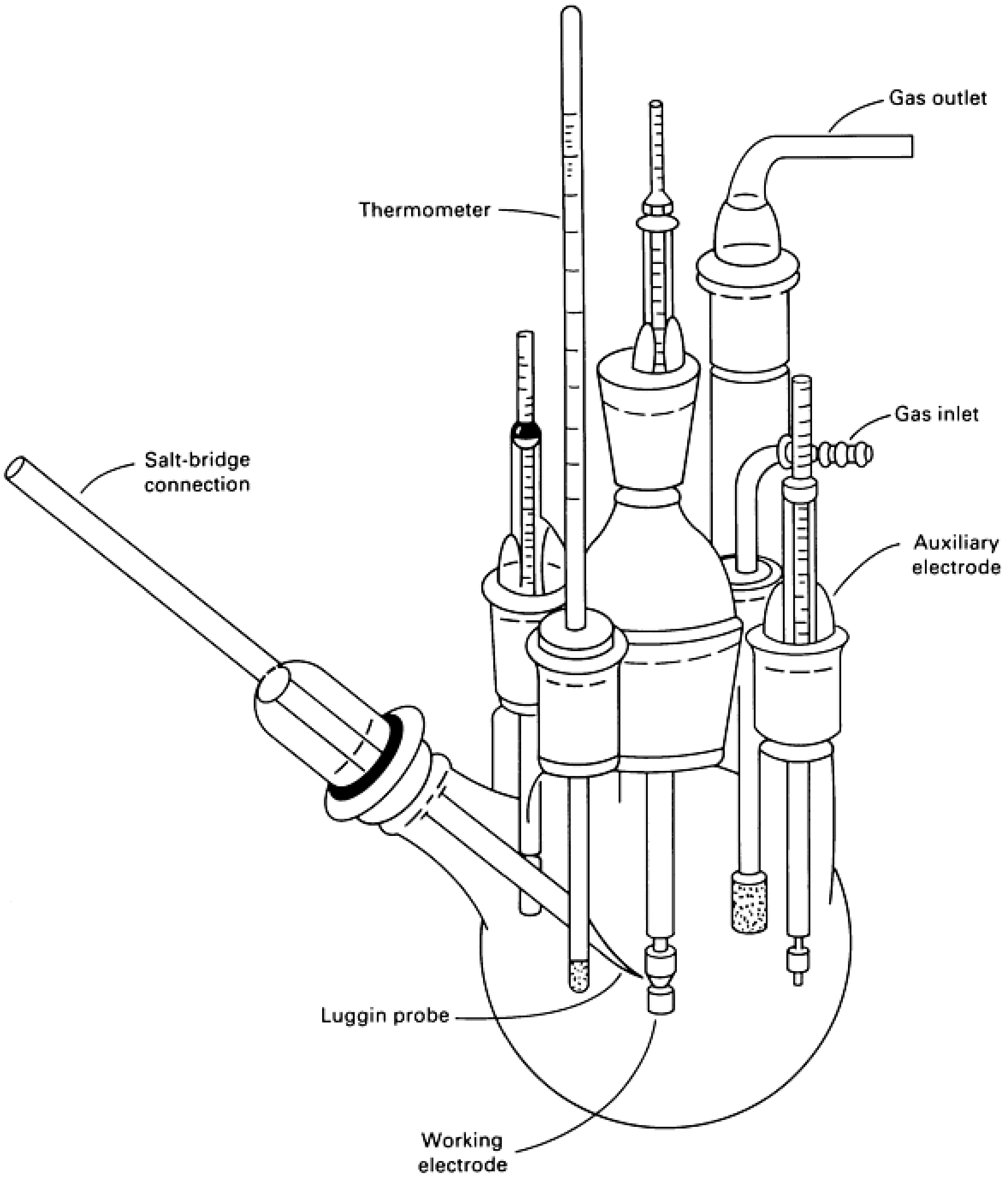

Fig. 3 Electrochemical measurement cell for corrosion investigations. Source: Ref 10

Current Measurements. The calculation of the corrosion rate of metal-electrolyte systems is based on Faraday's law if the reaction follows an electrochemical mechanism:

$$m = \frac{l.t.M}{n.F} \qquad \textbf{(Eq 1)}$$

where *m* is the amount of substance (in mol%) liberated or deposited by the passage of an electric current *I* (in amperes); *t* is time in seconds; *M* is the molecular weight of the electroactive species; *n* is the number of electrons involved in the electrochemical reaction; and F is the Faraday constant. Thus *m* is directly proportional to the quantity of charge passed, *Q*, where $Q = I \cdot t$.

The corrosion current of a homogeneous mixed electrode cannot be measured directly, because the surface is composed of a large number of "short-cut" corrosion elements uniformly distributed over the surface. In contrast, for electrode systems with separate areas of cathodic and anodic processes (e.g., different metals in contact), the corrosion current can be determined directly.

Potential measurements determine the potential established at the (working) electrode versus that established at the electrolyte. A standard reference electrode is used, such as Ag-AgCl-Cl^- (Argental) or Pt-Hg-Hg_2Cl_2-Cl^- (standard calomel electrode). These open-circuit measurements are made under equilibrium conditions (i.e., absence of current flow) to describe the thermodynamic equilibrium of an electrochemical system.

In the case of homogeneous mixed electrodes, the position of the reference electrode is of no importance because of the uniform potential distribution of the working electrode (sample). In contrast, potential measurements on heterogeneous mixed electrodes have to be performed locally. The Haber-Luggin capillary electrode is one of the easiest to use because it is positioned with its capillary tip close to the sample surface.

Potential measurements make it possible to describe the behavior of an electrode-electrolyte system (active or passive state) and the potential distribution of the corroding electrode.

Polarization measurements are based on the application of an external electrical load. The different methods are distinguished by the presetting of a potential or current that is controlled by a potentiostat. Methods using constant or time-dependent potentials are called potentiostatic and potentiodynamic, respectively. Likewise, current-controlled methods are called galvanostatic or galvanodynamic. The variation of the potential or current values can be performed continuously or in stepwise fashion. In the static methods, measurements need to be taken for a long enough period to reach steady-state conditions. In the dynamic measurements, parameters can be changed, such as scan rate or form of scan function. Quasi-steady-state conditions can be reached in the case of stepwise alterations at long holding times.

These polarization measurements involve three electrodes: a measurement electrode, a reference electrode, and a counter electrode. In this system the sample represents the measurement electrode (working electrode). The current flows only between the working electrode and the counter electrode, while the reference electrode is connected to a potentiostat or a high-impedance voltmeter and, hence, is without load. In potential-controlled measurements, the potential of the working electrode is kept constant or is definitely varied; in current-controlled measurements, a defined current flow is applied. In both methods, the potential of the measurement electrode is measured by use of the reference electrode.

Tafel Extrapolation. An application of polarization measurements is the determination of corrosion current density using the Tafel extrapolation. Under the conditions of a pure charge transfer-controlled process, the current density/polarization curves are given by:

$$j = j_{corr}\left[\exp\left(\frac{2.3h}{b_A}\right) - \exp\left(-\frac{2.3h}{b_c}\right)\right] \qquad \textbf{(Eq 2)}$$

where *j* is the applied current density, j_{corr} is the corrosion current density, $\eta$is the polarization, and β_A and β_C are the anodic and cathodic Tafel slopes.

In the case of a highly anodic polarization, the second part of Eq 2 becomes very small, and in the case of a highly cathodic polarization, the first part becomes small. These relationships can be shown as:

$$j_A = j_{corr} \exp\left(\frac{2.3h}{b_A}\right) \quad \textbf{(Eq 3)}$$

$$j_C = j_{corr} \exp\left(-\frac{2.3h}{b_C}\right) \quad \textbf{(Eq 4)}$$

The plotting of polarization versus the logarithm of the current density shows a linear relationship. The extrapolation of these Tafel straight lines to the open-circuit potential can be used to determine the current density of the corrosion process (Fig. 4).

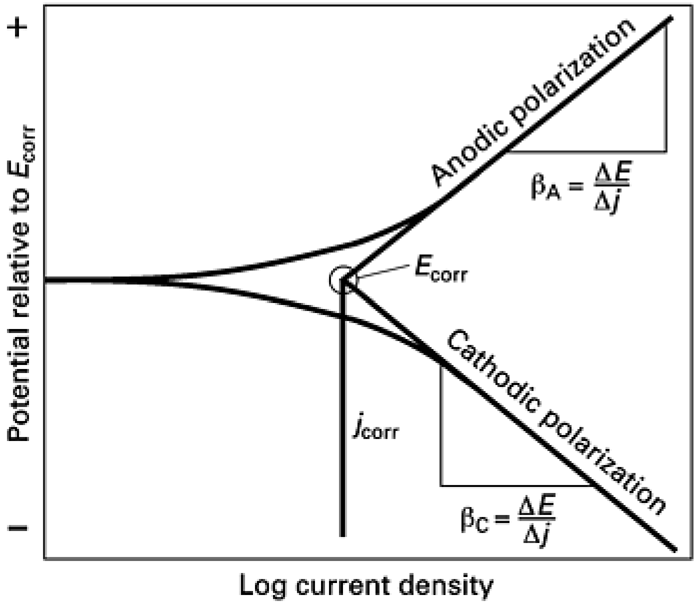

Fig. 4 Tafel plot to determine corrosion current density. β_A and β_C, anodic and cathodic Tafel coefficients; *j*, applied current density; j_{corr}, corrosion current density *E*, potential;E_{corr}, corrosion potential

These equations can be used only in the case of a pure charge transfer-controlled reaction. Therefore, it must be guaranteed that other polarization effects are negligible (e.g., concentration polarization or polarization resulting from the resistivity of the electrolyte depending on the distance of the used reference electrode from the sample surface).

Polarization Resistance. Another polarization technique is the determination of polarization resistance, R_p. This method is based on the fact that the cathodic or anodic current density change is approximately linear with the polarization in the range near the corrosion potential (Ref 11, 12). These relationships can be described by:

$$R_p = \frac{b_A . b_C}{2.3 . j_{corr} (b_A + b_c)} \quad \textbf{(Eq 5)}$$

The advantage of measuring polarization resistance is that only a very small potential range has to be scanned, and thus the measurements take less time. On the other hand, a charge transfer-controlled condition can be reached with very low scan rates without a large increase in total measuring time.

Impedance measurements involve applying a small-amplitude sinusoidal potential to the measurement system and registering the current response to the signal's amplitude and the phase. A corrosion process can be described by an equivalent electrical circuit model. A simple corrosion reaction can be viewed as a circuit, as illustrated in Fig. 5. The impedance of this circuit can be described by:

$$Z = R_\Omega + \frac{R_p}{(1+v^2.R_p{}^2.C^2)} - \frac{j.v\,.C.R_p{}^2}{(1+v^2.R_p{}^2.C^2)} \qquad \textbf{(Eq 6)}$$

where ω is the frequency of the applied signal. To determine *R*Ω and R_p in Fig. 5, it is necessary to make measurements over a wide range of frequencies and to plot the impedance of the system as a function of frequency. A Bode plot for the equivalent electrical circuit in Fig. 5 is shown in Fig. 6. To describe the system it is also necessary to measure the current response that is in phase with the alternating potential wave form, as well as the current response that is out of phase with the applied potential. From these data one can calculate the real and imaginary part of the impedance for each frequency. The plot of imaginary versus real impedance over a range of frequencies, the Nyquist plot, is shown in Fig. 7. When interpreted correctly and applied appropriately, impedance measurements are a powerful tool for describing corrosion processes (Ref 8, 13, 14, 15).

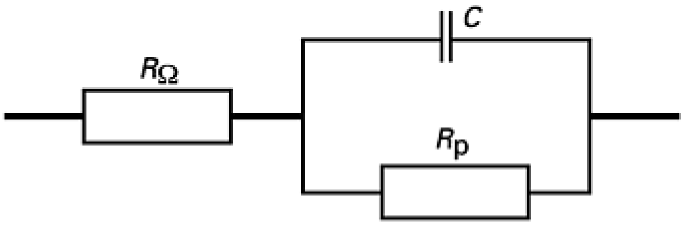

Fig. 5 Equivalent electric circuit model. *R*Ω, resistance between the reference electrode and the working electrode; R_p, polarization resistance of the electrochemical reaction; *C*, capacitance of the double layer

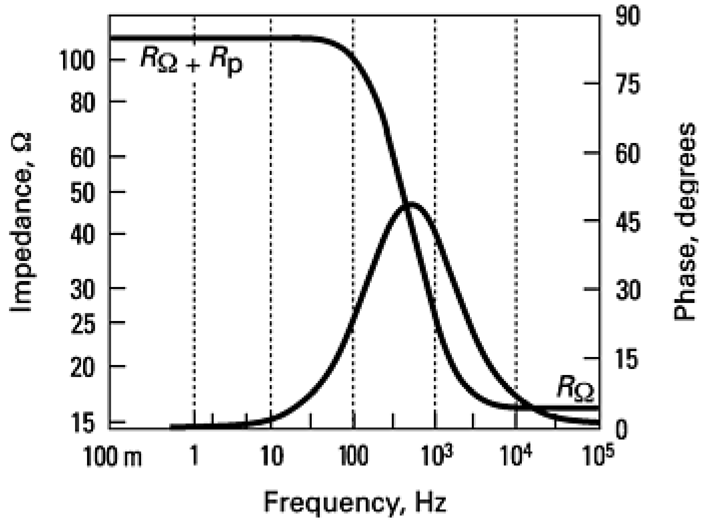

Fig. 6 Bode plot of the electrical circuit in Fig. 5. *R*Ω, resistance between the reference electrode and the working electrode; R_p, polarization resistance of the electrochemical reaction

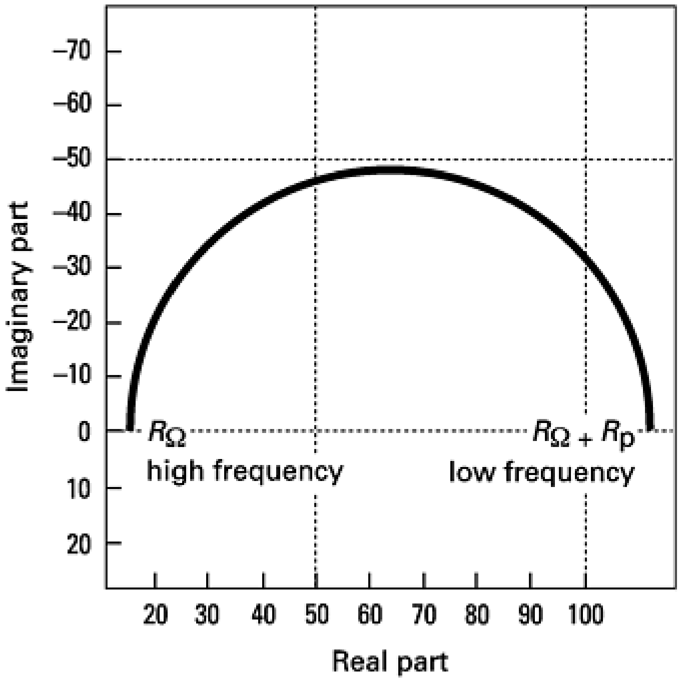

Fig. 7 Nyquist plot of imaginary versus real impedance over a range of frequencies. $R\Omega$, resistance between the reference electrode and the working electrode; R_p, polarization resistance of the electrochemical reaction

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References cited in this section

1. *Corrosion,* Vol 13, *ASM Handbook,* ASM International, 1987
2. *Corrosion and Metal Finishing,* John Wiley & Sons, 1987
7. A.T. Kuhn, *Techniques in Electrochemistry, Corrosion and Metal Finishing,* Wiley, 1987
8. *Annual Book of ASTM Standards,* ASTM, 1993
9. K.J. Vetter, *Elektrochemische Kinetik,* Springer Verlag, 1961
10. Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarisation Measurements, ASTM G 59-91, *Annual Book of ASTM Standards,* Vol 03.02, ASTM, 1993
11. M. Stern and A.L. Geary, Electrochemical Polarisation, *J. Electrochemical Soc.,* Vol 105, 1957, p 56
12. J.A.V. Butler, *Trans. Faraday Soc.,* Vol 28, 1932, p 379
13. J.R. Macdonald, *Impedance Spectroscopy,* John Wiley & Sons, 1987
14. J.R. Scully, D.C. Silvermann, and M.W. Kenaning, Ed., *Electrochemical Impedance: Analysis and Interpretation,* ASTM, 1993
15. P.T. Kissinger, *Laboratory Techniques in Electroanalytical Chemistry,* Marcel Dekker, Inc., 1987

Laboratory Corrosion Tests

To get information on the long-time corrosion behavior of parts, accelerated (short-time) tests have been used for decades. The environment used might simulate a humid tropical area, the salty air of a seaside area, a salted road in winter, a highly industrialized area, or one of many others. Even these few examples show the tremendous variety of aggressive environments that have to be considered.

Laboratory tests can easily compare the performance of materials and systems. They involve continuous exposure or increased corrosion activity so that results will be available within a short period of time. This means, however, that the mechanism of the corrosion reaction may be changed. It is not known for certain that lifelong corrosion can be simulated by a short-time test, considering that real conditions vary greatly and are sometimes much more complex. Nevertheless,

laboratory tests are most widely accepted as a tool for ensuring uniformity and quality of coatings. In general, they have to be verified by field tests.

Laboratory tests are standardized in part, but a huge number of specific test conditions can be applied, depending on the actual conditions of exposure. In principle, three types of tests can be distinguished: wetting of the surface by condensing media in humid atmospheres (simulated atmospheres), spraying of aggressive media, and immersion into corrosive liquid. All tests can be modified by certain intervals or changing conditions. In Table 2 the major laboratory corrosion tests are characterized by their media, procedures, and simulated environments. In general, laboratory corrosion tests are the same as those applied to bulk materials, although the type of deterioration is different.

Table 2 Laboratory corrosion tests

Test	**Conditions**	**Information**
Simulated atmospheres		
Condensed water climate test	Saturated water vapor	Behavior in humid environment
Condensed water alternating climate test	Water vapor + SO_2, temperature change	As in condensed water climate test, with polluted gas
Salt spray tests		
Salt spray test	NaCl solution	Ocean climate
Acetic acid salt spray test	NaCl + CH_3COOH	Salted roads
Copper-accelerated acetic acid salt spray test	As in acetic acid salt spray test	As in acetic acid salt spray test, but more aggressive
Immersion tests		
Artificial sweat test	. . .	Wearing of decorative parts
Immersion tests	Solutions of HCl, HNO_3, etc.	Wearing of decorative parts, corrosion in aqueous media

The samples treated in short-time tests normally are visually or optically inspected. The major information to be obtained is whether the coating or substrate material (at the defects) is corroded, the type of corrosion, if any, and the local distribution of the defect-related corrosion attack. The nature and color of the reaction product may be hints about the type of corrosion. The density and extent of corrosion give information about the coating properties (defect distribution) and coating quality (e.g., homogeneity of thickness).

Simulated atmosphere tests are performed in closed cabinets (humidity-temperature chambers). The samples are hung above the water-covered cabinet floor. The standard test procedure is to dry the samples and visually inspect them after a certain period (cycle), after which the test is repeated several times.

The simple condensed water climate test consists of 24 h cycles performed in saturated water vapor at 40 °C (104 °F) (Ref 16). A more aggressive atmosphere is produced by the addition of SO_2 gas. Alternating conditions may be chosen.

The condensed water alternating climate test consists of 24 h cycles of changing temperature conditions (e.g., water vapor plus 0.07 to 0.7 vol% SO_2 at 18 to 28 °C, or 64 to 82 °F, and 40% humidity, then 75 to 100 °C, or 166 to 212 °F, and 40% humidity) (Ref 17).

Salt spray (fog) tests have long been used to determine the corrodability of metals and the degree of protection provided by inorganic or organic coatings. The reproducibility of these tests and their correlation to actual service performance have been extensively discussed. However, they are easily performed, acceptable standards for comparing the behavior of materials and coatings. In several regulations the test procedures and specific conditions are standardized, but some companies and institutions have established their own standards and procedures.

All variations of the salt spray test are used to evaluate coatings for uniformity of thickness and degree of porosity. They are considered the most useful accelerated laboratory corrosion tests. In particular, they are used to evaluate different lots (for quality control in production) or different samples (for coating development in research). As can be seen from Table 2, the neutral salt spray test has been modified into acidified tests.

The neutral salt spray test is applied for periods ranging from 8 to 3000 h. A 5% NaCl solution of pH 6.5 to 7.2 is used that does not contain more than 200 ppm total solids. The temperature of the salt spray cabinet is kept at 35 °C (95 °F) +1.1 or -1.7 °C (+2.0 or -3.0 °F) (Ref 18).

The acetic acid salt spray test is normally applied for 144 to 240 h or more, but it can be applied for periods as short as 16 h. As in the neutral salt spray test, a 5% NaCl solution is used, but pH is adjusted to a value from 3.1 to 3.3 by adding acetic acid. The temperature is the same. This test is especially useful for decorative chromium platings (Ref 19).

The copper-accelerated acetic acid salt spray (CASS) test is applied for 6 to 720 h. Once again, a 5% NaCl solution is used, but with 1 g $CuCl \cdot H_2O$ (Cu-II chloride) per 3.8 L salt solution. The pH value is adjusted to a value from 3.1 to 3.3 by adding acetic acid. The temperature is somewhat increased, 49 °C (120 °F) +1.1 or -1.7 °C (+2.0 or -3.0 °F) (Ref 20).

Immersion Tests. In certain cases, complete immersion of the test sample in a corrosive solution is the best simulation. However, the test conditions need to be controlled to ensure reproducible results. The solutions are usually selected according to the actual problem (e.g., seawater or wastewater, liquids used in technical processes, or biological agents such as sweat or saliva). They are often of increased concentration in order to accelerate the corrosion process. For the most part, standardized test conditions are applied (Ref 21, 22). The parameters are solution composition, temperature, aeration, velocity, duration, and cleaning at the conclusion of the exposure.

Immersion of the test samples can be complete or partial (the latter simulates local corrosion, especially at the liquid line). It can also be continuous or intermittent (the latter simulates the moving of liquids in chemical plants, for example). The evaluation of immersion tests is by visual inspection.

An example of a specific test is alternate immersion in 3.5% NaCl. The samples are tested in 1 h cycles that include 10 min of immersion in 3.5% NaCl, followed by 50 min of immersion (Ref 23). The total test period can reach 90 days or longer.

References cited in this section

16. "Corrosion Tests in Artificial Atmospheres," ISO 7384-1986, American National Standards Institute
17. "Practice for Conducting Moist SO_2 Test," G 87-84, *Wear and Erosion, Metal Corrosion,* Vol 03.02, *Annual Book of ASTM Standards,* ASTM, 1993.
18. "Test Method of Salt Spray (Fog) Testing," B 117-90, *Wear and Erosion, Metal Corrosion,* Vol 03.02, *Annual Book of ASTM Standards,* ASTM, 1993.
19. "Practice for Modified Salt Spray (Fog) Testing," G 85-85, *Wear and Erosion, Metal Corrosion,* Vol 03.02,

Annual Book of ASTM Standards, ASTM, 1993

20. "Copper-Accelerated Acetic Acid--Salt Spray (Fog) Testing (CASS Test)," B 368-85, *Wear and Erosion, Metal Corrosion,* Vol 03.02, *Annual Book of ASTM Standards,* ASTM, 1993
21. "Practice for Laboratory Immersion Corrosion Testing of Metals," G 31-72, *Wear and Erosion, Metal Corrosion,* Vol 03.02, *Annual Book of ASTM Standards,* ASTM, 1993
22. "Test Method--Laboratory Corrosion Testing of Metals for Process Industries." TM-01-69, National Association of Corrosion Engineers, 1976
23. "Practice for Evaluating Stress Corrosion Cracking Resistance of Metals and Alloys by Alternate Immersion in 3.5% Sodium Chloride Solution," G 44-88, *Wear and Erosion, Metal Corrosion,* Vol 03.02, *Annual Book of ASTM Standards,* ASTM, 1993

Field Corrosion Tests

Field tests show the real performance of a coated part that is exposed to all the variations in environmental conditions that cannot be simulated by laboratory tests. As with laboratory tests, the same field test procedures are applied for coating-substrate systems as for bulk materials. Evaluation is by visual inspection or surface analytical techniques. For reliable predictions of corrosion behavior, a thorough comparison of field test results with accelerated laboratory tests and electrochemical tests is indispensable.

Corrosion Performance of Coated Parts

Deposition of a more noble material provides good corrosion protection in the case of a pore-free or defect-free coating. Defects, however, may allow severe local corrosion to occur. As shown schematically in Fig. 2, corrosion of the substrate or interlayers may result in caves underneath the coatings. This effect is further illustrated in Fig. 8 for TiN deposited by physical vapor deposition onto NiP deposited on brass by electrochemical deposition. Already dezincification can be detected. Similar results are found in coatings and thin films deposited by other techniques, such as electroplating or electroless plating, plasma spraying, or chemical vapor deposition.

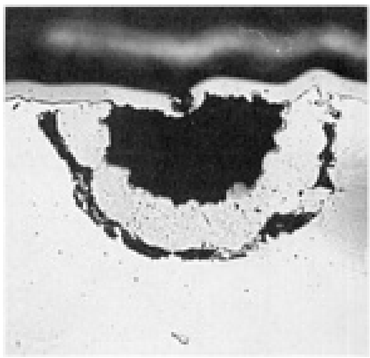

Fig. 8 Pitting corrosion after salt spray testing of the coating-substrate system TiN deposited by physical vapor deposition NiP electrochemically deposited on brass. Source: Ref 24

Polarization (electrode potential versus current density) curves provide useful information about the corrosion behavior of coating-substrate systems. The more noble and defect-free the coating, the greater the reduction in the measured current density. In general, thicker films exhibit fewer defects penetrating from the surface to the base material. Figure 9(a) shows polarization curves for TiN films deposited by plasma-assisted chemical vapor deposition onto 304 stainless steel. Even at a coating thickness of 10 μm, the behavior of the coated steel does not correspond to that of pure TiN deposited on glass (Ref 25). The deposition parameters also influence the coating morphology; this holds true for all deposition techniques. For PVD coatings, the substrate temperature, among other factors, determines the morphology (porosity) of the coatings (Fig. 9b).

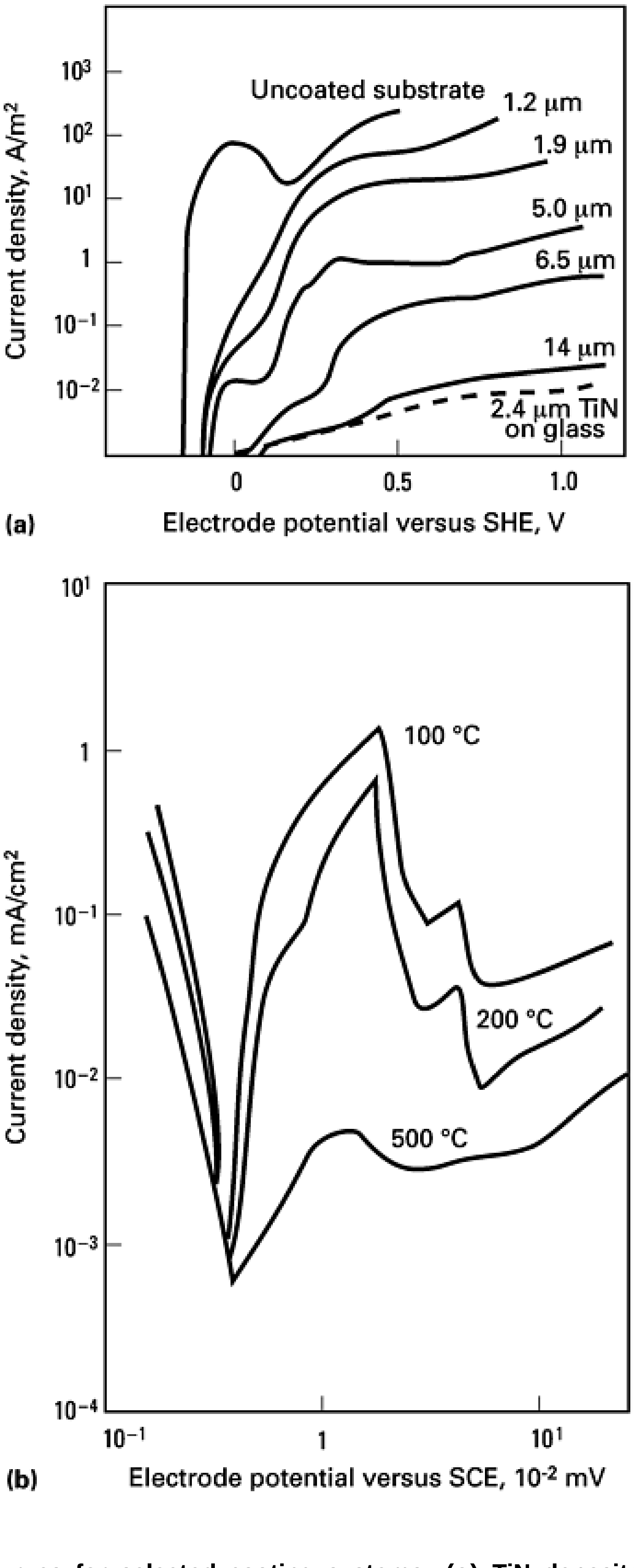

Fig. 9 Anodic polarization curves for selected coating systems. (a) TiN deposited on 304 stainless steel by plasma-assisted chemical vapor deposition. Curves for TiN deposited on glass and for the uncoated base metal are provided for comparison. Environment: 1 *M*/L HCl. Source: Ref 25. (b) TiN ion-plated onto ball bearing steel. Environment: 1 *N* H_2SO_4. Source: Ref 26

Polarization curves also show that corrosion resistance can be improved by the deposition of dense electrochemical or physical vapor deposition interlayers, alone or in combination. The polarization curves for reactively magnetron-sputtered

TiN on brass in Fig. 10 demonstrate the marked influence of interlayers. The coating with a 5 μm thick electrochemically deposited 80Pd-20Ni interlayer performs almost as well as pure TiN deposited on glass. The coating with a 2 μm PVD titanium interlayer does not perform quite as well, but much better than the TiN coated on brass without an interlayer. The titanium film was sputter-etched before the TiN was deposited.

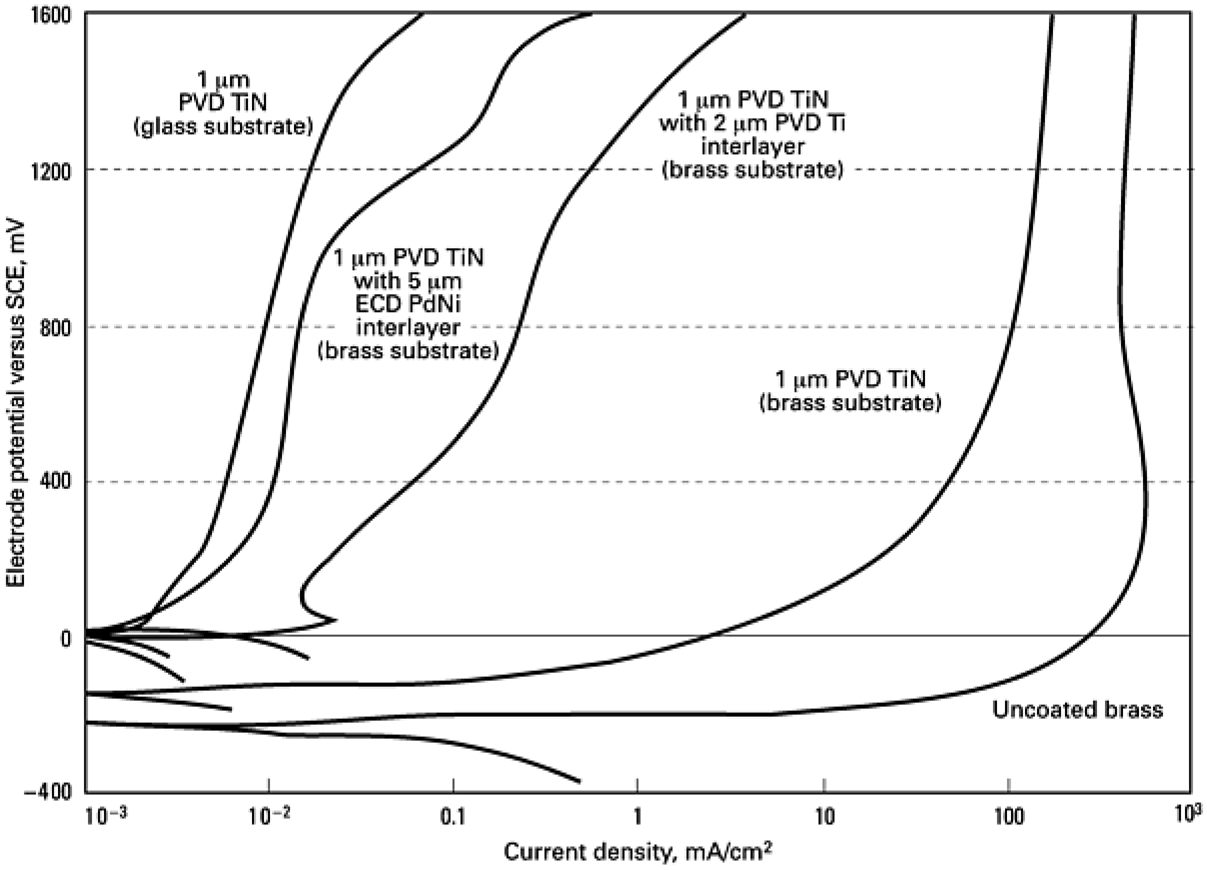

Fig. 10 Polarization curves for selected coating systems with and without interlayers. Environment: 0.8 *M* NaCl. Source: Ref 6

References cited in this section

6. H.A. Jehn, I. Pfeifer-Schäller, and M.E. Baumgärtner, Korrosion von Hartstoffschichten, Teil 3: Elektrochemische Korrosionsuntersuchungen an Dekorativen Hartstoffschichten, *Galvanotechnik,* Vol 84 (No. 12), 1993, p 4059-4064
24. H.A. Jehn and M.E. Baumgärtner, Corrosion Studies with Hard Coating-Substrate Systems, *Surf. Coat. Technol.,* Vol 54/55, 1992, p 108
25. T. Kado, R. Makabe, S. Modizuk, S. Nakajima, and M. Araki, *Corros. Eng.,* Vol 36, 1987, p 503
26. A. Edemir, W.B. Carter, R.F. Hochmann, in *Surface Modification Technologies IV, T.S. Gundarsham and D.G. Bhat, Ed., TMS-AIME, 1989, p 261*

Conclusion

Electrochemical measurements provide useful information about the fundamental corrosion behavior of coating-substrate systems in particular environments. However, it is not valid to draw conclusions about one aspect of a system from the results of one test. For example, a relatively low current density measurement for one coating system in a specific environment does not necessarily mean that the coating material is better than the others being tested. For a fairly complete analysis of corrosion mechanisms and behavior of a particular system, a combination of tests and measurements is needed.

Accelerated tests can only partially simulate the actual corrosion behavior of a given system. However, they are able to provide qualitative and reproducible results for the development and quality assurance of coating systems. Often, a combination of tests is used in practice.

In general, the corrosion resistance of a system can be improved by producing dense coating structures through the optimization of deposition techniques and process parameters, by selecting noble coating materials, and by using dense and noble interlayers.

Evaluation of Mechanical Properties of Thin Films

Franz R. Brotzen, Rice University

Introduction

THE TERM "THIN FILMS" is usually applied to metallic and nonmetallic layers of thickness of the order of microns or fractions of microns that are deposited on a variety of substrates. Their mechanical resistance is of particular interest, because high stresses often develop in the films during deposition or in service as a result of differences between the thermal expansion coefficients of the films and their substrates. This is a matter of special concern in the manufacture of microelectronic devices, where metallic films having high thermal expansion are often deposited on low-expansivity semiconductor substrates and where service temperatures vary by several hundred degrees Celsius. Similar conditions may prevail when thin films are deposited on bulk materials for the purpose of providing protective coatings.

The mechanical behavior of a given material in the form of thin films may differ substantially from that of the same material in bulk. Consequently, specialized thin-film testing methods have been developed. In these methods, one must differentiate between testing of freestanding films, that is, films removed from their substrates, and in situ films, that is, films still adherent to their substrates. Substantial differences may be observed between test results obtained from the two types of samples, mainly because of epitaxial and interfacial effects on adherent films.

Evaluation of Freestanding Films

Testing of freestanding films requires that the films be removed from their substrates without impairing their integrity. A relatively simple procedure can be applied in which the films are deposited on substrates or intermediate layers that will readily dissolve in water or some other medium. Alkali halides, such as sodium chloride or cesium iodide, have been used to this end. Organic substances (e.g., collodion or certain polymers) have also been used as substrates. However, inherent properties of films deposited on different substrates may vary, so it is often desirable to use films deposited on a specific substrate. This is particularly true of microelectronic circuits in which metallizations, such as aluminum, are deposited on silicon or silicon oxide. In these cases, the metal films are separated from the substrate by exposure to a stream of fluorine in an inert carrier gas. The silicon is removed in the form of gaseous silicon tetrafluoride, while the metal is covered by a very thin protective metal fluoride film. As the substrate is consumed, a freestanding film is produced.

Uniaxial Tensile Testing of Films. The most direct way to obtain the stress-strain relations of thin films in tension is by uniaxial testing. In principle, this procedure is analogous to conventional tensile testing of bulk materials, yet the fragility of the films and their extreme sensitivity to even the smallest flaws make uniaxial tensile testing a difficult and often frustrating task. In view of the high surface-to-volume ratio in thin films, specimens must be virtually free of surface flaws, because even the smallest defects will lead to premature failure. Tensile specimens usually have the form of a "dog bone." This shape, which has proved to be most advantageous, is obtained either by covering the substrate with a mask during deposition or by standard photolithographic techniques.

Problems are caused also by internal stresses that are created in the films during the deposition process. When the films are separated from the substrates, the stresses often cause films to wrinkle or to curl severely, rendering them useless for testing. To alleviate this condition, special devices have been developed that keep the films stretched during ablation (Ref 1).

Equipment used for uniaxial tensile testing of thin films is generally based on the simple principle of deforming a freestanding film by a known amount through the application of a known force to the ends of the specimen. The testing devices can be divided into two categories:

- *"Soft" machines*, in which the loading rate is constant and the ensuing elongation is measured
- *"Hard" machines*, in which the elongation rate is constant and the applied loads are measured

An example of tensile curves obtained by uniaxial testing of plasma-deposited aluminum films of 1μm thickness is given in Fig. 1. The initial portion of the curves often contains a clearly noticeable "unwrinkling" stage that can be ignored or discarded.

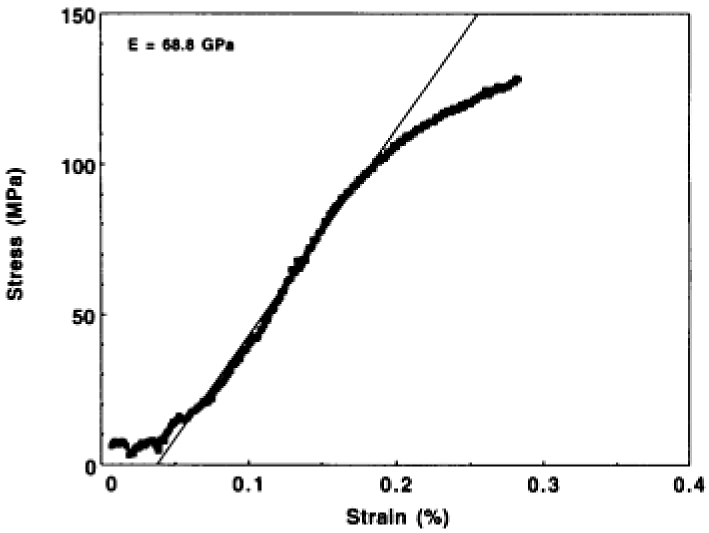

Fig. 1 Stress-strain curve obtained by uniaxial testing of a freestanding 1 μm thick annealed aluminum film

The absence of a well-defined yield point is characteristic for aluminum in bulk and, as evidenced by Fig. 2, for thin films.

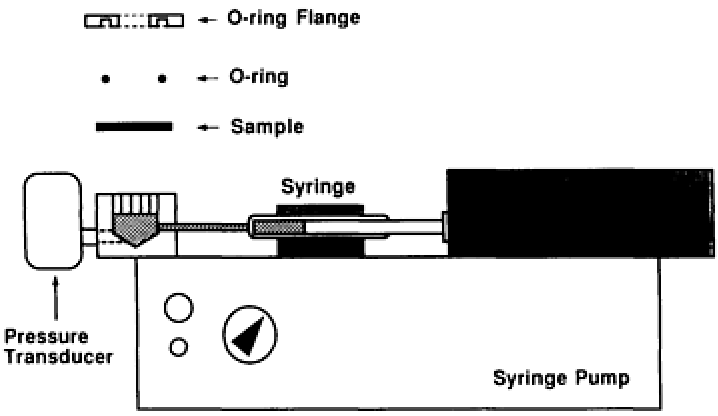

Fig. 2 Schematic drawing of a bulge-testing device. Source: Ref 3

The effect of film thickness on film strength has been the subject of intense study. Tests indicate that the strength of metallic films rises dramatically when the thickness falls below about 0.3 μm. There is evidence that the strength of films obeys the Hall-Petch relation:

$$Strenght = K + \frac{b}{\sqrt{t}}$$

where K and b are constants and t is the film thickness. However, the details concerning the thickness effect in films are still open to question and appear to be greatly influenced by the deposition conditions.

Whereas the elastic properties of metal films closely approach those of metals in bulk form, some investigations reveal a substantially higher fracture-strength level for thin films than for the corresponding bulk materials. The fracture stress of metallic polycrystalline and single-crystal films tends to rise sharply as the film thicknesses drop below 0.2 μm.

Uniaxial Creep Testing of Films. Uniaxial testing equipment can be readily employed in creep tests of freestanding thin films by keeping the load constant. In such tests, characteristic creep curves consisting of a primary and a secondary stage are obtained. The stress and temperature dependence of the secondary creep rates is very similar to that of bulk materials. For high strain rates, secondary creep rates are modeled as:

$$\varepsilon = B \exp - [(Q_0 - \beta\sigma) / kT] \quad \textbf{(Eq 1)}$$

For low strain rates, the relation is:

$$e = \frac{ADGb}{KT}\left(\frac{s}{G}\right)n \quad \textbf{(Eq 2)}$$

where B, A, $\beta$and n are constants, Q_0 is the activation energy at zero stress, $\sigma$is the applied tensile stress, k is Boltzmann's constant, T is the absolute temperature, D is the diffusion coefficient (i.e., D_0 exp [Q_D/kT]), G is the shear modulus, b is the interatomic distance, D_0 is a constant, and Q_D is the activation energy for self-diffusion. The values of the stress exponent n are usually in the range between 4 and 10 and are highly sensitive to the grain structure of the material. The material constant βin Eq 1 for thin aluminum films, for example, is close to 10^{-27} m^3/atom and about half of that in aluminum-silicon alloy films of 1 μm thickness. The activation energy at zero stress, Q_0, for steady-state creep in unannealed, vapor-deposited copper films is about 1.3 eV. In sputtered 1 μm thick aluminum and aluminum-1% silicon-alloy films, Q_0 is 0.56 and 1.10 eV, respectively (Ref 2). The low activation-energy value for aluminum approaches that of grain-boundary diffusion of vacancies in that metal.

In summary, the uniaxial testing method provides an excellent means for obtaining readily interpretable results in terms of tensile stress and strain. These results can be applied to well-known descriptions of the fundamental processes of plastic deformation. On the other hand, the uniaxial testing technique requires extreme care in specimen preparation and handling, and the elongations that can be obtained are often limited.

Biaxial Testing of Films. The bulge-testing technique is a biaxial testing method that can be applied to freestanding thin films. A film whose edges are fixed may be viewed as an impermeable membrane. Applying a known fluid pressure, liquid or gas, to one side of this membrane will cause it to bulge, so that the film material is strained biaxially. By monitoring the bulge expansion as a function of the fluid pressure, a stress-strain relationship is obtained. In principle, bulge testing is a straightforward technique by which problems associated with defects on the sample edges are eliminated. However, the interpretation of bulge-testing results is far more complex than that of uniaxial-test results.

Bulge testing can be performed by applying fluid pressure through a hole drilled on the back of the substrate without damaging the deposited film. An alternative procedure (Fig. 2) employs films that are removed from their substrates (Ref 3). The films are fastened by an O-ring on top of a small cylindrical chamber. A syringe pump then injects glycerol into the chamber at a constant rate. The glycerol pressure is monitored by a pressure transducer, and the injected volume is determined by the elapsed time. The bulge extension can be determined either by the displaced fluid volume or by the height of the bulge. In general, when designing bulge-testing equipment, the ratio of the bulge orifice to the film thickness should be at least between 200 and 300, so that the effect of flexural rigidity is minimized.

Films used in the bulge-testing technique must be separated from their substrates. The film-ablation techniques are identical to those described in the preceding section. It should be noted that metal films, such as aluminum or aluminum alloys, deposited on a silicon substrate tend to dissolve silicon, which often precipitates in the form of silicon-rich nodules. These nodules are removed during the ablation process together with the silicon substrate, producing very fine pinholes in the film that vitiate the bulge-testing procedure.

The analysis of the pressure-bulge deformation is generally based on a model proposed by Hill (Ref 4), which gives the meridional stress as:

$$s_m = \frac{\Pr_0}{2t} = \frac{Pa^2}{4th} \qquad \textbf{(Eq 3)}$$

where P is the fluid pressure, r_0 is the radius of curvature at the top of the bulge, t is the thickness of the film, a is the radius of the orifice, and h is the height of the bulge. This is an approximate expression that is predicated on the bulge height's being much less than the radius of the orifice. The calculation of the meridional strain, also based on Hill's work, is:

$$e_m = a\,\frac{h^2}{a^2} \qquad \textbf{(Eq 4)}$$

where α is a constant that is generally taken to be $\frac{2}{3}$. This, too, is an approximation based on the premises that the bulged film assumes a spherical shape and that the film is a plane at zero tension. The realization of true sphericity is questionable, but experimental results have shown that the meridional strain may be accurate within about 8% for strains up to 1% (Ref 5).

A serious criticism of bulge testing centers about the initial state of the film, that is, its flatness at zero pressure. Whenever bulge testing is carried out on films adherent to the substrate by removing the substrate over a given area, there may be residual compressive or tensile stresses in the film. In the former case, this results in buckling or wrinkling of the film, and in the latter case, in a film stressed in tension (Ref 6). These conditions must be taken into account when calculating the stress-strain relations obtained from the tests.

The bulge test presents an attractive method for determining mechanical properties of thin films, mainly because--in contrast to the uniaxial test--flaws at the edges of the film specimens do not affect bulge-test results. It is seen from the above comments, however, that the value of this method for the accurate determination of mechanical behavior of freestanding thin films is diminished because of the many imponderables with which the interpretation of bulge-testing data is fraught.

Beam-Bending Methods Applied to Free-standing Films. When a specimen in the shape of a beam is bent, the portion on one side of a longitudinal "neutral" plane is strained in tension, while the portion of the other side of the plane is strained in compression. If the specimen has a uniform composition, such as a freestanding film, the stress-strain relation of the material can be readily calculated from the load-deflection data determined during bending. In this technique, very small cantilever-beam specimens are used, which are produced by microelectronic fabrication methods. In such test, a Nanoindenter device can be employed that applies the load to the free end of the cantilever beam and simultaneously measures the deflection (Fig. 3). The elastic modulus and the yield strength of the material are determined from the load-deflection curve. The specimens for the microbeam method are prepared by creating the required pattern of the film and the subsequent removal of the substrate. Microbeam fabrication and testing are briefly reviewed in Ref 8. A detailed review of micromachining of beam specimens is given in Ref 9.

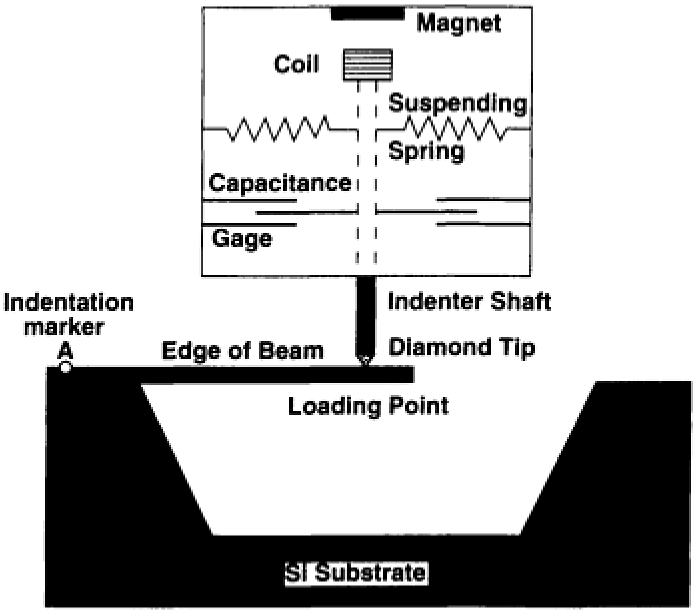

Fig. 3 Schematic drawing of a Nanoindenter used as a loading device on a microcantilever beam. Source: Ref 7

When the deflections are small and the material is considered to be uniform and isotropic and to deform elastically, the well-known equation for the cantilever-beam deflection δ under a load *P* applied to the free end of a beam is given by:

$$d = \frac{PL^3}{3EI} = \frac{4PL^3}{bEh^3} \qquad \textbf{(Eq 5)}$$

where *L* is the length of the beam, *E* is Young's modulus, *I* is the moment of inertia, *b* is the width of the beam, and *h* is the thickness of the beam. This equation is modified, for the case of thin and broad plate-like specimens (*b* ? *h*), where plane stress is applied in the direction of the beam thickness and plane strain is applied in the direction of its width, to read:

$$d = \frac{4(1-v^2)PL^3}{bEh^3} \qquad \textbf{(Eq 6)}$$

where ν is Poisson's ratio. Young's modulus is derived from the slope of δ(*P*).

The simple beam theory described above can also be employed in the determination of the yield strength of the beam material. When the beam is bent under a downward load applied to its free end, the maximum tensile stress occurs at the fixed end. When this stress reaches the yield strength, the load-deflection curve ceases to be linear. The load that marks this deviation from linearity is denoted by P_v, so that the yield stress is (Ref 7):

$$s_y = \frac{6LP_v}{bh^2} \qquad \textbf{(Eq 7)}$$

An interesting modification of the simple curved-beam method has led to a resonance technique for the determination of the elastic modulus. Specimens similar to the ones used in the technique described above were vibrated electrostatically, and Young's modulus was obtained from the observed natural frequency (Ref 10).

The beam-bending method is well suited for the determination of elastic and some plastic properties of freestanding films. The principal drawback to this technique is the inherent difficulty of specimen preparation.

References cited in this section

1. C.T. Rosenmayer, F.R. Brotzen, and R.J. Gale, *Thin Films: Stresses and Mechanical Properties,* J.C. Bravman, W.D. Nix, D.M. Barnett, and D.A. Smith, Ed., Symp. Proc. Mater. Res. Soc., No. 130
2. F.R. Brotzen, C.T. Rosenmayer, C.G. Cofer, and R.J. Gale, in *Vacuum,* Vol 41, 1990, p 1287-1290
3. A.J. Griffin, Jr., F.R. Brotzen, and C.F. Dunn, in *Thin Solid Films,* Vol 150, 1987, p 237-244
4. R. Hill, in *Phil. Mag.,* Vol 41, 1950, p 1133-1142
5. T. Tsakalakos, in *Thin Solid Films,* Vol 75, 1981, p 293-305
6. M.K. Small and W.D. Nix, in *J. Mater. Res.,* Vol 7, 1992, p 1553-1563
7. T.P. Weihs, S. Hong, J.C. Bravman, and W.D. Nix, in *J. Mater. Res.,* Vol 3, 1988, p 931-942
8. W.D. Nix, Mechanical Properties of Thin Films, *Met. Trans. A,* Vol 20, 1989, p 2217-2245
9. J.Â. Schweitz, in *MRS Bull.,* Vol 17, 1992, p 34-45
10. K.E. Petersen and C.R. Guarnieri, in *J. Appl. Phys.,* Vol 50, 1979, p 6761-6766

Evaluation of Films Adherent to Their Substrates

Indentation testing of thin films resembles in many aspects the well-known hardness measuring techniques, such as the Vickers and Brinell hardness tests. However, in the "nanoindentation" technique, the indentations extend only to extremely shallow depths, often as low as nanometers. A hard indenter, usually an accurately ground diamond, is gradually pressed into the film, which is deformed first elastically and then plastically. Upon gradual removal of the load, the elastic deformation is recovered (Fig. 4). Analysis of the load-displacement curves provides information not only on the hardness, but also on the elastic and creep properties of the films. In contrast to traditional hardness measurements, the nanoindentation technique furnishes a continuous record of both load and indentation depth during loading and unloading, so that imaging of the indentation is no longer required.

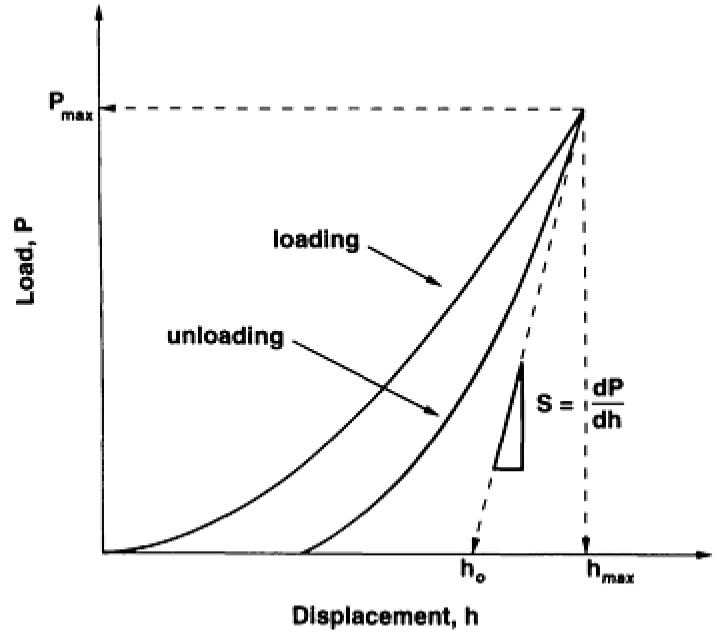

Fig. 4 Typical curve of load as a function of indenter-penetration depth. Source: Ref 11

The determination of mechanical properties of thin films by nanoindentation has gained widespread use in recent years. Its popularity stems not only from the high spatial resolution of the indentations--less than 1 μm^2--but also from the simplicity with which mechanical properties of surface layers on bulk materials and of films adherent to their substrates can be determined under essentially compressive conditions. Details of nanoindentation testing techniques and equipment can be found in the literature (see the "Selected References" in this article. The most common means of applying the load

in nanoindentation equipment is through electromagnetic or piezoelectric devices, in which the resolution obtained is often better than 0.01 μN. The displacements are typically measured by a capacitive device giving resolutions as small as 0.1 nm. The most commonly used indenter is a diamond of the Berkovich type, a triangular pyramid with the same depth-to-area relation as the standard Vickers indenter (square pyramid)--that is, the cross-sectional area varies as the square of the depth of the indentation.

Determination of Elastic Properties by Indentation. The indentation technique provides a simple means for determining the elastic modulus of the film. During penetration of the film by the indenter, both elastic and plastic deformations occur. Upon withdrawal of the indenter, the depth of the permanent indentation changes as a result of the elastic recovery of the film. Repeated applications of the load generate a truly elastic recovery for which mathematical solutions are known, so that the unloading curves can be related effectively to the elastic properties of the material, that is, the elastic modulus, E, and Poisson's ratio, ν. The effective modulus is obtained from the slope of the unloading curve:

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{p}} b \sqrt{AE_r} \qquad \textbf{(Eq 8)}$$

where S, P, and h are given in Fig. 4, A denotes the contact area of the indenter, E_r is the effective elastic modulus, which takes into account the small deformation of the indenter, and βis a dimensionless parameter that depends on the geometry of the indenter. For any indenter that can be described as a solid of revolution of a smooth function, β= 1. Although neither the Vickers nor the Berkovich indenters falls into this category, βdeviates only very slightly from unity for these indenters. To compute the modulus E_r, according to Eq 7, the slope of the unloading curve dP/dh must be known and the projected contact area, A, at the maximum load would have to be known as well. The area is obtained from an area function F(h), which relates the cross section of the indenter to the appropriate depth, h, of the indentation measured from the tip of the indenter. As an example, for an ideally sharp Berkovich indenter the area function is $F(h) = 24.5\ h^2$. In reality, this function is much more complex because of the impossibility of achieving ideal tip sharpness. To determine the appropriate depth of indentation, various models for elastic unloading were proposed (Ref 11). An improved method for determining the contact area at peak load uses the contact depth h_c found by the equation

$$h_c = h_{max} - e \frac{P_{max}}{dP/dh} \qquad \textbf{(Eq 9)}$$

whose terms are defined in Fig. 4. The value of ε depends on the geometry of the indenter and can be taken to be 0.75 for the Berkovich indenter. Once h_c is determined from the above equation, the appropriate contact area can be calculated from the area function $A = F(h_c)$. The effective elastic modulus, E_r, can now be determined from the unloading curve in accordance with Eq 7.

Indentation Hardness Testing of Films. The indentation technique is very well suited for determining the hardness of films adherent to their substrates. Hardness is a measure of resistance to local deformation and is defined by the ratio $H = P(\max)/A$, where P(max) is the peak load applied to a given type of indenter and A is the projected area of the hardness impression. In general, the determination of the contact area A follows the procedure outlined in the preceding section.

The effect of indentation depths on hardness measurements has been a matter of concern. It has been shown, however, that a variation in the applied load has little effect on the hardness of several different materials, provided that the projected area has been properly determined. When the hardness of films deposited on a substrate is measured, the region deformed by the indentation may extend to the film/substrate interface, which affects the hardness measurements. As the plastic zone under the indentation in the film reaches the substrate, the measured hardness becomes a function of the ratio of maximum penetration depth to film thickness and ceases to be the true hardness of the film. A rule of thumb suggests that the indentation depth should not exceed 10% of the film thickness.

It should be noted that silicon, as well as ceramic materials, may develop cracks when indentation strains are not accommodated by plastic deformation. These cracks affect the measured load-displacement relations. To overcome the troublesome substrate effects in very thin films, extremely shallow indentation techniques have been applied successfully.

Strength Measurements by Indentation Testing. It would be, of course, very desirable to derive plastic properties, such as the ultimate tensile strength or the yield strength, from indentation measurements. Because of the complexity of the mechanics of the indentation process, such a task is very difficult. In 1951, Tabor (Ref 12) formulated

an equation that related the ultimate tensile strength, σ_{UT} (in kg/mm^2), to the Vickers hardness number, H_v, for a material whose work-hardening exponent (n) is as follows:

$$\frac{s_{UT}}{H_v} = \frac{1-n}{2.9}\left(\frac{12.5n}{1-n}\right)n \quad \textbf{(Eq 10)}$$

This equation yielded reasonable agreement with experimental data.

Actual stress-strain curves were obtained by indentation of 1 μm thick gold and aluminum-copper metallizations deposited on silicon (Fig. 5). Here, spherical diamond indenters of radii of 5, 10, and 22 μm were used. The analysis of the load displacement data was based on Tabor's work and presupposed a strain-hardening equation in which the flow stress, σ, was exponentially related to strain, ε, such that $\sigma \approx \varepsilon^n$. While the application of Tabor's analysis has been helpful, correlations fo pressure-indentation results with stress-strain curves of ductile materials have not been promising.

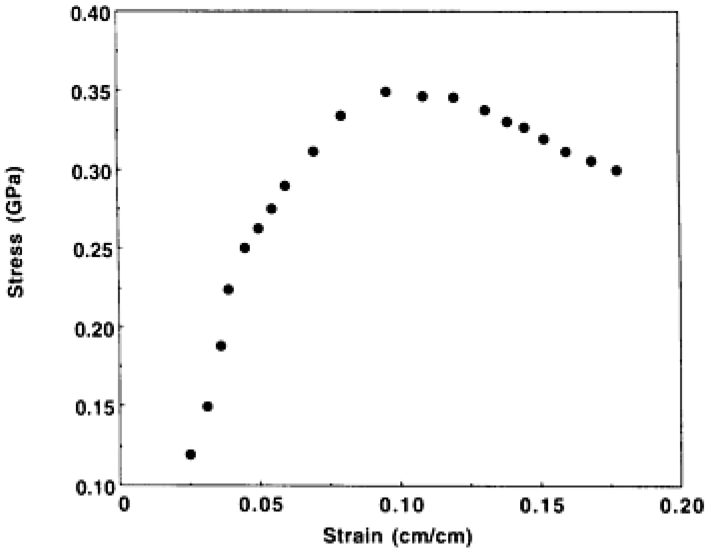

Fig. 5 Stress-strain curve for an annealed gold film, obtained by the indentation technique using a spherical-tipped diamond indenter of 20 μm radius. Source: Ref 13

Creep and Stress-Relaxation Testing by Indentation. Modern indentation equipment is designed to monitor the movement of the indenter under a given load as a function of time as well as the changes in load at a fixed depth of penetration. The equipment is therefore capable of measuring the equivalents of creep and stress relaxation.

When recording the penetration rate under a constant indenter load, curves are obtained that bear a strong resemblance to typical creep curves of bulk materials (Fig. 6). The classical stress dependence for secondary creep rate (ε) = constant σ^n can be applied, where ε is the stain rate, σis the stress, and n is the stress exponent. The latter is close to the one found by uniaxial creep testing of films (see the section "Uniaxial Creep Testing of Films" in this article).

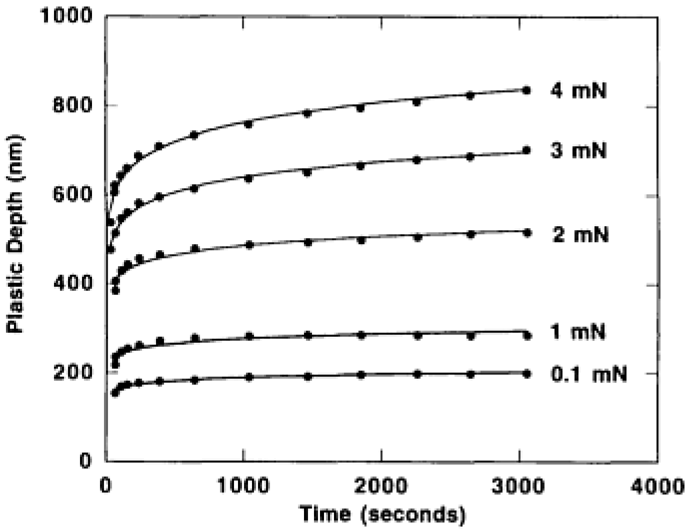

Fig. 6 Penetration depth (plastic deformation only) in a 1.6 μm thick sputtered aluminum film at constant indenter loads. Source: Ref 14

Valuable information can also be obtained from stress-relaxation experiments. In a typical experiment of this kind, the indenter is pressed into the specimen at a constant rate, usually of the order of 10 nm · s^{-1}, to a predetermined depth while monitoring the change in load. After the displacement is halted, a record is made of the relaxation effected by the specimen and the elastic reactions of the testing equipment. The modulus describing these elastic reactions is obtained from the initial slope of the unloading curve at a constant displacement rate. The relaxation curve yields data on the plastic strain rate, ε, as a function of stress, σ, the strain-rate sensitivity being defined by:

$$m = \frac{\partial \ln e}{\partial \ln s} \quad \textbf{(Eq 11)}$$

One concludes from the above that the indentation method provides a consistent picture of elastic modulus, hardness, and strain-rate sensitivity measurements of surface layers of bulk materials, including thin films deposited on substrates. It is particularly well suited for use with hard surface films, in which plastic deformation plays only a minor role. Indentation testing is attractive in view of its simplicity and the absence of complex sample preparation. The principal drawbacks of the indentation method lie in uncertainties of interpretation, particularly in ductile materials.

Beam-Bending Methods Applied to Adherent Films. This technique is based on the same principles as the beam-bending technique applied to freestanding films, described earlier. In the case of testing of adherent films by the beam-bending technique, the specimen is a composite of two materials, the film and the substrate. If the mechanical characteristics of the substrate are known, the stress-strain relation for the deposited material can be inferred from the load-deflection curve.

The elastic deflection at the free end of a bilayer cantilever beam under an external load is related to the elastic constant by an equation similar to Eq 6:

$$d(L) = \frac{PL^3}{3(EI)_{eff}} \quad \textbf{(Eq 12)}$$

where Young's modulus *E*, and the moment of inertia, *I*, are replaced by the product of the effective modulus and the effective moment of inertia:

$$(EI)_{eff} = b\left[\frac{1}{3}(E_{ps}h_s^3 - E_{pf}h_f^3) - C_i^2(E_{ps}h_s - E_{pf}h_f\right] \quad \textbf{(Eq 13)}$$

Here, the subscripts "p," "s," and "f" refer to "plate," "substrate," and "film,"respectively, and $E_p = E/(1 - u^2)$. The distance between the film/substrate interface and the neutral plane of the beam is given by:

$$C_i = \frac{(E_{ps}h_s^2 - E_{pf}h_f^2)}{2(E_{ps}h_s - E_{pf}h_f)} \qquad \textbf{(Eq 14)}$$

A comparative beam-bending technique can also be employed, in which the load-deflection curve of a cantilever-beam sample consisting only of the substrate is registered. This operation is repeated after a film is deposited on the substrate. The difference between the two tests is used to find the elastic modulus of the film. The modulus can be evaluated by this method without prior knowledge of the properties of the substrate material, as shown in Ref 9.

Elastic properties of thin films adherent to the substrates are sometimes investigated by subjecting the specimen to temperature changes. In this case, calculable thermal stresses are introduced that produce an observable curvature in the specimen. It is possible to derive elastic and certain plastic properties of thin films from the curvature-vs.-temperature records by techniques shown in Ref 15.

The cantilever-beam technique in its different forms is a useful tool for determining elastic and yield properties in films. However, although it provides a means to determine these properties in situ, that is, properties of films adherent to their substrates, it suffers from the difficulty of specimen preparation.

References cited in this section

9. J.Â. Schweitz, in *MRS Bull.,* Vol 17, 1992, p 34-45
11. G.M. Pharr and W.C. Oliver, in *MRS Bull.,* Vol 17, July 1992, p 28-33
12. D. Tabor, *The Hardness of Metals,* Clarendon Press, 1951
13. T.J. Bell, J.S. Field, and M.V. Swain, in *Thin Films: Stresses and Mechanical Properties III,* W.D. Nix, J.C. Bravman, E. Arzt, and L.B. Freund, Ed., Symp. Proc. Mater. Res. Soc., No. 239
14. V. Raman and R. Berriche, in *J. Mater. Res.,* Vol 7, 1992, p 627-638
15. M.F. Doerner, S.D. Gardner, and W.D. Nix, in *J. Mater. Res.,* Vol 1, 1986, p 845-851

Stress Determination for Coatings

J. Albert Sue, Praxair Surface Technologies, Inc.; Gary S. Schajer, University of British Columbia

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Introduction

COATINGS AND THIN FILMS can be produced by a large variety of deposition techniques. Typical processes are physical vapor deposition (PVD), chemical vapor deposition (CVD), electroplating, electroless deposition, anodizing, thermal growth, and thermal spraying. Since the early 1980s, considerable progress has been made in improving deposition processes for a wide range of high-technology applications. Consequently, many new ceramic coatings and films have been introduced in various industries. Typical examples are metal-oxide semiconductors for microelectronics; titanium nitride, titanium carbide, aluminum oxide, and silicon nitride for machining tools; and thermal-sprayed tungsten carbide/cobalt, M-chromium-aluminum-yttrium (where M stands for iron, cobalt, or nickel), and yttrium oxide/partially stabilized zirconia coatings for aerospace applications.

Residual stresses, which are internal and therefore locked in, are contained in materials that are produced by nearly every mechanical, chemical, and thermal process, either alone or in combination. As a result, most coatings are in a state of internal stress, including metallics and ceramics. The stress can be either compressive or tensile. It is generally recognized that compressive stresses in coatings are more favorable than tensile stresses, because they increase resistance to fatigue failure. However, extremely high compressive stresses may cause either coating separation from the base metal or intra-coating spallation. Generally, if a tensile stress causes strain that exceeds the elastic limit of the coating, then it will cause cracking in the coating perpendicular to the direction of the stress. Therefore, understanding the formation of residual

stress in the coating is important to prevent the coating from peeling or cracking during service. Furthermore, residual stresses have significant influences on the mechanical and physical properties of the coatings, particularly electrical resistivity, optical reflectance, fatigue, and corrosion.

There are three types of residual stresses:

- Macrostresses, which are nearly homogeneous over macroscopic areas of the material
- Microstresses, which are nearly homogeneous over microscopic areas, such as one grain or subgrain
- Inhomogeneous microstresses, which are inhomogeneous even on a microscopic level

Residual macrostresses are the ones of most interest in engineering practice, because they can substantially affect component service performance. Both residual and inhomogeneous microstresses are of more interest in material science.

This article intends to provide a useful guide for measuring residual macrostress on a coating. The most commonly used measurement methods are mechanical deflection, x-ray diffraction, and hole-drilling strain-gage. After a discussion on the origins of residual stress, the fundamental principles, as well as examples of practical measurements, are described for each method.

Origins of Residual Stress

Residual macrostress in a coating combines the intrinsic stress and the thermal stress acting in the coating plane parallel to the coating/substrate interface:

$$\sigma_t = \sigma_i + \sigma_{th} \qquad \textbf{(Eq 1)}$$

where σ_t is the total macrostress, and σ_i and σ_{th} are intrinsic stress and thermal stress, respectively. Intrinsic stress results from the growth processes, depending primarily on deposition parameters, whereas thermal stress arises from a mismatch in coefficients of thermal expansion between the coating and the substrate.

Many phenomenological models have been proposed to explain the occurrence of intrinsic stresses by correlating them with a variety of coating microstructure and process features. To varying degrees, the intrinsic stress of a coating is associated with these deposition conditions and coating features:

- Incorporation of residual gas atoms in the coating
- Grain size, microvoid, and dislocation density in the coating
- Energetic particle bombardment during coating growth
- Lattice misfit between the substrate and the growing coating
- Combined effect of surface tension and growth process at grain boundaries
- Deposition temperature relative to the melting temperature of the coating material
- Annealing and shrinkage of disordered material buried behind the advancing surface of a growing coating

Although many studies have described the intrinsic stresses, information on the corresponding structural details is limited. It seems unlikely that one can formulate a generalized model of intrinsic stress for various coating materials and deposition processes.

Any coating that is prepared at elevated temperatures (T_2) and then cooled to room temperature (stress measurement temperature, T_1) will be thermally stressed because of the difference in the coefficients of thermal expansion between the coating and the substrate. Assuming no deformation of the substrate, the magnitude of the thermal stress in the coating is:

$$\sigma_{th} = (\alpha_c - \alpha_s)\,(T_2 - T_1)\,E_c/(1 - u_c) \qquad \textbf{(Eq 2)}$$

where α_c and α_s are the coefficients of thermal expansion for the coating and the substrate, respectively, and E_c and ν_c are the Young's modulus and Poisson's ratio of the coating, respectively. A coating deposited at an elevated temperature exhibits compressive stress if $\alpha_s > \alpha_c$, but tensile stress if $\alpha_s < \alpha_c$. In the case of $\alpha_s > \alpha_c$, the substrate shrinks more than the coating does during cooling from the deposition temperature and compresses the coating to maintain dimensional compatibility.

In some cases, thermal stress is the primary residual stress of the coating. For example, a titanium nitride coating can be deposited on a cemented carbide substrate (tungsten carbide-1 wt.% tantalum-10 wt.% cobalt) via a CVD process at 1000 °C (1830 °F). With the values of $\alpha_s = 5 \times 10^{-6}$/K, $\alpha_c = 9.54 \times 10^{-6}$/K, E_{TiN} = 411 GPa (60 × 10^6 psi) and $\nu_{TiN} = 0.24$, the stress in the coating, as calculated from Eq 2, is 2.39 GPa (0.35 × 10^6 psi) in tension at 25 °C (77 °F).

Deflection Method

The deflection method is the most widely used technique for determining the residual stress in a coating. In terms of basic principles, it involves measuring the amount of bending in a strip that is due to the deposition of the coating. A formula for calculating the residual stress in an electrodeposited coating was first derived by Stoney (Ref 1) in 1909. Subsequent researchers have derived more complex formulas to improve the accuracy of the stress evaluation. Comparative studies on those stress-evaluation formulas are reviewed and discussed elsewhere (Ref 2, 3, 4). Nearly all formulas are variants of Stoney's formula.

Consider a coating deposited on one side of a strip substrate. Both coating and substrate are assumed to be homogeneous. A mismatched force at the coating/substrate interface results in residual stress in the coating, which bends the strip either upward (concave) or downward (convex), depending on whether the stress is tensile or compressive. For overall force and moment equilibrium of the coating/substrate composite, it can be shown that the residual stress in the coating is (Ref 5):

$$\sigma_c = (E_s d_s^2) / [6(1 - \nu_s) R d_c] (d_s \ ? \ d_c) \qquad \textbf{(Eq 3)}$$

or, in general,

$$\sigma_c = \{E_s d_s^2 / [6(1 - \nu_s) R d_c]\} \{(1 + \Gamma \Theta^3) / (1 + \Theta)\} \qquad \textbf{(Eq 4)}$$

where

$$\Gamma = [E_c(1 - \nu_s)] / [E_s(1 - \nu_c)], \ \Theta = d_s / d_c, \text{ and } R \approx L^2 / 8f \approx L^2 / 2\delta \qquad \textbf{(Eq 5)}$$

where E is Young's modulus; ν is Poisson's ratio; d is thickness, with the subscript c denoting coating and s denoting substrate; R is the radius of curvature of the bent strip, L is the length of the strip, f is the deflection from the free end of the strip, and δ is the deflection at the center of the strip (Fig. 1).

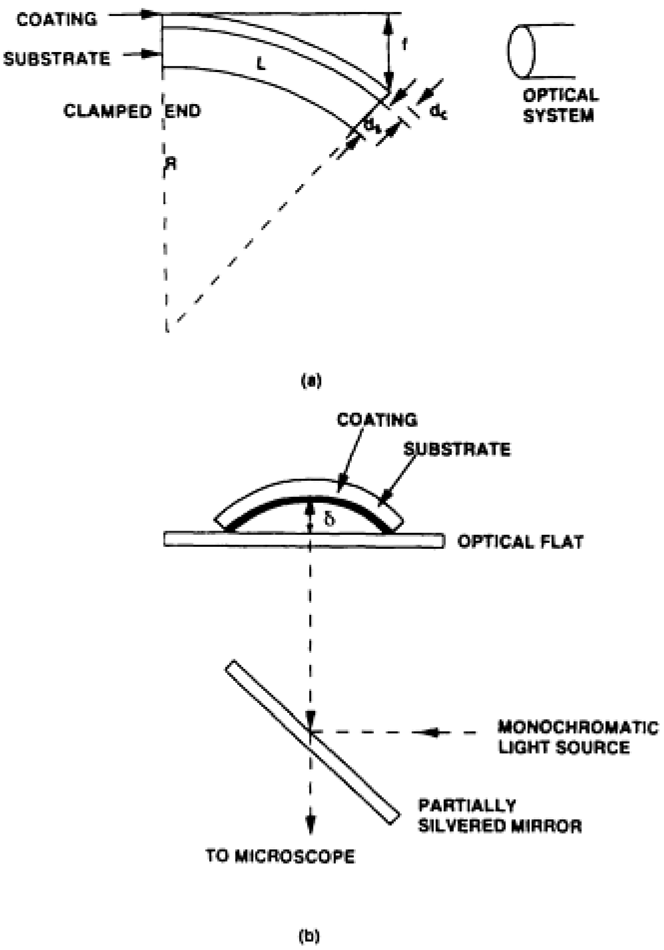


Fig. 1 Stress measurement techniques. (a) Bending of cantilever beam. (b) Disk deflection. Source: Ref 7

Although Eq 3 is most often used in practice and represents a generalized Stoney's formula for a planar state of stress, it tends to overestimate the value of measured stress. However, it does not require knowledge of the elastic properties of the coating. Equation 4 provides a much better approximation than Eq 3, but it does require knowledge of elastic properties. Equation 4 differs from Eq 3 in terms of a correction factor $[(1 + \Gamma \Theta^3)/(1 + \Theta)]$. Table 1 compares stresses as a function of d_s/d_c, calculated from both Eq 3 and 4. In the calculation, it was assumed that E_c = 400 GPa (60 × 10^6 psi), E_s = 200 GPa (30 × 10^6 psi), and $\nu_c = \nu_s$. It is clear that both equations are in good agreement when $d_s/d_c > 50$. By choosing a large value of d_s/d_c, the error can be minimized if Eq 3 is used.

Table 1 Comparison of average residual stress calculated using Eq 3 and 4

d_s/d_c	Calculated stress			
	Eq 3		Eq 4	
	MPa	ksi	MPa	ksi
200	-1143	-165.7	-1137	-164.9
100	-571	-82.8	-565	-81.9

50	-286	-41.5	-280	-40.6
20	-114	-16.5	-109	-15.8
10	-57	-8.3	-52	-7.5

Cantilever Beams. To measure the deflection of cantilever beams, various techniques have been developed (Ref 6), including optical, capacitance, mechanical, electromechanical, interferometric, and electromechanical or magnetic restoration. Figure 1(a) shows the setup for the deflection measurement when an optical system is used. In this example, a titanium nitride coating was deposited on a quartz beam via a PVD process, and the average residual stress in the coating was determined by measuring the amount of deflection at the free end, *f*, of the bent beam, according to the relation:

$$\sigma_c = [4E_s d_s^2 f] / [3(1 - \nu_s)L^2 d_c] \qquad \textbf{(Eq 6)}$$

With the values of E_s = 71.7 GPa (10.4×10^6 psi), ν_s = 0.16, d_s = 3 mm (0.12 in.), $d_c = 3 \times 10^{-6}$ m (1.2×10^{-4} in.), L = 50 mm (2 in.), and $f = 2 \times 10^{-6}$ m (8.0×10^{-5} in.), the stress in the coating is determined to be 273 MPa (40 ksi) in compression.

Disks. The average stress in the coating on a disk substrate can be determined from the amount of deflection, δ, at the center of the disk caused by the deposition of a coating on one side. This value can be measured optically by interferometry or microstylus profilometry. Figure 1(b) shows a typical interferometry apparatus setup. Either technique measures deflection at the same position, across a diameter of the disk, both before and after coating deposition. The stress in the coating is then calculated:

$$\sigma_c = \{E_s d_s^2 [(\Delta\delta_x + \Delta\delta_y) / 2]\} / [3(1 - u_s)r^2 d_c] \qquad \textbf{(Eq 7)}$$

where $\Delta\delta_x$ and $\Delta\delta_y$ are deflection changes measured before and after coating deposition, and *r* is the radius of the disk. Whether the stress is tensile or compressive, it is determined by the curvature of the disk before and after coating deposition, as determined by a depth microscope. When the change in curvature is upward (concave), viewed from the coating side, the stress in the coating is tensile. The opposite change in curvature indicates a compressive stress in the coating.

Typical interference fringe patterns are shown in Fig. 2. Figures 2(a) and 2(b) correspond to equal and unequal principal stresses of the same sign, whereas Fig. 2(c) corresponds to a biaxial stress state with principal stresses of opposite signs. Using Fig. 2(a) as an example, the measured defection, δ, is equal to the wavelength of monochromatic light multiplied by the number of light fringes (δ = 632.8 nm × 17).

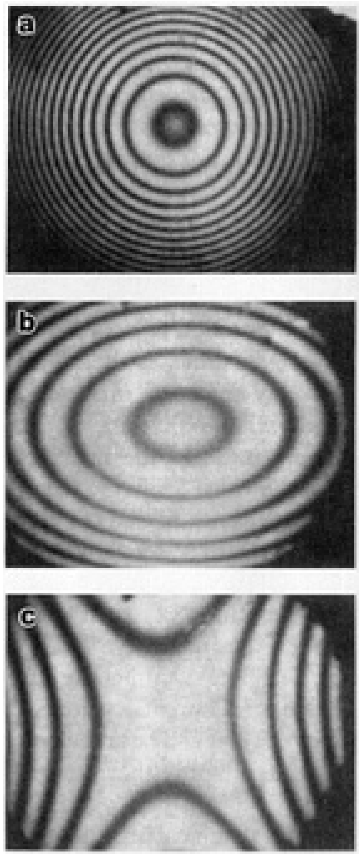


Fig. 2 Typical patterns of interference fringes. (a) $\sigma_x = \sigma_y$. (b) $\sigma_x \neq \sigma_y$, where both components are in compression or tension. (c) $\sigma_x \neq \sigma_y$, where one component is in compression and the other is in tension. Source: Ref 8

Figure 3 shows typical microstylus traces on the titanium nitride coated surface of an AISI 304 stainless steel disk, both before and after coating deposition. The curvature of the coated surface was downward (convex), viewed from the coated side. With the values of E_s = 193 GPa (28 × 10^6 psi), ν_s = 0.28, d_s = 4.74 mm (0.186 in.), r = 11.94 mm (0.4700 in.), d_c = 20 μm (800 μin.), and the deflection $\Delta\delta$= 6.3 × 10^{-6} m (2.5 × 10^{-4} in.), the stress in the titanium nitride coating is 4.44 GPa (0.644 × 10^6 psi) in compression. The measurement errors from both the optical and the microstylus trace setups are within one-half light band and ±0.1 μm (4 μin.), respectively.

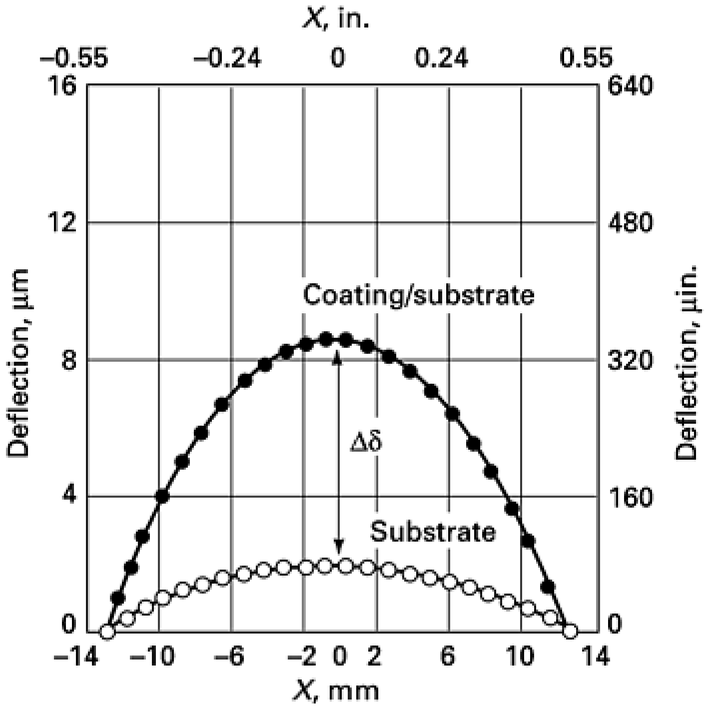


Fig. 3 Typical microstylus trace on titanium nitride-coated AISI 304 stainless steel disk before and after coating deposition

Practical Considerations. First, either strip or disk-shape substrate specimens should be parallel within 0.02 mm (0.001 in.) over their length or diameter. Specimen edges should be free from visible flaws and chips. In addition, the surfaces on which the deflection measurements (interferometer or profilometer) will be performed should be ground and lapped to a finish better than 0.08 μm R_a (3 μin. R_a).

Second, the dimensions of a strip of length L, width w, and substrate thickness d_s should obey $L > 10\ w > 10\ d_s$. The substrate thickness of a strip or disk depends on the coating thickness to be deposited. The thickness ratio of the substrate to the coating, d_s/d_c, should be greater than 50 to ensure the accuracy of the stress calculation from Eq 3.

Third, substrate specimens should be stress relieved before coating deposition. They should be placed between two stainless steel surface plates under at least an 8.8 kPa (1.3 psi) normal load, at an annealing temperature, in a vacuum furnace for at least 1 h. The annealing temperature is dependent on the substrate material.

Fourth, for coatings with an inherently smooth surface, such as those produced by PVD and CVD, the deflection can be determined either by interference fringe or microstylus profilometer measurements on the coated surface. For a coating with a relatively rough surface, such as those produced by thermal spraying and electroplating, the measurements can be made on the surface that is opposite the coated surface.

Significance and Use. The deflection measurement method is recommended for determining the average stress in the cross section of a coating with a thickness ranging from several hundred angstroms to several hundred micrometers. Typically, the elastic constants of a thin coating are much different from those of a bulk material. Equation 3 provides a means for stress measurement on a thin coating without any knowledge of its elastic constants. The measurement normally applies only to a test sample. The disk deflection method is particularly useful for the direct inspection of silicon wafers used in solar cells or integrated circuits.

References cited in this section

1. G.G. Stoney, *Proc. R. Soc. (London) A,* Vol 82, 1909, p 172

2. C.N. Kouyumdjev, *Surf. Technol.,* Vol 26, 1985, p 35
3. C.N. Kouyumdjev, *Surf. Technol.,* Vol 26, 1985, p 45
4. G. Sotirova and S. Armyanov, *Surf. Coat. Technol.,* Vol 28, 1986, p 33
5. M. Ohring, in *The Materials Science of Thin Films,* Academic Press Inc., 1991, p 461
6. D.S. Campbell, in *Handbook of Thin Film Technology,* L.I. Maissel and R. Glang, Ed., McGraw-Hill, 1970, p 12-21
7. R.W. Hoffman, in *Physics of Thin Films,* Vol 3, 1966, p 211
8. R.E. Cuthrell, D.M. Mattox, C.R. Peeples, P.L. Dreike, and K.P. Lamppa, *J. Vac. Sci. Technol.,* Vol 6A (No. 5), 1988, p 2914

X-ray Diffraction Method

Basic Principles. Stress measurement, using the x-ray diffraction method, is based on the change in the interplanar spacing (strain) close to the surface of the specimen material. The details of the theory and interpretation of residual stress measurements are well described in the article "X-Ray Diffraction Residual Stress Techniques" in Volume 10 of the *ASM Handbook*, as well as in Ref 9, 10, and 11. Consider an isotropic material with a lattice parameter d_0^{hkl} for unstressed material in the sample plane normal. The strain in a direction inclined by an angle y to the surface normal of the coating and the stress acting in the surface plane of the coating at an angle φwith the principal axis of the specimen are related by:

$$e_{jy}^{hkl} = (d_{jy}^{hkl} - d_0^{hkl}) / d_0^{hkl} = [(1 + \nu^{hkl}) / E^{hkl}] \\ (\sigma_x\cos^{2\varphi} + t_{xy}\sin^{2\varphi} + \sigma_y\sin^{2\varphi} - \sigma_z)\sin^2\psi \\ + [(1 + \nu^{hkl}) / E^{hkl}]\,\sigma_z - (\nu^{hkl} / E^{hkl})(\sigma_x + \sigma_y + \sigma_z) \\ + [(1 + \nu^{hkl}) / E^{hkl}]\,(t_{xz}\cos\varphi + t_{yz}\sin\varphi)\sin^2\psi \qquad \textbf{(Eq 8)}$$

where *h*,*k*, and *l* are the indices of the Bragg reflection; e_{jy}^{hkl} and d_{jy}^{hkl} $d\varphi\psi$ are the strain and interplanar spacing of (*hkl*) in the direction of (φ, ψ) respectively; ν^{hkl} and E^{hkl} are Poisson's ratio and Young's modulus in (*hkl*) in the coating; σ_x, σ_y and σ_z are normal stresses; t_{xy}, t_{yz}, and t_{xz} are shear stresses; σ_x is the normal stress acting in the *x* direction on a plane perpendicular to the *x* axis; and t_{yz} is the shear stress on a plane normal to the *y* axis (the first subscript) in the *z* direction (the second subscript). Residual stresses of the coating in various stress states can be determined using Eq 8.

Biaxial Stress. At a free plane, the out-of-plane stress components σ_z, τ_{xz}, and τ_{yz} are all zero, at a free surface. Because the penetration depth of x-rays is very small, the resulting measurements refer specifically to near-surface material. Plane stress conditions therefore often apply to x-ray measurements, and Eq 8 is simplified to:

$$e_{jy}^{hkl} = (d_{jy}^{hkl} - d_0^{hkl} / d_0^{hkl} = [(1 + \nu^{hkl}) / E^{hkl}] \\ \sigma\varphi\sin^2\psi + (\nu^{hkl} / E^{hkl})(\sigma_x + \sigma_y) \qquad \textbf{(Eq 9)}$$

where $\sigma\varphi = \sigma_x\cos^2\varphi + \sigma_y\sin^2\varphi$ is the macrostress in the coating parallel to its surface at an angle φwith the principal axis of the sample.

For a biaxial stress state, $\sigma_x = \sigma_y = \sigma\varphi$, and at $\psi = 0$,

$$(d_{j,y}^{hkl} = 0 - d_0^{hkl})/d_0^{hkl} = 2\nu^{hkl}\sigma\varphi / E^{hkl} \qquad \textbf{(Eq 10)}$$

From Eq 9 and 10,

$$d_{jy}^{hkl} = d_{j,y}^{hkl} = 0 + \sigma\varphi\, d_0^{hkl}\ [(1 + \nu^{hkl}) / E^{hkl}]\sin^2\psi \qquad \textbf{(Eq 11)}$$

In practice, high-angle diffraction peaks of an (*hkl*) reflection are obtained from -ψ to +ψ at a given angle φ. Lorentz polarization, absorption, and background corrections are applied to the diffraction peak profile. The peak positions are

determined by profile fitting or other methods and are subsequently converted to interplanar spacing $d_{\varphi\psi}^{hkl}$ for stress analysis.

In the linear plot of $d_{\varphi\psi}^{hkl}$ vs. $\sin^2\psi$, the intercept is $I = d_{\varphi\psi}^{hkl} = 0$ and the slope is $M = \sigma\varphi\, d_0^{hkl}\ [(1 + \nu^{hkl})/E^{hkl}]$ .The stress of the coating can then be determined by:

$$\sigma\varphi = M / \{ d_0^{hkl}\ [(1 + \nu^{hkl}) / E^{hkl}]\} \qquad \textbf{(Eq 12)}$$

Triaxial Stress State Without Shear Stress. For a material in a three-dimensional (triaxial) stress state without shear stress, but with the stress component σ_z having a finite value within the x-ray penetration volume, Eq 8 becomes (Ref 9, 11, 12):

$$\begin{aligned} e_{\varphi\psi}^{hkl} &= (d_{\varphi\psi}^{hkl} - d_0^{hkl}) / d_0^{hkl} \\ &= [(1 + \nu^{hkl}) / E^{hkl}](\sigma_x\cos^2\varphi + \sigma_y\sin^2\varphi - \sigma_z)\sin^2\psi \\ &\quad + [(1 + \nu^{hkl}) / E^{hkl}]\, \sigma_z \\ &\quad -(\nu^{hkl} / E^{hkl})\, (\sigma_x + \sigma_y + \sigma_z) \end{aligned} \qquad \textbf{(Eq 13)}$$

Two data sets, φ= 0° and φ= 90°, are needed to obtain σ_x, σ_y, and σ_z. The slopes and intercepts of a linear function of $d_{\varphi\psi}^{hkl}$ vs. $\sin^2\psi$ at φ= 0° and φ= 90° are given by:

$$\begin{aligned} M\varphi=0° &= d_0^{hkl}\ [(1 + \nu^{hkl}) / E^{hkl}]\, (\sigma_x - \sigma_z); \\ M\varphi=90° &= d_0^{hkl}\ [(1 + \nu^{hkl}) / E^{hkl}]\, (\sigma_y - \sigma_z); \\ I &= d_0^{hkl}\, \{[(1 + \nu^{khl}) / E^{hkl}]\, \sigma_z \\ &\quad -(\nu^{hkl} / E^{hkl})\, (\sigma_x + \sigma_y + \sigma_z)\} \end{aligned} \qquad \textbf{(Eq 14)}$$

Stresses σ_x, σ_y, and σ_z can be determined from the sum of the slopes and the intercept in Eq 14.

Triaxial Stress State With Shear Stress. A coating with a three-dimensional (triaxial) stress state, including shear stresses, is fully described by Eq 8. The shear stresses, t_{xz} and t_{yz}, have a $\sin^2\psi$ dependence. The $d_{\varphi\psi}^{hkl}$ vs. $\sin^2\psi$ distribution is no longer linear and has two branches of an ellipse for ψ> 0 and ψ< 0. This effect is termed "ψ splitting," which is an indication of the presence of shear stress.

To obtain these stress-tensor components, three data sets (φ = 0°, φ= 45°, and φ= 90°) are obtained for both -ψ and +ψ. The average strain a_1 and the deviation a_2 from the strains of "ψ splitting" are determined to be (Ref 9, 11, 12):

$$\begin{aligned} a_1 &= (e_{\varphi\psi}^{hkl} + e_{\varphi\psi}^{hkl} -) / 2 = [(d_{\varphi\psi}^{hkl} + d_{\varphi\psi}^{hkl}) / 2\, d_0^{hkl}] -1 \\ &= [(1 + \nu^{hkl}) / E^{hkl}]\, (\sigma_x\cos^2\varphi + t_{xy}\sin^2\varphi \\ &\quad + \sigma_y\sin^2\varphi - \sigma_z)\, \sin^2\psi + [(1 + \nu^{hkl}) / E^{hkl}]\, \sigma_z \\ &\quad - (\nu^{hkl} / E^{hkl})\, (\sigma_x + \sigma_y + \sigma_z), \end{aligned} \qquad \textbf{(Eq 15)}$$

$$\begin{aligned} a_2 &= (e_{\varphi\psi}^{hkl} + - e_{\varphi\psi}^{hkl} -) / 2 = (d_{\varphi\psi}^{hkl} - d_{\varphi\psi}^{hkl}) / 2\, d_0^{hkl} \\ &= [(1 + \nu^{hkl}) / E^{hkl}]\, (t_{xz}\cos\varphi + t_{yz}\sin\varphi)\, \sin^2\psi \end{aligned} \qquad \textbf{(Eq 16)}$$

The stress-tensor components can be calculated from the slopes of linear plots of a_1 vs. $\sin^2\psi$ and a_2 vs. $\sin^2\psi$. For a_1 vs. $\sin^2\psi$, (σ_x - σ_z) is obtained at φ= 0°, (σ_y - σ_z) at φ= 90°, and t_{xy} at φ= 45°, whereas σ_z is evaluated from the intercept if d_0^{hkl} is known. Similarly, t_{xz} and t_{yz} are obtained when φ= 0° and φ= 90 °, respectively, from the slope of a_2 vs. $\sin^2\psi$.

Stress Measurement. Modern diffractometers are fully automated and equipped with computer software for performing numerically intensive analyses. Diffractometers are capable of measuring residual stresses efficiently and economically. Typically, the measurement can be completed in several hours. The following examples illustrate some

stress measurements using Cu Kα radiation on cathodic arc PVD titanium nitride coatings on a substrate with various stress states.

Biaxial. An approximately 10 μm (400 μin.) thick coating of highly (111) oriented titanium nitride was deposited on AISI 304 stainless steel at 500 °C (930 °F). The x-ray diffraction $\sin^2\psi$ technique was applied to determine the residual stress in the (333)/(511) reflection of the coating. Figure 4 shows the linear distribution of d_{jy}^{hkl} vs. $\sin^2\psi$, indicating typical biaxial stress in the coating. As shown, the slope M = -1.1933 × 10^{-3} nm (4.698 × 10^{-11} in.) and the intercept I = $d_{jy}^{hkl} = 0$ = 0.082123 nm (0.003233 μin.). Young's modulus and Poisson's ratio for titanium nitride in (333)/(511) are 364 GPa (52.8 × 10^6 psi) and 0.245, respectively (Ref 13). The calculated residual stress for titanium coating is -4248 MPa (-615 ksi) in compression. For highly (111) oriented titanium nitride film, (511) contribution is negligible. This is addressed in Ref 13. The (422) reflection has 2θ < 130°, which is not desirable.

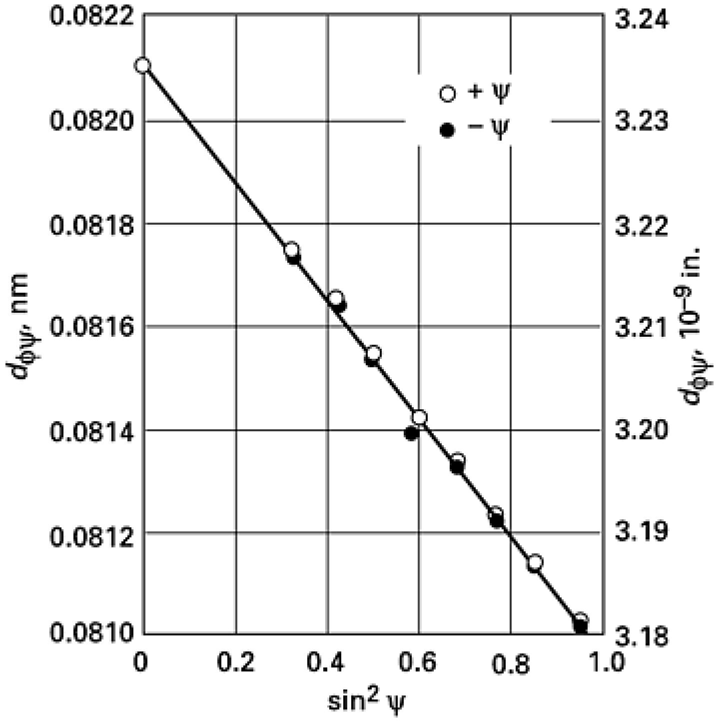


Fig. 4 Linear distribution of d_{jy}^{hkl} as a function of $\sin^2\psi$ of titanium nitride coating from (333)/(511) reflection

Triaxial Without Shear Stress. To exemplify a triaxial stress distribution, without shear stresses, triaxial stress analysis was applied to a titanium nitride coating deposited on Inconel 718 substrate at 550 °C (1020 °F). The d_{jy}^{hkl} vs. $\sin^2\psi$ distributions were obtained from (333)/(511) for φ= 0° and φ= 90° (Fig. 5). The slopes *Mφ=0* and *Mφ=90°* are -0.96782 and -1.01415 × 10^{-3} nm (-3.8103 and -3.9927 × 10^{-11} in.), respectively, and the intercept I is 0.082083 nm (0.003231 μin.). The strain-free interplanar spacing for (333)/(511) is 0.08160 nm (0.003213 μin.). Based on Eq 14, the stress tensor (σ_{ij}) from this analysis, in units of MPa, is:

$$s_{ij} = \begin{pmatrix} s_x & t_{xy} & t_{xz} \\ t_{yx} & s_y & t_{yz} \\ t_{zx} & t_{zy} & s_z \end{pmatrix} = \begin{pmatrix} -2653 \pm 151 & 0 & 0 \\ 0 & -2819 \pm 150 & 0 \\ 0 & 0 & 815 \pm 140 \end{pmatrix}$$

The result shows that the planar stresses are equal biaxial within experimental error and that the stress perpendicular to the coating surface is in tension.

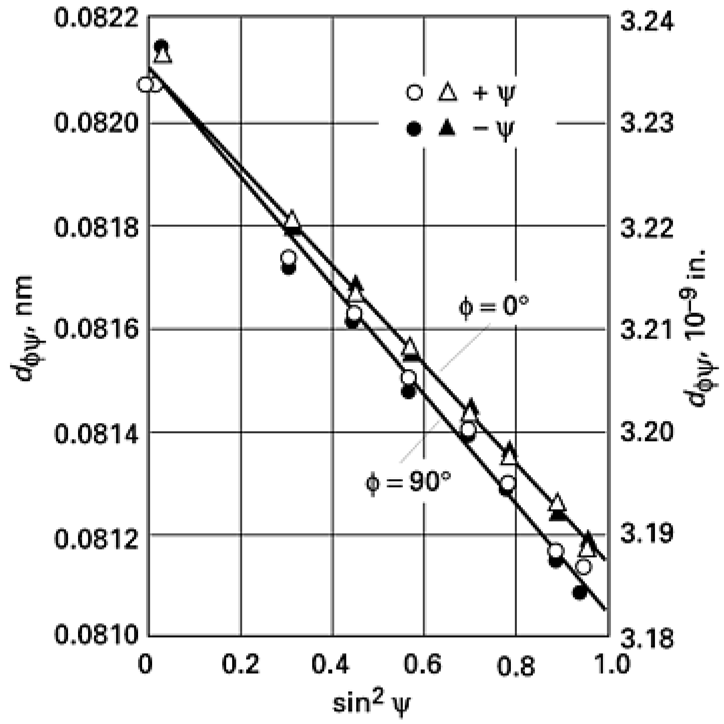


Fig. 5 Linear distribution of d_{jy}^{hkl} as a function of sin^{2}ψ of titanium nitride coating from (333)/(511) reflection at φ= 0° and φ= 90°

Triaxial With Shear Stress. A triaxial stress distribution, including shear stresses t_{xy}, t_{yz}, and t_{xz}, was studied in a cathodic arc PVD titanium nitride coating on AM-355 stainless steel. The d_{fy}^{hkl} vs. sin^{2}ψ distributions were obtained from (333)/(511) at φ= 0°, φ= 45°, and φ= 90° using Cu Kα radiation. Figure 6 shows the typical ellipse distribution of d_{jy}^{hkl} vs. sin^{2}ψ at φ= 0°. Based on analysis discussed at the beginning of this section, the stress tensor in the titanium nitride coating, in units of MPa, is:

$$s_{ij} = \begin{pmatrix} -2899 \pm 148 & 1 \pm 181 & 110 \pm 32 \\ 1 \pm 181 & -2776 \pm 148 & -34 \pm 34 \\ 110 \pm 32 & -34 \pm 34 & 833 \pm 148 \end{pmatrix}$$

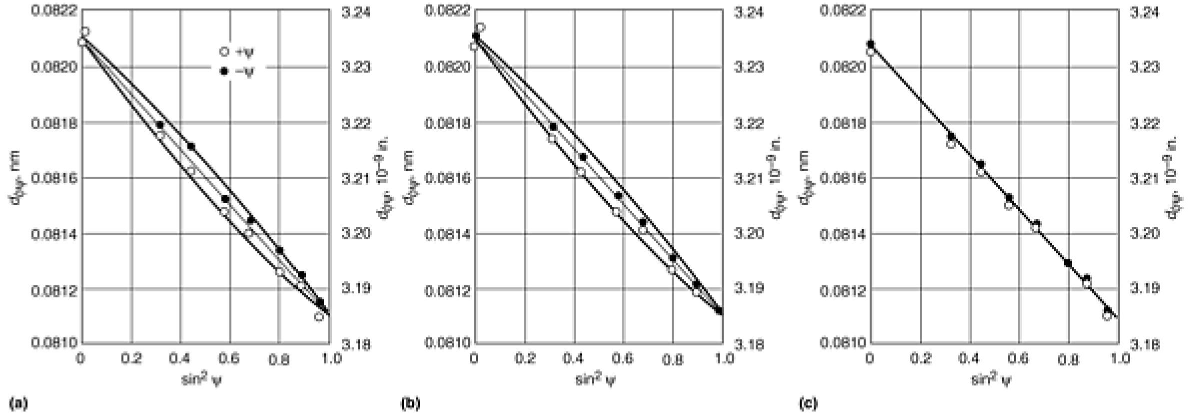


Fig. 6 Typical ellipse distribution of d_{jy}^{hkl} as a function of sin^{2}ψ of titanium nitride coating from (333)/(511) reflection at varying angles. (a) φ= 0°. (b) φ= 45°. (c) φ= 90°

Practical Considerations. First, a ψ-diffractometer is preferable for conducting stress measurements. The Ω-and ψ-diffractometers are defined on the basis of the sample axis for ψ tilt perpendicular or parallel to the plane of the incident and detected x-ray beam, respectively. A ψ-diffractometer gives symmetric irradiated areas in -ψ and +ψ tilted angles at a given (*hkl*) reflection line and a greater range of $\sin^2\psi$ (from 0 to 0.95 for a ψ-diffractometer and 0 to 0.5 for an Ω-diffractometer).

Second, the diffractometer should be mechanically aligned and calibrated using a stress-free standard sample (NIST SRM 660 lanthanum hexaboride powder or SRM 640 silicon powder) to obtain the peak position of the (*hkl*) reflection line within ±0.01° at Bragg angles 2θ in the range of ψ> 0 and ψ< 0.

Third, an appropriate x-ray wavelength should be selected to achieve the desired sampling volume (penetration depth) for a particular set of (*hkl*)planes. The penetration depth, which is defined as the distance from the surface to the depth with 63% or 1/*e* of the intensity of the reflection line, is calculated for Ω- and ψ-diffractometers, respectively:

$$t\ \Omega = (\sin^2\theta - \sin^2\psi) / [2\mu(\sin\theta \cos\psi)]$$
$$t\ \psi = (\sin\theta \cos\psi) / 2\mu$$

where μ is the linear absorption coefficient, which can be obtained from Ref 14 for various materials and radiations.

Fourth, to achieve high accuracy in residual stress, the measurement should only be carried out on an (*hkl*) reflection line with Bragg angles 2θ > 130° and with sufficient intensity for peak position determination.

Fifth, an appropriately sized collimator should be selected. It should have an irradiated area large enough to ensure that a statistically relevant number of grains or subgrains in the coating are included in the measurement. The angular resolution is essential in stress measurement. If the spot mode of x-ray beam cannot sample a sufficient number of grains, one should use another method.

Sixth, appropriate methods (Ref 9, 10, 15, 16, 17), such as modified Lorentzian, Gaussian, Cauchy, Pearson VII, parabola, center of gravity, gravity line, and cross correlation should be applied to determine the peak positions of the reflection line (*hkl*).

Seventh, a sufficient number of measurements in the -ψ and +ψ directions should be conducted to obtain an accurately linear distribution or ψ-splitting of d_{jy}^{hkl} vs. $\sin^2\psi$. The significance of this distribution should be verified by repeating measurements at different φangles. If a nonlinear relation other than ψ-splitting is obtained in the d_{jy}^{hkl} vs. $\sin^2\psi$ distribution, then the coating being measured is inhomogeneous and, therefore, the x-ray diffraction $\sin^2\psi$ method is no longer applicable.

Eighth, the x-ray elastic constants of the coating for an (*hkl*) plane, $S_1^{hkl} = -\nu^{hkl}/E^{hkl}$ and $S_2^{hkl}/2 = (1 + \nu^{hkl})/E^{hkl}$, can be calculated from single-crystal compliance, according to an appropriate model (Ref 11, 12), or measured experimentally in uniaxial tension or bending tests with a series of loads (Ref 13, 18, 19). X-ray elastic constants and applied loads (σ_a) obey these equations:

$$S_2^{hkl} / 2 = (1 + \nu^{hkl}) / E^{hkl}$$
$$= (1 / d_0^{hkl})[\partial / \partial \sigma_a(\partial d_{jy}^{hkl} / \partial \sin^2\psi)]$$
$$S_1^{hkl} = -\nu^{hkl} / E^{hkl} = [1 / (2 d_0^{hkl})](\partial d_{jy}^{hkl} = 0 / \partial\sigma_a)$$

Ninth, a stress-free interplanar spacing, d_0^{hkl}, for a coating may not be readily available in practice. For biaxial stress analysis, the lattice spacing measured at ψ= 0, $d_{jy}^{hkl} = 0$, can be substituted for d_0^{hkl}. In this case, the contribution to the total error is less than 0.1%. For a triaxial stress analysis, the difference between $d_{jy}^{hkl} = 0$ and d_0^{hkl} is included in the calculation. Consequently, a small error in d_0^{hkl} can lead to a relative large error in the measured stress. To obtain acceptable stress results, d_0^{hkl} must be within 0.01% of its true value. The stress-free interplanar spacing d_0^{hkl} in the strain-free direction ψ* is given by (Ref 20):

$$\sin^2\psi^* = [-S_1^{hkl} / (S_2^{hkl} / 2)] \{1 + [(\sigma_y - \sigma_z) / (\sigma_x - \sigma_z)] + [3 + (S_2^{hkl} / 2 S_1^{hkl}) \sigma_z] / (\sigma_x - \sigma_z)\}; \varphi=0$$

$$\sin^2\psi^* = [-S_1^{hkl} / (S_2^{hkl} / 2)] \{1 + [(\sigma_y - \sigma_z) / (\sigma_x - \sigma_z)]\}$$
$$\text{when } | \sigma_x + \sigma_y - 2\sigma_z | \ ? \ 2 | \sigma_z |$$

$$d_0^{hkl} = d_{jy}^{hkl} = 0 / [1 + S_1^{hkl} (\sigma_x + \sigma_y + \sigma_z) + (S_2^{hkl} / 2)\sigma_z]$$

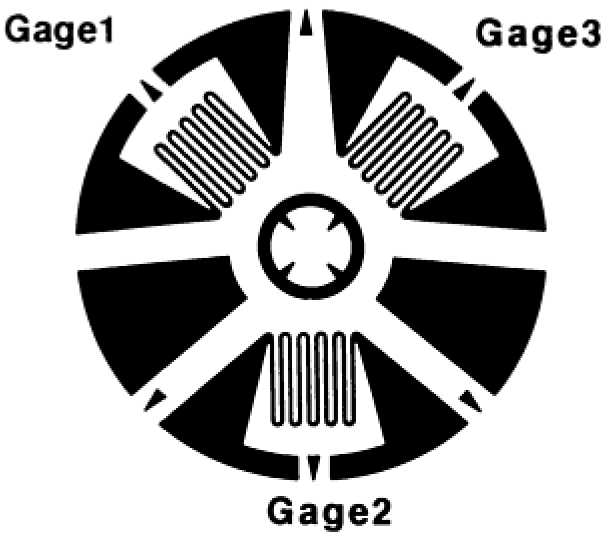
Significance and Use. The advantage of the x-ray diffraction method is its capability for measuring residual stress directly and nondestructively on a product component. Portable diffractometers are commercially available and can be used for on-site measurement. The method can apply to a coating with a thickness ranging from 0.5 to 350 μm (2×10^{-5} to 1.4×10^{-2} in.). However, it is difficult to measure residual stresses in extremely thin coatings and, in some cases, highly textured coatings. Furthermore, x-ray diffraction is inapplicable to amorphous coatings, and a large scatter in stress measurement is often encountered in coatings with large grain size.

References cited in this section

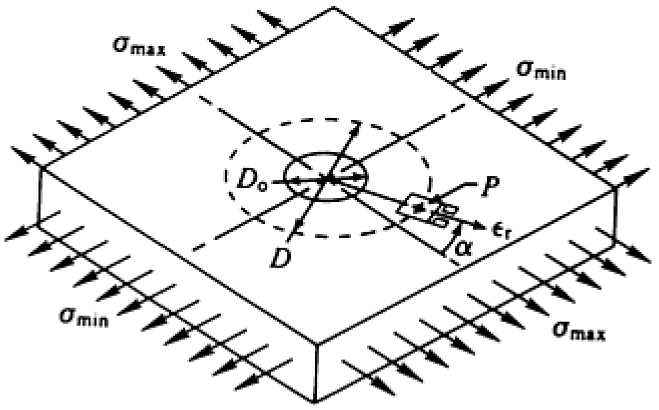
9. V.M. Hauk, *Adv. X-ray Anal.,* Vol 27, 1984, p 81
10. *Residual Stress Measurement by X-ray Diffraction,* SAE Handbook J784a, 2nd ed., Society of Automotive Engineers, 1971
11. I.C. Noyan and J.B. Cohen, in *Residual Stress Measurement by Diffraction and Interpretation,* B. Ilschner and N.J. Grant, Ed., Springer, 1987
12. H. Dolle, *J. Appl. Cryst.,* Vol 12, 1979, p 489
13. J.A. Sue, *Surf. Coat. Technol.,* Vol 54/55, 1992, p 154
14. C.H. Macgillavry and G.D. Rieck, Ed., *International Tables for X-ray Crystallography,* The Kynoch Press, Birmingham, 1962
15. W. Parrish, T.C. Huang, and G.L. Ayers, *Trans. Am. Cryst. Assoc.,* Vol 12, 1976, p 55
16. A. Brown and J.W. Edmonde, *Adv. X-ray Anal.,* Vol 23, 1980, p 361
17. A. Brown and S. Linde, *Adv. X-ray Anal.,* Vol 30, 1987, p 343
18. V. Hauk, in *International Conference on Residual Stresses,* ICRS2, G. Beck, S. Denis, and A. Simon, Ed., Elsevier, London, 1989, p 292
19. H. Behnken and V. Hauk, in *International Conference on Residual Stresses,* ICRS2, G. Beck, S. Denis, and A. Simon, Ed., Elsevier, London, 1989, p 341
20. V.M. Hauk, *Adv. X-ray Anal.,* Vol 27, 1984, p 101

Hole-Drilling Method

Basic Principles. The hole-drilling method for measuring residual stresses involves drilling a shallow hole in the test specimen to a depth approximately equal to the hole diameter. Typical hole diameters range from 0.8 to 5.0 mm (0.030 to 0.200 in.). The creation of the hole redistributes the stresses in the material surrounding the hole. A specially designed three-element strain-gage rosette, such as that shown in Fig. 7(a), measures the associated partial strain relief. The in-plane residual stresses that originally existed at the hole location can then be calculated from the measured strain reliefs using the method described in ASTM E 837-92 (Ref 21). The ASTM standard also gives details of practical drilling procedures.



(a)



(b)

Fig. 7 (a) Typical three-element strain-gage rosette. (b) In-plane strain components caused by release of residual stress through introduction of a hole. Source: Ref 21

The partial strain relief measured by one of the three strain gages in the rosette in Fig. 7(b) is related to the principal in-plane residual stresses by:

$$\varepsilon_r = (\sigma_{max} + \sigma_{min})A + (\sigma_{max} - \sigma_{min})B \cos 2\alpha \quad \textbf{(Eq 17)}$$

where σ_{max} and σ_{min} are maximum and minimum principal residual stresses, and α is the angle from the gage axis to the maximum principal stress direction. *A* and *B* are calibration constants, the values of which depend on the specimen material properties, the rosette geometry, the hole diameter, and the hole depth. ASTM E 837-92 tabulates the calibration constants for the standard rosette pattern shown in Fig. 7.

Equation 17 can be inverted to determine the principal residual stresses from the measured strain reliefs. The result is:

$$s_{max}, s_{min} = [(e_3 - e_1)/4A] \pm \{[(e_3 - e_1)^2 + (e_3 + e_1 - 2e_2)^2]^{1/2}/4B\}$$
$$b = \tfrac{1}{2}\arctan[(e_3 + e_1 - 2e_2)/(e_3 + e_1)]$$
(Eq 18)

where β is the angle measured clockwise from the location of gage 1 to the direction of σ_{max}. The above equations are valid for a homogeneous isotropic material that is wide, when compared with the hole diameter, and thick, when compared with the hole depth. The equations also apply to a through-the-thickness hole in a material in the form of a thin sheet, provided that the sheet thickness is uniform near the hole. The associated calibration constants have slightly different values than those of the thick-material case. Table 2, reproduced from ASTM E 837-92, lists the dimensionless calibration coefficients for both the thin-sheet and thick-material cases. *A* and *B* can be determined from the dimensionless coefficients using:

$$A = -(1 + \nu)\,\bar{a}/2E$$
$$B = -\bar{b}/2E$$
(Eq 19)

Table 2 Numerical values of dimensionless calibration coefficients $\bar{a}$ and $\bar{b}$

D_0/D	Through-the-thickness hole[(a)]		Blind hole[(b)], depth = 0.4 D	
	$\bar{a}$	$\bar{b}$	$\bar{a}$	$\bar{b}$
0.30	0.089	0.278	0.111	0.288
0.31	0.095	0.295	0.118	0.305
0.32	0.101	0.312	0.126	0.322
0.33	0.108	0.329	0.134	0.340
0.34	0.114	0.347	0.142	0.358
0.35	0.121	0.364	0.150	0.376
0.36	0.128	0.382	0.158	0.394
0.37	0.135	0.400	0.166	0.412
0.38	0.143	0.418	0.174	0.430
0.39	0.150	0.436	0.182	0.448
0.40	0.158	0.454	0.190	0.466
0.41	0.166	0.472	0.199	0.484

0.42	0.174	0.490	0.208	0.503
0.43	0.183	0.508	0.217	0.521
0.44	0.191	0.526	0.226	0.540
0.45	0.200	0.544	0.236	0.558
0.46	0.209	0.562	0.246	0.576
0.47	0.218	0.579	0.255	0.594
0.48	0.228	0.596	0.265	0.612
0.49	0.237	0.613	0.275	0.630
0.50	0.247	0.629	0.285	0.648

Source: ASTM E 837-92

(a) In a thin sheet.

(b) In a thick material.

Residual stress measurements in coated materials create an additional complication because the combination of coating and substrate is no longer a homogeneous material. The calibration coefficients provided in ASTM E 837-92 no longer accurately apply. However, the above two equations are still valid for coated materials, if the coating has a uniform thickness. If the substrate is less than several times greater than the hole depth, then it is also necessary for the substrate thickness to be uniform.

The calibration coefficients A and B for hole drilling in a coated material differ from the standard values given in ASTM E 837-92. The actual values depend on the elastic properties of the coating and the substrate, the coating thickness, and the hole diameter and depth. These coefficients can be determined by either experimental calibrations (Ref 22) using known externally applied stresses or finite-element calculations (Ref 23).

Approximate values of A and B for thick coatings can be estimated from the values given in ASTM E 837-92. For this purpose, a "thick" coating is one that is at least 0.25 times the mean radius of the strain-gage rosette. For the smallest commercially available hole-drilling rosette, the mean radius is about 1.25 mm (0.050 in.). Therefore, the minimum acceptable coating thickness is about 0.3 mm (0.012 in.).

An approximate estimation of A and B for a coated material is based on the observation that the hole-drilling method is most sensitive to the stresses closest to the specimen surface. Almost all of the measured strain relief is due to the stresses in the material within a depth of about 0.25 times the mean radius of the hole-drilling rosette. Thus, a specimen coated to at least this depth is likely to behave similarly to a homogeneous thick specimen consisting only of coating material. Thus, the A and B calibration coefficients for a "thick" coating are approximately equal to the ASTM tabulated values for a homogeneous material with the elastic properties of the coating.

The *A* and *B* coefficients for coatings that are thinner than 0.25 times the mean radius of the hole-drilling rosette will deviate significantly from the ASTM tabulated values. The coefficients must be determined on an individual basis, either by experimental or computational means. The use of the hole-drilling method with such "thin" coatings is not generally recommended because the sensitivity of the resulting strain measurements is rather low. As a result, small absolute errors in the strain measurements can cause large relative errors in the computed residual stresses.

Stress Measurement. The following example illustrates a hole-drilling measurement on a detonation gun type of tungsten carbide-cobalt (WC-Co) coating deposited on an AISI 1018 steel substrate. The coating was approximately 0.75 mm (0.03 in.) thick and had a macroscopically homogeneous structure. The elastic properties of the coating were E_c = 172 GPa (25 × 10^6 psi) and u_c = 0.3.

A 062-RE hole-drilling strain-gage rosette (5.13 mm, or 0.202 in., strain-gage mean diameter) was attached to the coated specimen. A 2.44 mm (0.096 in.) diameter hole was cut in the WC-Co coating by abrasive-jet drilling using 27 μm (1080 μin.) alumina particles. Drilling proceeded in four approximately equal depth increments, up to a final depth of 0.356 mm (0.014 in.). The strain measurements listed in Table 3 were made after each hole-depth increment. Using the *A* and *B* calibration coefficients from ASTM E 837-92, adjusted for the elastic properties of the coating material, the principal residual stresses in the coating were found to be -260 MPa (-38 ksi) and -286 MPa (-41 ksi), respectively. As might be anticipated, the residual stresses in the coating are approximately isotropic.

Table 3 Hole-drilling residual stress measurements on a detonation gun WC-Co coating

Depth		Strains, με			Average stress												α
					σ_x		σ_y		t_{xy}		σ_{max}		σ_{min}		t_{max}		
mm	in.	ε_1	ε_2	ε_3	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi	
0.00	0.000	0	0	0	-271	-39.3	-275	-39.9	-13	-1.9	-260	-37.7	-286	-41.5	13	1.9	41°
0.10	0.004	56	52	52	...	...	...	...	...	...	...	...	...	...	...	...	...
0.20	0.008	116	107	109	...	...	...	...	...	...	...	...	...	...	...	...	...
0.28	0.011	163	155	168	...	...	...	...	...	...	...	...	...	...	...	...	...
0.36	0.014	210	200	218	...	...	...	...	...	...	...	...	...	...	...	...	...

Note: Rosette type, EA-XX-062RE; Young's modulus, 172.0 GPa (25 × 10^6 psi); Poisson's ratio, 0.3; hole diameter, 2.440 mm

Practical considerations for the use of the hole-drilling method are:

- A high-speed drilling technique using carbide drills is recommended for producing a hole in a ductile coating. Abrasive-jet drilling is recommended for a brittle, hard coating (Ref 24).
- The use of specially made hole-drilling strain-gage rosettes is essential. The application of the strain-gage should follow the procedure recommended by the manufacturer.
- A smooth coating surface less than 0.41 μm R_a (16 μin. R_a) is desirable for secure strain-gage adhesion. An abrading or grinding process that does not induce significant residual surface stress should be used for surface preparation.
- The selection of an appropriately sized strain gage should be based on coating thickness, as well as on

the depth and diameter of the hole to be drilled. The diameter of the drilled hole, D_0, should be related to the diameter of the gage circle, D, where $0.3 < (D/D_0) < 0.5$.

- A depth microscope with a resolution better than 12.7 μm (0.0005 in.) should be used to measure the depth of the drilled hole at each depth increment.
- The center of the drilled hole should coincide with the center of the strain-gage circle within $\pm 0.015\ D_0$. A measurement microscope should be used to align the drill holder or abrasive-jet nozzle with the center of the rosette.
- Precautions should be taken to ensure that the walls of the drilled hole are square to the coating surface on which the rosette is cemented. It is important to protect the strain gage from abrasive-particle erosion or mechanical damage during the drilling operation.
- Values for the Young's modulus and Poisson's ratio of the coating should be independently measured in order to determine the residual stress from strain relaxations.

Significance and Use. The hole-drilling strain-gage method is a semidestructive technique for measuring residual stress on a coating with a thickness of at least 0.1 mm (0.004 in.). The method, which is quite versatile, can apply to test samples as well as to actual components with complex geometries. Furthermore, it can be used for on-site measurements.

References cited in this section

21. "Determining Residual Stresses by the Hole-Drilling Strain-Gage Method," E 837-92, *Annual Book of ASTM Standards,* ASTM
22. "Measurements of Residual Stresses by Hole-Drilling Strain Gage Method," TN503-4, Measurements Group, Wendell, NC, 1993
23. G.S. Schajer, *J. Eng. Mater. Technol. (Trans. ASME),* Vol 103 (No. 2), 1981, p 157
24. M.T. Flaman and J.A. Herring, *Exp. Tech.,* Vol 9 (No. 8), 1985, p 30

Method Comparison

The mechanical-deflection method is capable of measuring the average stress throughout the coating thickness, but requires the stress to be uniform over large distances in the in-plane directions. In contrast, the x-ray diffraction and hole-drilling methods can make a much more localized measurement in-plane, but they have a significantly more limited depth capability. A good agreement in stress measurements between the deflection and x-ray diffraction methods has been demonstrated (Ref 13). With the extrapolation of blind-hole measurements to the near surface, the stress measurement is in good agreement with that measured by x-ray diffraction (Ref 25). A user can select the most suitable method based on economics, environment, coating microstructures, and the geometry of the component to be measured.

References cited in this section

13. J.A. Sue, *Surf. Coat. Technol.,* Vol 54/55, 1992, p 154
25. C.O. Ruud, P.S. DiMascio and J.J. Yavelak, *Exp. Mech.,* Vol 25 (No. 4), 1985, p 338

Testing of Stability and Thermal Properties of Thermal Barrier Coatings

Thomas A. Taylor, Praxair Surface Technologies, Inc.; Ray E. Taylor, Purdue University

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Introduction

THERMAL BARRIER COATINGS (TBCs) are applied to metallic components of advanced heat engines to reduce the metal temperature, increase the environmental resistance and life of the component, and in some cases reduce noxious exhaust emissions. This thin coating usually consists of a metallic bond coat applied to the metal component, followed by a layer of magnesia- or yttria-stabilized zirconia (YSZ). If the TBC is on nickel- or cobalt-base superalloy components

intended for high-temperature operation, it is advisable to heat treat the TBC to achieve bond coat densification and diffusion bonding to the substrate. The selection of the TBC system involves many considerations, principally knowledge of the intended service conditions, temperature reduction expectations, component life estimates, cost, and in some cases the external surface finish requirements. It is implicit that a successful TBC will also survive the rigors of service without spalling or eroding. This article discusses the various tests applied to the TBC system, and to the zirconia layer separately, to establish thermal design properties and thermomechanical and environmental stability.

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Thermomechanical Stability

The TBC system is expected to survive the thermal shock of rapid cycle heating and cooling, as experienced in gas turbine or diesel engines, without spallation. Spallation is the result of the thermal stress pattern created when the thermal cycle repeatedly exceeds the stress for crack growth within the zirconia layer. This results in a time-dependent extension of pre-existing cracks within the plane of the coating until critical link-up and spallation. In many tests, the location of the spall line is in the zirconia layer, but near the bond coat interface. In the finite element modeling studies of Chang et al. (Ref 1), the near-interface area in the zirconia layer was shown to be the high-stress zone in simulated thermal cycling. In the thermal spray process, the crack nuclei are probably the interfaces between splats in the coating.

Two strategies to improve the resistance to in-plane crack growth in thermally sprayed zirconias are to use a low-density coating, with the pores acting to blunt growing cracks, or to increase the cohesive strength between splats, which requires high-density coating conditions. In the first case, 12 to 15% porosity is useful, and in the latter case, it is critical to generate macrocracks vertical to the plane of the coating, spaced about 0.2 to 1 mm apart, to relieve short-range stress (Ref 2). In physical vapor deposition coating, the zirconia deposition conditions are adjusted to grow columnar grains, which similarly reduce the in-plane modulus and limit the accumulation of coating stress during a thermal cycle.

Thermal Fatigue Testing. Laboratory testing has been used, particularly in the coating development stage, to cycle thermally a TBC specimen followed by post-test microscopic examination for spallation-type cracks. The thermal cycle for evaluation of thermal shock resistance employs rapid heating and cooling rates, using direct impingement flames or heating jets on the oxide face of the specimen, with little hold time at the maximum temperature. This test principally challenges the oxide layer, because the bond coat remains at relatively low temperatures due to the insulating nature of the zirconia layer and the short time at high temperatures.

Figure 1 illustrates a cycle that simulates the thermal shock of first-stage gas turbine outer airseals with a zirconia layer 1.27 mm (0.050 in.) thick. Detail of the flame impingement on the button sample is shown in Fig. 2. The test sample is a 25 mm (1 in.) diameter button, 3.2 mm (0.125 in.) thick, made from the substrate alloy of interest. After the button is coated with the TBC system, the edges are ground and polished to produce a square edge to allow examination of the coating layers.

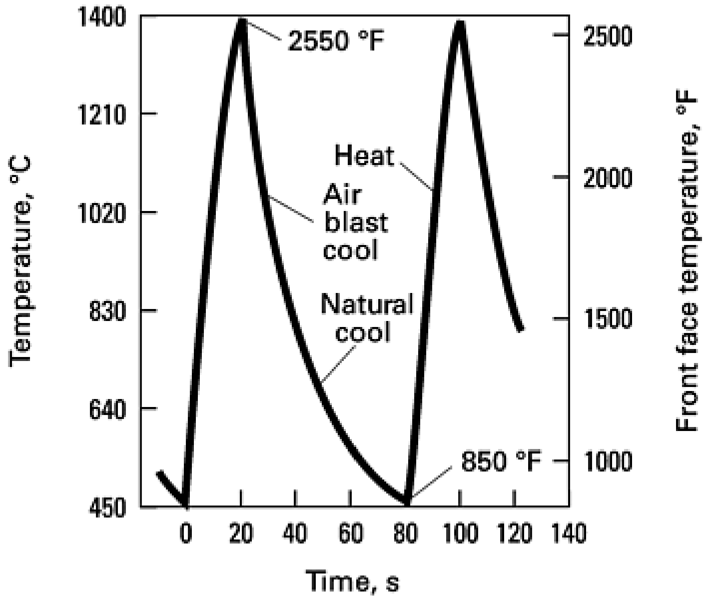

Fig. 1 Schematic illustration of oxide surface temperature cycle used for thermal fatigue testing of ZrO_2-coated test buttons 1.27 mm (0.050 in.) thick, simulating a first-stage gas turbine outer airseal application

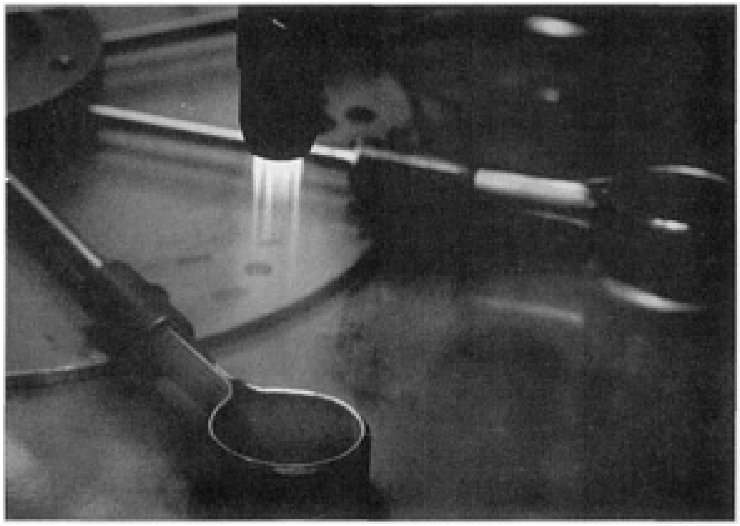

Fig. 2 Flame impingement on the button sample in a thermal fatigue test rig

The test rig consists of an oxygen-propane or propylene burner, a fixture arm to hold the button sample, a stepping motor system to advance quickly between stations and to hold for prescribed times in the heating and cooling positions, and a means to record at least the front oxide face temperature during the heating cycle. Two-color infrared optical pyrometers are widely used for the latter task, with the output connected to a chart recorder or computer. One word of caution concerning the temperature measured. If the zirconia coating is not an ideal gray body, that is, the emissivity is not the same at the two wavelengths used by the pyrometer, the reading may be in error. This issue is under study at several test facilities, and it could affect burner rig tests as well. If the samples being tested are all the same material, such as plasma-sprayed 8% YSZ coatings of common thickness, the measured temperatures should be relatively correct.

In one test configuration, the heating cycle is 20 s, followed by a 20 s air blast and two 20 s periods of natural convection cooling. The burner-to-specimen standoff, burner size, and gas flows are set to heat the oxide face of a standard specimen rapidly to 1400 °C (2550 °F) in the first 20 s. The air blast then drops the front face temperature to about 815 °C (1500 °F), and it finally reaches about 454 °C (850 °F) after 40 s of natural cooling. After the cycle is repeated 2000 times, the

edge of the coated button is examined at 10× to 30× for evidence of separation-type cracking in the zirconia layer. The specimen edge should also be inspected before the test, with few to no starting cracks expected.

The post-test cracking of good TBC systems having zirconia thicknesses of about 1.27 mm (0.050 in.) should be less than 15% of the circumference, and typically much less. If a tested specimen is mounted in cross section and serially polished, it will be seen that the crack is indeed at the edge of the coating and extends inward toward the center of the button. The cracks will continue to extend around the circumference and grow inward until eventual spallation, for the case of a TBC with poor thermal fatigue resistance. In good TBC systems, additional sets of 2000 cycles will show little crack growth, if any, and typically at a lower rate than in the first test period.

It has been found that the edge-cracking rate is a function of the zirconia coating density (Ref 2), as shown in Fig. 3. In addition, use of the conventional tensile bond-cap test (ASTM C 633-79) has shown that the higher-density coatings have increasing cohesive strength within the zirconia (Ref 2). The result of Fig. 3 must be further qualified. The coatings of density above about 90% of theoretical density (below 10% porosity) also had intentional long macrocracks throughout the coating running perpendicular to the coating plane. Without these macrocracks, the higher-density zirconia coatings will spall quickly, perhaps even on the first thermal cycle.

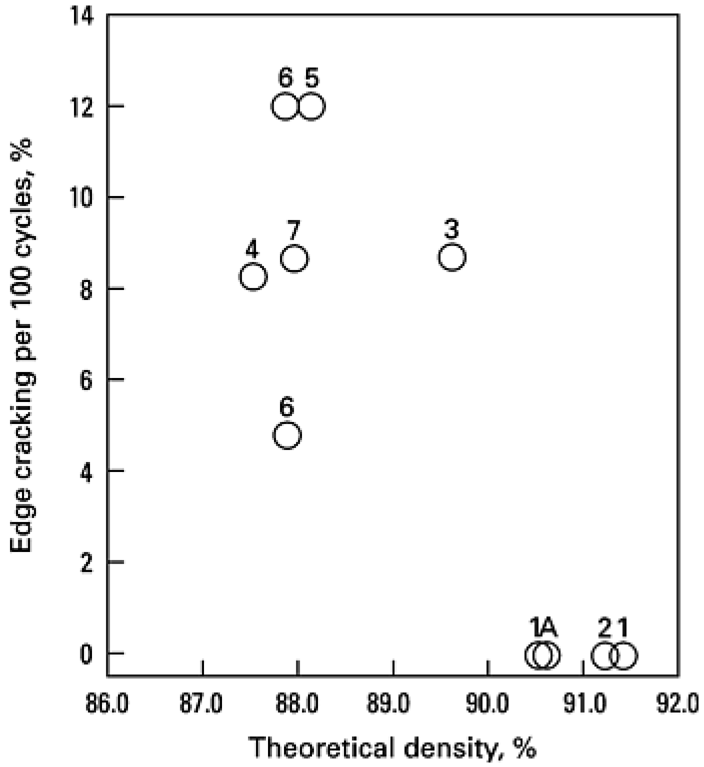

Fig. 3 Thermal fatigue edge-cracking rate for thick ZrO_2 coatings as a function of coating density. Thermal fatigue test with peak temperature of 1400 °C (2550 °F) and 1.1 to 1.3 mm (0.4 to 0.5 in.) thick oxide. Specimen numbers allow correlation to Fig. 4. Source: Ref 2

If the back metal side of the button specimen also has temperature instrumentation, the differential front-to-back temperature drop, ΔT, can be measured at the peak of the heating cycle. Figure 4 shows that ΔT is also related to coating density, with lower-density coatings having greater thermal insulation.

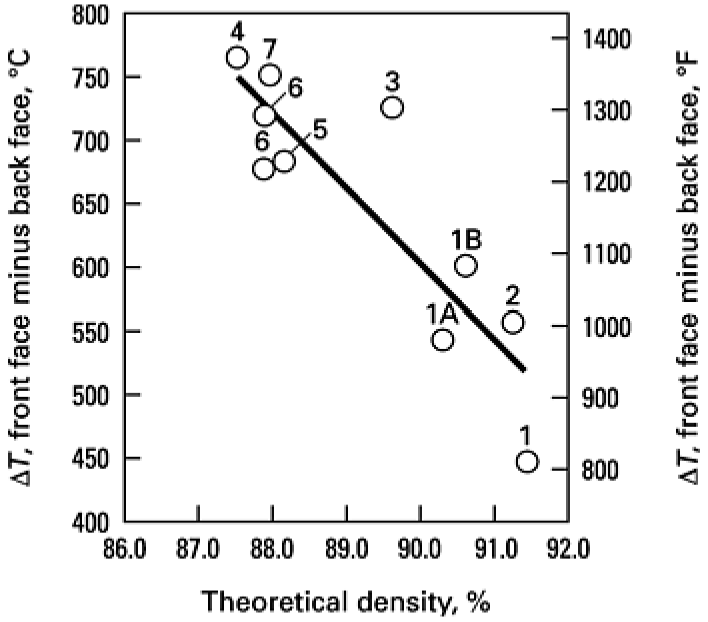

Fig. 4 Temperature drop across thick ZrO_2 coatings on an IN 718 substrate (thickness, 3.2 mm) as a function of ZrO_2 coating density. Thermal fatigue test with peak temperature of 1400 °C (2550 °F) and 1.1 to 1.3 mm (0.4 to 0.5 in.) thick oxide. Specimen numbers allow correlation to Fig. 3. Source: Ref 2

The same rapid heating test rig can be used to evaluate thin TBCs. On aircraft turbine components such as first-stage blades or vanes, the zirconia thickness required may be from 0.13 to 0.30 mm (0.005 to 0.012 in.), and on combustion chambers, 0.30 to 0.38 mm (0.012 to 0.015 in.). If the front face oxide peak temperature is set at 1400 °C (2550 °F) on a standard YSZ sample of 90 to 91% theoretical density and 1.27 mm (0.050 in.) thickness, specimens with thinner zirconia layers will reach lower temperatures in the same test cycle, while those with thicker layers will reach higher temperatures. Figure 5 shows this dependence on oxide layer thickness when other conditions are constant. For this reason, the burner parameters should be set using a standard sample to ensure a constant heat flux for all tests. One way to do this is to have a rotary carousel of samples, including one standard sample, that provides a check on the test conditions every time it cycles through the heating station. The parameter ΔT will also increase with zirconia thickness, as one would expect. Furthermore, the edge-cracking rate will depend on coating thickness for constant coating density and structure. For example, a dense macrocracked TBC specimen 0.30 to 0.38 mm (0.012 to 0.015 in.) thick can easily sustain 20,000 or more of the above cycles without edge cracking.

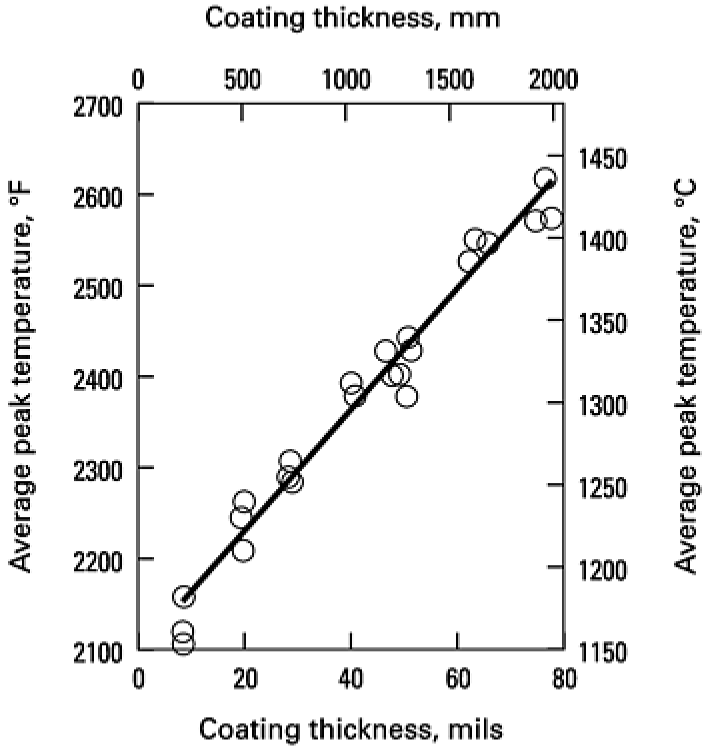

Fig. 5 Peak temperature of zirconia surface for ZrO_2 coatings as a function of coating thickness, in standard thermal cycle test of Fig. 1 (20 s cycle to 1400 °C, or 2550 °F). All samples were run at the same relative heat flux (1330 °C, or 2423 °F, on a nominal coating 1270 μm, or 50 mils, thick).

A similar thermal fatigue test cycle can be established for testing TBCs for the diesel environment. In this case, the heat flux across the TBC is expected to be greater than in gas turbines, but the peak temperature is expected to be lower. In one test configuration, the burners were moved closer to the oxide face of the coated button, the heating cycle was reduced to 8 s, and the peak oxide temperature was held to 982 °C (1800 °F).

Another testing approach, used by aircraft gas turbine manufacturers and the National Aeronautics and Space Administration, is to coat solid 1.2 cm (0.5 in.) diameter burner bars and expose a rapidly rotating carousel of bars to a high-velocity fuel-oxygen burner. This test has the advantage of allowing use of commercial engine fuel, with controlled doping of known impurities such as sulfur or vanadium if desired. Substrate-side air cooling is sometimes introduced by using hollow bars, to make the test a better simulation of actual coated hardware conditions where back-side cooling is typical.

Although the button tests establish the capability of the basic coating candidate, the button and burner bar coating conditions are usually ideal. Only on real components will practical issues such as the effect of component geometry on the coating structure be faced. One further stage of testing might be considered: putting actual coated components in large thermal cycling chambers. Even so, the laboratory screening tests described above should be followed by actual engine tests of components with TBCs.

References cited in this section

1. G.C. Chang, W. Phucharoen, and R.A. Miller, Finite Element Thermal Stress Solutions for Thermal Barrier Coatings, *Surf. Coat. Technol.,* Vol 32, 1987, p 305-325
2. T.A. Taylor, D.L. Appleby, A.E. Weatherill, and J. Griffiths, Plasma-Sprayed Yttria-Stabilized Zirconia Coatings: Structure-Property Relationships, *Surf. Coat. Technol.,* Vol 43/44, 1990, p 470-480

Environmental Stability

A TBC must also resist environmental degradation. This may occur as oxidation of the bond coat, phase transformation stress deterioration of the zirconia layer, or chemical destabilization of the oxide layer. The severity of these effects depends on the oxidation resistance of the bond coat, the initial crystalline phase mixture of the zirconia coating, the service temperature, and the environmental impurities present.

Bond Coat Oxidation. To test the oxidation resistance of the bond coat and its effect on the spallation of the TBC, a thermal cycle needs to combine extended soak time at high temperatures with periodic heating and cooling cycling to induce thermal stress. One such cycle used to test TBCs for aircraft gas turbine applications is a simple tube furnace that operates at a constant temperature of 1121 °C (2050 °F), with the sample set pneumatically moved in and out of the hot zone. The TBC samples rest on an alumina firebrick boat, with dense alumina pushrods made from thermocouple insulator ceramics, for an all-oxide hot-zone support system. The samples heat to furnace temperature in about 5 min, soak for 50 min, and then are quickly pulled out for a 5 min cooling period. At the end of every 25 cycles, the samples are held out and visually examined at room temperature. After 200 cycles, the samples are inspected for spallation or edge cracking, then are mounted in plastic for evaluation in polished cross section. There the extent of bond coat oxidation and interface cracking can be measured. The test temperature is as much as 110 °C (200 °F) higher than expected for the component in service and is thus an accelerated test for oxidation of the bond coat. To make this comparison test valid, care should be taken that the furnace temperature profile is uniform and covers the full zone occupied by the TBC samples.

A cycle for testing coatings for diesel applications can be similarly designed by setting the soak temperature about 110 °C (200 °F) higher than the measured steady-state temperature of the substrate metal of the component in question. In the case of coatings for steel or cast iron substrates, the bond coat is typically not heat treated, which may allow internal oxidation of the Ni-Cr or Fe-Cr-Al-Y alloys used for thermally sprayed layers. Thus, a cycle soak temperature of 650 to 982 °C (1200 to 1800 °F) may still challenge inadequate coating systems.

Zirconium Oxide Phase Stability. Pure zirconium oxide is an allotropic material and has a cubic structure from its freezing point at 2680 °C (4856 °F) down to 2370 °C (4298 °F), where it transforms to a tetragonal structure of similar cell size. Because of this small difference in crystalline cell volume, thermal cycling across the cubic-tetragonal transition temperature does not impose severe internal stresses. Following further cooling to below 1170 °C (2138 °F), zirconia transforms to the monoclinic structure, which has about a 4% larger crystalline cell volume than the tetragonal structure (Ref 3). Large internal stresses are generated as the transformation front sweeps through the material, which can lead to crack initiation. Commercially useful zirconia is alloyed with yttria, which has a cubic-plus-tetragonal two-phase field in its phase diagram (Fig. 6) and inhibits the low-temperature tetragonal-to-monoclinic transformation (Ref 3, 5, 6).

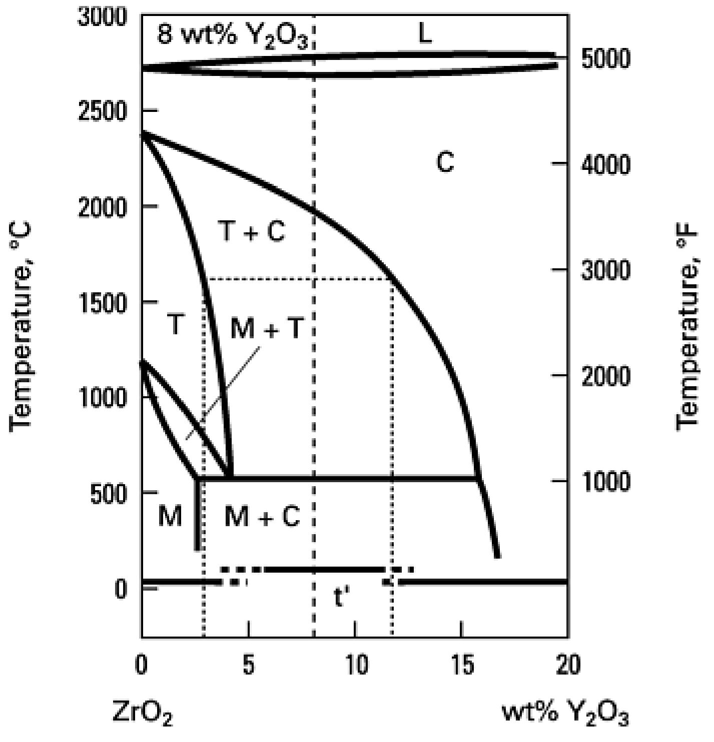

Fig. 6 Phase diagram of the ZrO_2-rich region of the ZrO_2-Y_2O_3 system. M, monoclinic phase; C, cubic phase; T, tetragonal phase; L, liquid; t, nontransformable tetragonal. Source: Ref 4

In thermally sprayed yttria-stabilized coatings, the feedstock is powder, which may be fabricated by a variety of methods (Ref 7). Partially stabilized zirconia, with about 6.5 to 9 wt% Y, mostly avoids the monoclinic phase and the fully stabilized cubic-only phase, which is known to have less thermal shock resistance than the dual-phase cubic-plus-tetragonal structure (Ref 8). A powder feedstock may have the correct average yttria content, but it may not be homogeneous at the crystalline grain level. An inhomogeneous powder may have some local volumes that have no yttria and others with yttria concentrations far higher than the bulk analysis. The x-ray diffraction pattern of such a powder thus shows the monoclinic phase characteristic of the nearly pure zirconia grains, along with tetragonal and cubic phases from the volume of the material that was sufficiently combined with yttria. When an inhomogeneous powder is plasma sprayed to form a coating, the particle melting in the arc improves the degree of homogeneity. However, this may not be sufficient to fully homogenize the material, depending on the state of the starting powder and the chosen spray parameters.

Figure 7 shows the x-ray diffraction patterns of an inhomogeneous powder and a sprayed coating. In this example, the spray conditions did eliminate nearly all of the starting monoclinic phase. The following table gives the phase distribution for the two materials in Fig. 7, based on the areas under the diffraction peaks:

Material	**Phase, mol%**		
	Monoclinic	**Tetragonal**	**Cubic**
Starting powder	6	76	18

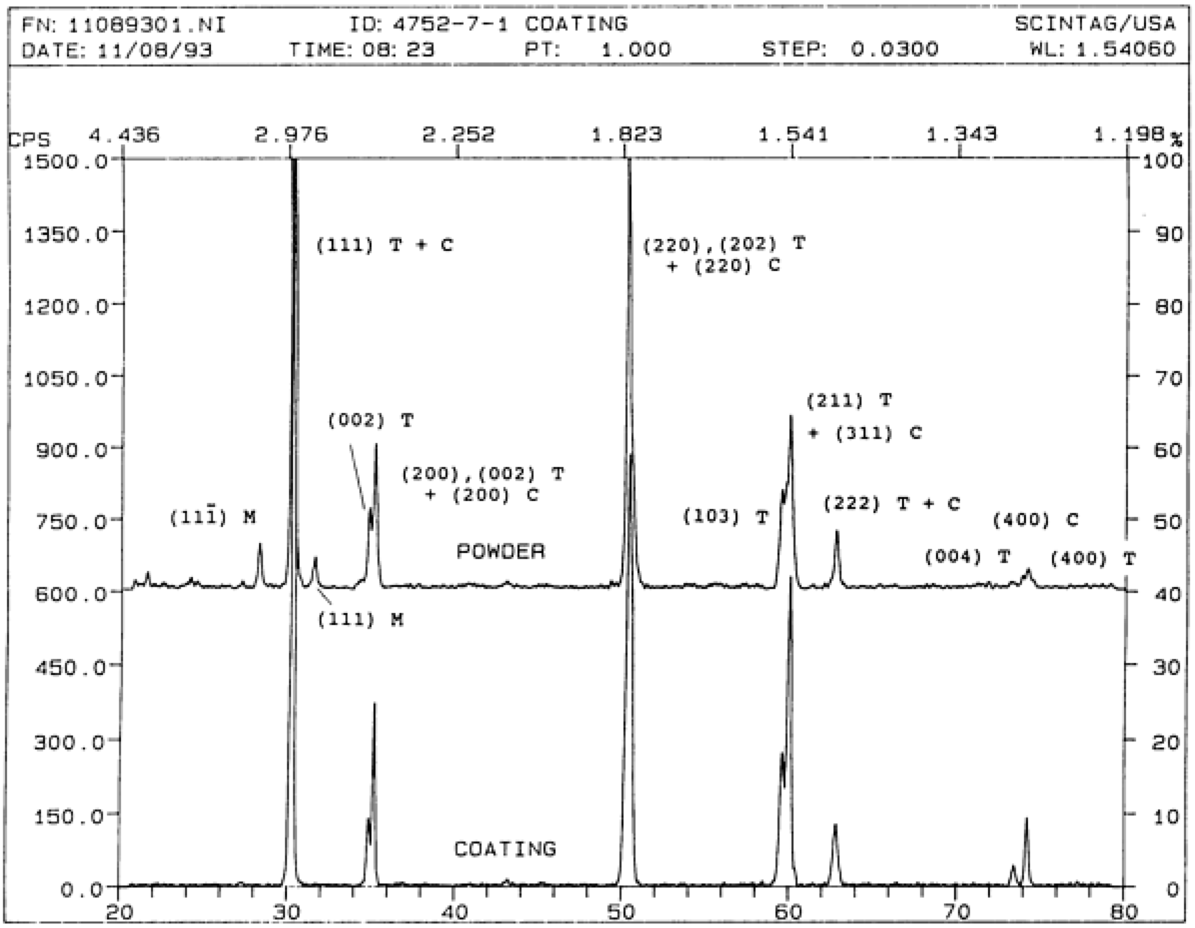

Fig. 7 X-ray diffraction patterns of yttria-stabilized zirconia powder showing some monoclinic phase, and of a coating made from that powder. M, monoclinic phase; C, cubic phase; T, tetragonal phase; T + C, overlapping tetragonal and cubic reflection

The values in the table were obtained with the Miller algorithm (Ref 6):

$$\frac{M}{T+C} = 0.82\frac{I_{(11\bar{1})M} + I_{(111)M}}{I_{(111)T+C}} \qquad \textbf{(Eq 1)}$$

$$\frac{C}{T} = 0.82\frac{I_{(400)C}}{I_{(400)T} + I_{(004)T}} \qquad \textbf{(Eq 2)}$$

$$M+T+C = 1.00 \qquad \textbf{(Eq 3)}$$

where M, T, and C denote the mole percentages of the monoclinic, tetragonal, and cubic phases, respectively, and $I_{(hkl)}$ is the integrated intensity for the (hkl) diffraction peak. For the high-angle (400) peaks, a deconvolution routine was used first to separate the three overlapping peaks.

Not all TBCs need to be made from homogeneous 6 to 9 wt% YSZ. The importance of the degree of homogeneity and the allowable amount of monoclinic phase in the starting powder depend on the maximum temperature to be experienced by the TBC. Consider the zirconia-yttria phase diagram in Fig. 6 in the following argument. Assume that a coating made from inhomogeneous 8% YSZ powder has some fraction of grains of very low yttria content. These grains will behave as if they were a separate entity and experience the phase transitions characteristic of nearly pure zirconia. At room temperature these grains should exist in the monoclinic structure. The other grains may be partially stabilized with yttria and exist mainly as the nontransformable tetragonal phase, and possibly some cubic-phase material. These higher-yttria-content nontransformable tetragonal grains exist as a nonequilibrium phase because of the rapid quench from the liquid

state upon deposition at the substrate. They have high thermal fatigue resistance because they will not transform to the monoclinic phase and experience the large volume change. On the other hand, the nearly pure zirconia grains having the monoclinic structure may be safe from transformation stresses as long as they remain below the temperature of the M + T two-phase field, which can be as high as about 1100 °C (2000 °F).

Therefore, coated components that have a maximum exposure of only 760 °C (1400 °F) should be stable against deleterious phase transformation, even though they may have a zirconia coating composed of both stabilized and unstabilized grains. As the operating temperature of the component increases, the need for a homogeneous coating increases. Applications at temperatures above about 1100 °C (2000 °F) should require fully homogeneous coatings. For applications at 760 to 1100 °C, thermal cycle testing is needed to determine whether the powder and coating process selected are adequate. If monoclinic-phase material exists in the coating and is tested with flame impingement on the oxide face to temperatures that cycle through the transformation temperature, the surface layer will begin to flake away small particles. Because of the insulating effect of zirconia, the lower layers of the coating would be at a lower temperature and thus remain intact. If the same nonhomogeneously stabilized coating is exposed to a uniform temperature test, the whole zirconia layer could develop cracks, leading to early spallation if the whole layer is cycled through the phase-transformation temperature.

Although the use of fully homogeneously stabilized coatings may seem warranted for all applications, regardless of operating temperature, economic considerations argue against this. Fully homogeneous powders, which are more costly, must either be fused and crushed or sintered from pure zirconia and yttria components at high temperatures. If the exposure temperature of the TBC does not demand monoclinic-phase-free material, a less costly powder will still meet the thermal barrier performance required. The key is to know the relation between operating temperature limits and the phase content of the coating.

Chemical Effects on Phase Stability. As discussed above, powders that are inhomogeneous in regard to yttria concentration could lead to coatings with phase-transformation-induced cracking if used at high temperatures. It has also been found that fully homogeneous yttria-stabilized coatings used in high-temperature environments containing vanadium and/or sulfur can experience surface degradation. In this case, the impurities can form yttrium vanadate and yttrium sulfide by leaching yttrium from the coating (Ref 5, 9). This leads to a surface layer that is progressively depleted in yttria content, and eventually to a material that is in the fully monoclinic structure when cooled and has a large volume change and disruptive stresses when thermally cycled. This surface transformation can also be detected by x-ray diffraction, which will give the evidence needed to understand the failure mechanism.

References cited in this section

3. J.R. VanValzah and H.E. Eaton, Cooling Rate Effects on the Tetragonal to Monoclinic Phase Transformation in Aged Plasma-Sprayed Yttria Partially Stabilized Zirconia, *Surf. Coat. Technol.,* Vol 46, 1991, p 289-300
4. H.G. Scott, Phase Relationships in the Zirconia-Yttria System, *J. Mater. Sci.,* Vol 10 (No. 9), 1975, p 1527-1535
5. R.J. Bratton and S.K. Lau, Zirconia Thermal Barrier Coatings, *Adv. Ceram., Vol. 3: Science and Technology of Zirconia,* American Ceramic Society, 1981, p 226-240
6. E.C. Subbarao, Zirconia --An Overview, *Adv. Ceram.,* Vol. 3: Science and Technology of Zirconia, American Ceramic Society, 1981, p 1-13
7. M.F. Gruninger and M.V. Boris, Thermal Barrier Ceramics for Gas Turbine and Reciprocating Heat Engine Applications, *Proc. ITSC,* C.C. Berndt, Ed., ASM International, 1992, p 487-492
8. R.A. Miller, J.L. Smialek, and R.G. Garlick, Phase Stability in Plasma-Sprayed Partially Stabilized Zirconia-Yttria, *Adv. in Ceram., Vol. 3: Science and Technology of Zirconia, American Ceramic Society,* 1981, p 241-253
9. B.A. Nagaraj and D.J. Wortman, Burner Rig Evaluation of Ceramic Coatings with Vanadium Contaminated Fuel, *J. Eng. Gas Turbines Power,* Vol 112, 1990, p 536-542

Thermal Property Measurements

Coefficient of Thermal Expansion. The coefficient of thermal expansion (CTE) of the TBC in the in-plane direction should match as closely as possible the CTE of the bond coat. The expansion in the through-thickness direction is not of

great interest, which is fortunate because this measurement is relatively difficult to perform. The in-plane expansion on a freestanding sample can be determined using a conventional pushrod dilatometer (ASTM C 228). In the case of a differential pushrod dilatometer, the differential expansion between the sample and a known standard reference material is measured as a function of temperature. The expansion of the sample is computed from this differential expansion and the expansion of the standard. The measurements are made under computer control, and linear expansion is calculated at preselected temperature intervals. The expansion can be monitored with the visual display during the measurement process. Seven standard reference materials for expansion are available from the National Institute of Standards (NIST, formerly the National Bureau of Standards), including materials with low, moderate, and large expansion. For purposes of calibration and checkout, one NIST standard is measured against another NIST standard.

Specific Heat. Measurements of the specific heat of TBCs can be easily performed using differential scanning calorimetry (ASTM E 1269). Reference and sample holders are equipped with heaters and temperature sensors that detect temperature fluctuations of the sample holder with respect to the reference holder as both are heated. A high-gain, closed-loop electronic system provides differential electrical power rate that can be read out directly in millicalories per second and that is equivalent to the rate of energy absorption or evolution of the sample. The specific heat is calculated by comparing this rate with the rate measured during the heating of a known mass of sapphire. The experiments are performed under computer control, and specific heat is automatically calculated at equal temperature intervals.

The procedure is to measure the differential power required to heat the empty pan at the same rate as the reference empty pan (blank amplitude). The data are collected and stored in the computer. The sapphire standard (whose mass and specific heat are known) is then placed in the empty pan, and the differential power required to heat this pan at the same rate as the reference empty pan is measured to obtain the standard amplitude. Next, the sample is substituted for the sapphire standard and the sample amplitude is determined. The computer then calculates the specific heat. The results for ZrO_2-8wt%Y_2O_3 coatings are very close to those predicted from the rule of mixtures, as calculated using values for the pure oxides (Ref 10).

Thermal Transport Properties. Thermal conductivity can be calculated from:

$$\lambda = q/A\,(dT/dx) \qquad \textbf{(Eq 4)}$$

where λ is the thermal conductivity, *q* is the heat flux, *A* is the cross-sectional area conducting the flux *q*, and *dT*/*dx* is the temperature gradient. Alternatively, conductivity can be determined from:

$$\lambda = \alpha C_p \rho \qquad \textbf{(Eq 5)}$$

where α is the thermal diffusivity, C_p is the specific heat, and ρ is the density. It should be noted that thermal conductivity cannot be measured directly. Equation 4 involves steady-state determinations, and Eq 5 involves transient determinations. Relatively large errors have been documented for steady-state determinations, even under good conditions (Ref 11). Because specific heat and density (expansion) measurements are straightforward, and because diffusivity measurements involve only length and time, transient techniques are more attractive, especially for the small samples associated with coatings in the through-thickness direction. In addition, the diffusivity technique is much faster and costs less.

A particularly useful diffusivity technique (Ref 12) is the laser flash method, ASTM E 1461-92. It is shown schematically in Fig. 8. The sample, normally the size of a nickel, is held at the desired measurement (e.g., room temperature, 100 °C, 200 °C, etc.). The front surface receives a pulse of energy from the laser, which soon raises the back face temperature a degree or two. The rear face temperature response is normalized and compared with the theoretical model based on Carslaw and Jaeger's solution to one-dimensional heat flow (Ref 13). Using that model, diffusivity values can be obtained at any percent rise of the curve. For example, at 50% rise, the diffusivity is calculated from:

$$\alpha = 0.1338\, l^2/t_{0.5} \qquad \textbf{(Eq 6)}$$

where *l* is the sample thickness and $t_{0.5}$ is the elapsed time needed for the rear-face temperature to reach one-half of its maximum rise (Fig. 8).

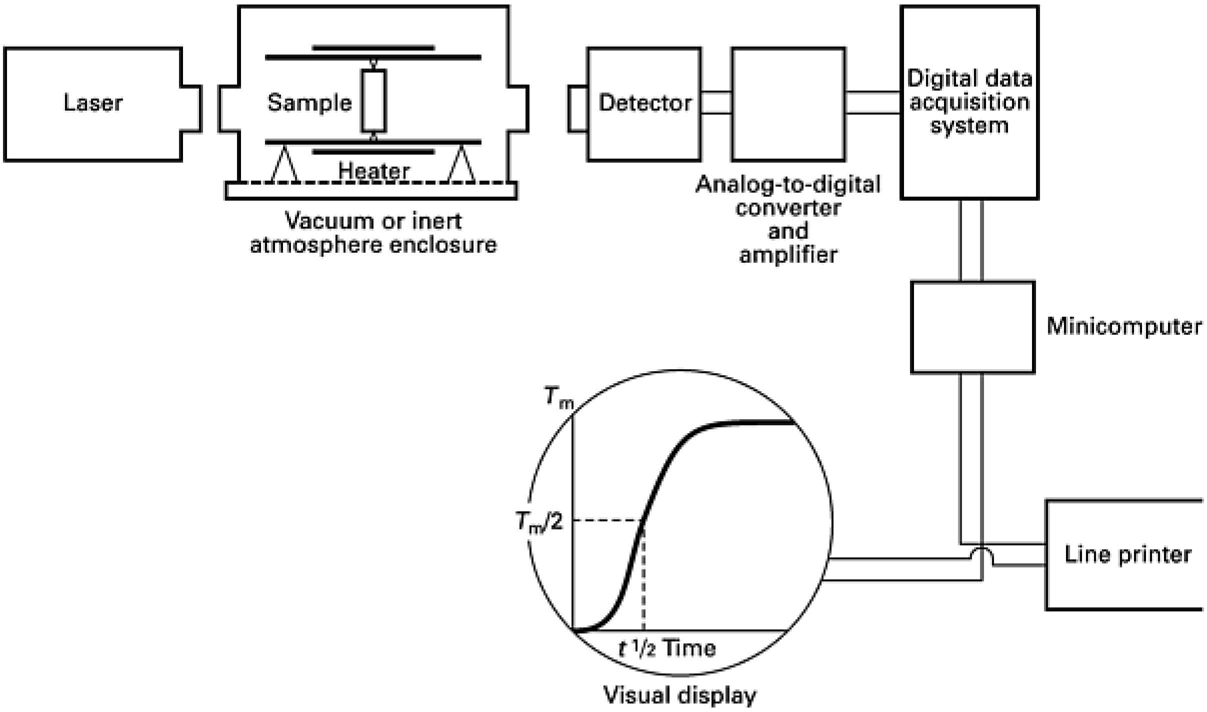

Fig. 8 Schematic diagram of laser-flash method for thermal diffusivity measurement. T_m**, maximum temperature measured by the liquid nitrogen-cooled infrared detector**

It is possible to measure freestanding coatings, but it is also possible to measure the coatings on the substrate. In the latter case, the effects of any interfacial resistance are included in the calculated diffusivity/conductivity of the coating. Because TBCs may be translucent, part of the laser beam could penetrate significantly into the sample, violating an assumed boundary condition. Thus, for freestanding coatings, it is necessary to put a very thin opaque layer on at least one surface. In the case of TBCs on substrates, this is not a problem because the substrate side faces the laser.

Thermal conductivity values in the literature have rarely been corrected for thermal expansion, because the expansion correction has been within the accuracies of steady-state determinations of conductivity. This general practice is usually followed when computing thermal conductivity from transient measurements: density and diffusivity values are not corrected for expansion. If one does correct density for expansion by dividing by $(L_0 + \Delta L)^3$, one must also correct the diffusivity values by multiplying by $(L_0 + \Delta L)^2$, where L_0 is the length at the reference (room) temperature and ΔL is the length change at any temperature from that at the reference temperature. Thus the total correction is a factor of $(L_0 + \Delta L)^{-1}$. For TBCs at operating temperature, this correction is less than 2%.

Thermal diffusivity and conductivity values may increase after thermal cycling (Ref 10, 14) or upon heat treatment to progressively higher temperatures (Fig. 9). These effects may be due to closing of horizontal microcracks. In addition, the conductivity/diffusivity of the TBCs can be thickness dependent due to the somewhat cone-shape structure. It should also be noted that the in-plane conductivity values of TBCs are different from the through-thickness values because of the lamellar nature of thermally sprayed coatings and the columnar structure of zirconia deposited by physical vapor deposition. In general, the in-plane values are relatively unimportant for TBC applications.

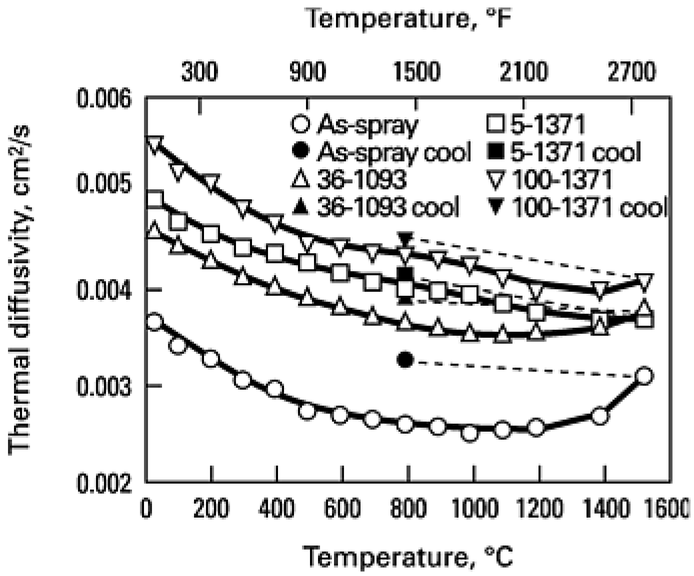

Fig. 9 Thermal diffusivity of plasma-sprayed ceramic coatings subjected to selected heat treatments

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References cited in this section

10. T.A. Taylor, Thermal Properties and Microstructure of Two Thermal Barrier Coatings, *Surf. Coat. Technol.*, Vol 54/55, 1992, p 53-57
11. R.E. Taylor, Things Mother Never Taught Me (About Thermophysical Properties of Solids), *Therm. Conduct.*, Vol 21, C.J. Creamers and H.A. Fine, Ed., Plenum Publishing Corp., 1991, p 41-49
12. R.E. Taylor and K.D. Maglic, Pulse Method for Thermal Diffusivity Measurements, *Compendium of Thermophysical Property Measurement Methods,* Vol 1, K.D. Maglic, Ed., Plenum Publishing Corp., 1984, p 305-336
13. H.S. Carslaw and J.C. Jaeger, *Conduction of Heat in Solids,* Oxford University Press, 1959
14. R.E. Taylor, On Material Changes and Heating Rate Dependent Properties, *Therm. Conduct.,* Vol 20, D.P.H. Hasselman and J.R. Thomas, Jr., Ed., Plenum Publishing Corp., 1989, p 93-101

Microstructural Characterization of Coatings and Thin Films

S.J. Bull, AEA Technology

Introduction

BOTH METALLURGY AND MATERIALS SCIENCE are concerned with the relationship between structure and the macroscopic properties of materials. Structure can be important at different levels. For example, on the atomic scale, structure dictates the strength of grain boundaries. On a larger scale, extending over many grain diameters, structure influences more complex phenomena, such as contact at surfaces or optical properties. For coatings, structure-property relationships are further complicated by the fact that coating microstructures are generally highly anisotropic and contain concentrations of defects that can vary from grain to grain for some coatings (e.g., plasma-sprayed coatings). Clearly, the ability to characterize coating microstructures is important in understanding the properties and behavior of coatings in many applications.

This article describes the structure of coatings produced by plasma spraying, vapor deposition, and electrodeposition processes. It also introduces the main techniques that can be used for microstructure assessment. Although examples are given for a limited range of deposition technologies, they are widely applicable to coatings produced by other processes.

Microstructure of Coatings

The microstructure of a coating is critically dependent on the deposition technology used to produce it (Ref 1). In some technologies, such as physical vapor deposition (PVD), the structure of the coating can be controlled to a certain extent by the choice of deposition parameters. In other technologies, such as weld surfacing or diffusion treatment, it is the thermal history of the component surface that dictates microstructure. Good process control is needed to ensure the production of a layer with the correct microstructure and the required properties for the application. A number of microstructural factors are important in dictating the properties of the coating:

- Phase composition
- Size and shape of grains
- Size and distribution of porosity
- Defects (vacancies, dislocations, etc.)
- Presence of cracks and pin holes
- Anisotropy
- Stress and strain

In most cases, the first three factors are the most important. However, the others can be critically important for certain applications. Stresses and strains occur when the microstructural units of the coating (e.g., columnar grains in PVD coatings or splats in plasma-sprayed materials) are moved with respect to their equilibrium positions by externally applied forces, which can be due to mechanical or thermal loading or the mismatch of properties with the substrate. Stresses can lead to bending of the coating, distortion of the microstructural units, and generation of defects within microstructural units where they contact (e.g., dislocation loops are created by compressive stresses forcing columnar grains together in PVD films). Strains usually manifest themselves as changes to the lattice parameter of the material. There are two types: macrostrains (changes that affect the whole coating, produced by thermal expansion mismatch) and microstrains (highly localized distortions of the structure around defects). Described below is the evolution of microstructure in several important deposition technologies.

In the thermal spraying process, the powder form of a coating material is injected into a flame, where it melts and is ejected against the component surface to build up the coating. Thermal spraying is actually a generic term for a number of processes that all produce coatings with similar microstructures, ranging from flame spraying and high-velocity combustion processes to plasma spraying. The structure and properties of the coatings depend on the stability of the particles within the flame and the choice of process parameters. Ideally, the powder particles are completely melted, but not vaporized, in transit between the injection point and the substrate surface. The molten particles then strike the substrate surface, where they flatten and freeze. Succeeding particles acquire the same lenticular shape over material that has already been deposited, so that the coatings develop an anisotropic lamellar structure parallel to the interface (Fig. 1). The extent of flattening depends on factors such as degree of melting, viscosity of the liquid, and wetting of the surface. Coatings may contain voids that are due to outgassing, shrinkage, or topographical effects (e.g., shadowing). Metal coatings processed in air will also probably contain oxide inclusions.

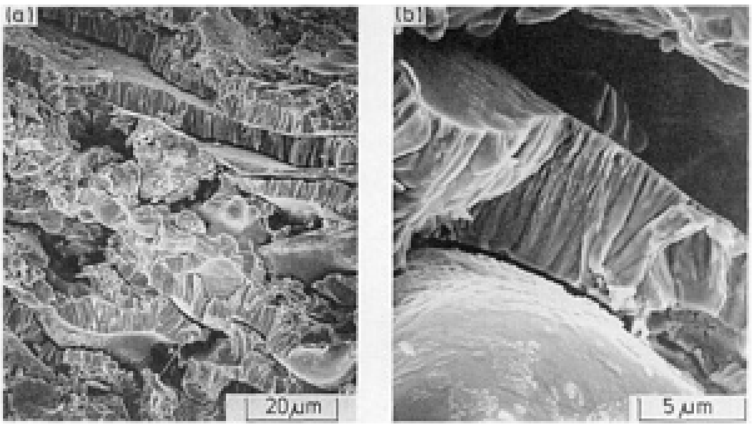

Fig. 1 Scanning electron micrographs of fracture cross sections of air plasma-sprayed tungsten coatings. (a)

Lamellar structure. (b) Presence of columnar structure within the splats

Cooling rates can be very high (as much as 10^6 K/s) for plasma-sprayed particles. This produces a very fine microstructure within the lenticular splats (Ref 2), as shown in Fig. 1(b). The rapid solidification can form amorphous deposits from some ferrous alloys (Ref 3), whereas metastable or nonstoichiometric phases can be observed in some ceramics. For instance, alumina coatings contain an increasing proportion of the λ phase as the energy of the spraying process increases or the particle size decreases (Ref 4).

Vapor Deposition Processes. The structure of coatings deposited from the vapor phase is controlled as much by the nucleation of the coatings as by the way in which they subsequently grow. One feature common to vapor-deposited coatings is that solid material is distributed in an array of fairly closely packed columns that run perpendicular to the substrate. It is this anisotropy in structure that controls many of the properties of the films.

A number of factors can influence the nucleation of vapor deposited coatings. The surface structure of the substrate is critically important, including grain size, defect density, texture, roughness, and surface composition, and it is often necessary to pretreat materials prior to coating to enhance nucleation. Surface contaminants introduced in the coating process can promote or inhibit nucleation, as can ion bombardment in PVD processes. In many cases a chemical or physical activation step is required to get the best surface structure for coating (e.g., a chemical etch is required to remove surface magnesium from aluminum alloys). This needs to be followed by careful control of the early stages of coating to ensure that reliable structures are produced.

Structure Zone Models. An essential feature of the structure of these thin films is that they are formed from a flux of atoms that approaches the substrate from a limited range of directions. This generates the columnar microstructure, but can lead to problems, because there are many boundaries running perpendicular to the interface that can act as planes of weakness (e.g., as short-circuit diffusion paths).

Movchan and Demchishin (Ref 5) were the first to classify thin-film microstructures. They identified three distinct structure zones as a function of the homologous temperature T/T_m, where T represents the substrate surface temperature and T_m represents the coating melting point. A low-temperature zone 1 structure (T/T_m < 0.25-0.3) corresponds to low adatom mobility and consists of tapered columns with domed tops. In a zone 2 structure (T/T_m = 0.3-0.5), surface diffusion becomes increasingly important, and the structure consists of straight columns with a smooth surface topography. With increasing temperature (T/T_m > 0.5), bulk diffusion becomes a dominant process. The zone 3 microstructure therefore consists of equiaxed grains, as are observed in recrystallized metals. For sputtered coatings, Thornton (Ref 6) later suggested that the presence of a sputtering gas could modify the model, and a further region was identified between zone 1 and zone 2. This region consists of poorly defined fibrous grains and is named zone T.

At the temperatures used in the chemical vapor deposition (CVD) process, surface diffusion of adatoms is actuated and structures of the zone 2 type are produced, in the case of most coating materials. However, the structure of the coating is often controlled by the nucleation density. In the early stages of coating, a very high density of small nuclei is established, which becomes constant after a time, that is, no new nuclei are formed, but newly deposited adatoms move to the existing nuclei and are trapped there. For longer deposition times, the nuclei grow until they eventually coalesce to form the film. In the case of some CVD coatings (e.g., diamond on silicon), the nuclei grow in both height and width, and the coalescence process may result in pores at the interface. Because porosity at the interface decreases adhesion, it is necessary to maximize the density of nuclei formed in order to obtain optimal adhesion. Porosity also remains at the triple points created as the nuclei grow together. These nuclei provide the seeds for the columnar units that compose the coating. Maximizing the nucleation density also reduces the size and extent of this through-thickness porosity.

Because the typical deposition temperatures in PVD processes is very low, many coatings are deposited with a zone 1 microstructure. Instead of increasing the deposition temperature, the occurrence of this microstructure can be overcome by bombarding the growing films with particles having sufficient energy so that the resulting momentum transfer will cause the coating atoms to fill the voided boundaries. Messier (Ref 7) has suggested a modification to the structure zone models that accounts for the evolution of morphology with increasing film thickness, as well as the effect of both thermal and bombardment-induced mobility. The model draws attention to the fact that ion bombardment promotes a dense structure of the zone T type, but it also indicates that the atomic rearrangement can have either thermal or ion-bombardment-induced origins.

Increasing the energy (or the flux) of ion bombardment, by applying a substrate bias, for example, has a significant effect on the structure of PVD films (Ref 8, 9). The coating on an unbiased substrate shows an open columnar structure (zone 1, Fig. 2a), whereas the film on a biased substrate appears more dense, because the individual columns are less well defined (zone T, Fig. 2b). The two coatings will have different properties that are due primarily to changes in the packing density of the columns.

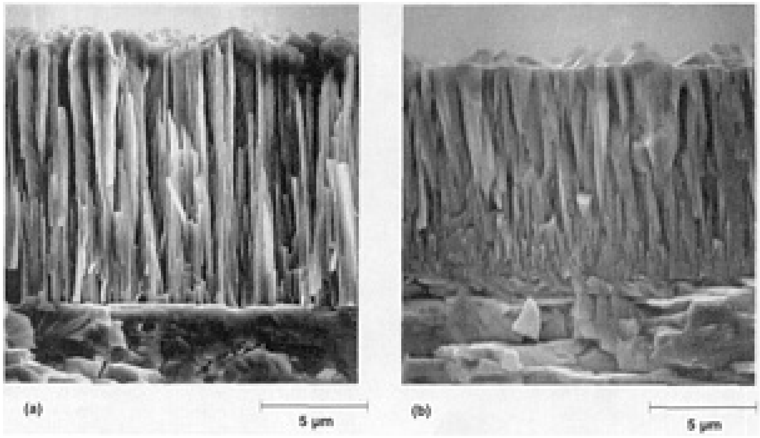

Fig. 2 Scanning electron micrographs of fracture cross sections of sputtered tungsten films on a tungsten substrate. (a) Unbiased (zone 1 structure). (b) -100V bias (zone T structure)

The deposition of predominantly covalent coatings, such as silicon carbide or diamond-like carbon, causes a further complication. Because of bonding directionality, it becomes very difficult to incorporate adatoms into their correct crystallographic location at low deposition temperatures. For this reason, amorphous coatings are produced with smooth, featureless, fracture cross sections. At a critical deposition temperature, some crystallization occurs, and structures of the zone T or zone 2 type can be produced. However, identifiable zone 1 structures are not usually observed.

Zone 1, zone T, and zone 2 microstructures are all associated with the development of texture in PVD films. For titanium nitride coatings, for example, a {111} orientation is commonly reported, although both {200} and {220} orientations have also been observed (Ref 10, 11, 12). The development of texture occurs in three stages:

- Nucleation, where crystallites are nucleated on the substrate from the vapor phase, the distribution and orientation of which depend on the substrate surface structure and deposition parameters
- Competitive growth, where certain favorably oriented nuclei will grow into the vapor phase faster than others, but which may not constitute the majority of the nuclei population
- Steady growth, which occurs once a preferred orientation has achieved dominance

The detailed deposition conditions in any PVD process can change any or all of the above stages and will also affect the morphology of the coating. At the interface region, a very fine grain size is established initially, but with increasing thickness, the columnar structure becomes established and the grain size increases. During the competitive growth phase, intercolumnar voids will open up because of shadowing processes. These voids will be increasingly closed up once the steady-state growth conditions are achieved. Clearly, if porous coatings are to be avoided, it is advisable to know in which thickness range these changes are taking place, as well as how to minimize their effects.

Electrodeposition was one of the earliest plating processes developed for depositing one metal onto another. The method is now widely used for both decorative and engineering purposes. The process involves the reduction of metallic ions at the surface of the substrate, which acts as the cathode of an electrolytic cell. The electrodeposit structure is controlled by the composition of the electrolyte, by the plating conditions, and, in particular, by the presence of growth-inhibiting substances and by the substrate itself (Ref 13). In solution, the metal ions (surrounded by their solvation sheath) migrate toward the deposit, where they lose their sheath and accept electrons to become atoms. The atoms are adsorbed onto the surface and migrate until they encounter a site where they can be incorporated into the existing structure. Impurities or bath additions (inhibitors) may block such sites and can thereby control the structure of the deposit. Under

growth-inhibiting conditions (i.e., when the current density is high and the bath temperature is low, so that atoms cannot readily diffuse), the deposit is finely grained and there is essentially continuous nucleation. Under other conditions, extended three-dimensional crystallite networks can grow.

The growth rate perpendicular to the surface is not the same for all grains, because the adsorption of inhibiting substances is anisotropic. As the deposit thickness increases, the slower-growing grains can become covered, and a texture will develop in the film. Slight misorientations between the grains lead to the need for misfit dislocations at boundaries. This is the reason for the high dislocation densities associated with coatings deposited under inhibited conditions. The microstructure of hard electrodeposits used for tribological applications (such as hard chromium) is equiaxed, and extremely finely grained, and it contains some oxide inclusions and microcracks, which give the coating some porosity (Fig. 3). Tensile residual stresses can be produced in the coating during plating and can lead to a network of larger cracks on the material. Similar structures are observed for autocatalytic coatings, such as electroless nickel, where phosphorus-containing reducing agents are present in the plating solution and get incorporated in the coating. Both electrolytic and autocatalytic coatings can be modified to incorporate fine particles (typically, 0.5-5 μm, or 20-200 μin. in size) into the growing film. They can be hard particles, such as silicon carbide, as well as solid lubricants, such as polytetrafluoroethylene. A nonuniform distribution of codeposited substances can lead to crevices or a banded structure (Ref 13).

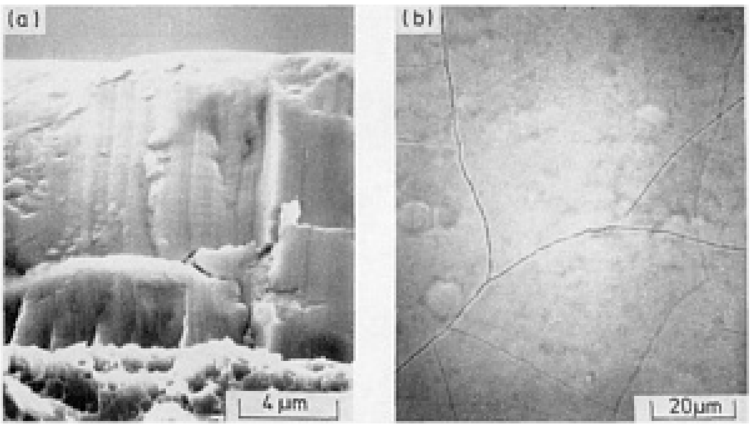

Fig. 3 Scanning electron micrographs of an electrodeposited chromium film. (a) Fracture cross section. (b) Plan view showing the presence of cracks within the coating

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References cited in this section

1. E. Hornbogen, *Acta Metall.,* Vol 32, 1984, p 615
2. S. Safai and H. Herman, *Proc. Advances in Surface Coating Technology,* Welding Institute, 1978, p 1
3. H. Herman and H. Bhat, in *Synthesis and Properties of Metastable Phase,* (E.S. Machlin and T.J. Rowland), Ed., TMS/AIME, 1980, p 115-137
4. A. Dauger, D. Fargeot, and J.P. Laval, *Mater. Res. Soc. Symp. Proc.,* Vol 21, 1984, p 207
5. B.A. Movchan and A.V. Demchishin, *Fiz. Met. Metalloved,* Vol 28, 1969, p 653
6. J.A. Thornton, *Annu. Rev. Mater. Sci.,* Vol 7, 1977, p 239
7. R. Messier, A.P. Giri, and R.A. Roy, *J. Vac. Sci. Technol.,* Vol A2, 1984, p 500
8. D.M. Mattox, *J. Vac. Sci. Technol.,* Vol 10, 1973, p 47
9. R.W. Knoll and E.R. Bradley, *Thin Solid Films,* Vol 117, 1984, p 201
10. P.N. Mattox and G.J. Kuminiak, *J. Vac. Sci. Technol.,* Vol 9, 1972, p 528
11. U. Helmersson, J.-E. Sundgren, and J.E. Greene, *J. Vac. Sci. Technol.,* Vol 4, 1986, p 500
12. A. Matthews and H.D. Sundquist, in *Proc. Int. Ion Engineering Congress, ISIAT '83,* T. Takagi, Ed., IEE (Japan), 1983, p 1311

13. R. Weil and K. Sheppard, *Mater. Char.,* Vol 28, 1992, p 103-112

Microstructure / Property Relationships

In the preceding section, it was shown that although the same coating materials can be deposited by a number of different processes, the tructure of the coatings produced will be very different. Whereas a very fine equiaxed grain structure is produced by electrodeposition, a columnar structure is produced by vapor-deposition processes (grain boundaries perpendicular to the interface), and a splat structure is produced by plasma spraying (splat boundaries parallel to the interface). Thus, it should be intuitive that the coatings will not have the same properties, and this is what is observed in practice. Considerable attention should be paid to the microstructure of the coating if performance is to be understood. There are numerous techniques that can provide relevant information.

Structure/property relationships have been determined empirically for many deposition processes for a restricted range of coating materials (e.g., Ref 13, 14). However, theoretical modeling of coating properties based on microstructure is not well advanced. A characterization of the structures and properties of commercially available coatings produced by different deposition technologies is often necessary to aid in coating selection and specification. Because some control of coating structure is possible for most deposition technologies, optimizing the microstructure of the coating for a given application is also a possibility. Structural characterization is a necessary step in achieving this rather ambitious goal.

References cited in this section

13. R. Weil and K. Sheppard, *Mater. Char.,* Vol 28, 1992, p 103-112

14. D.S. Rickerby and S.J. Bull, *Surf. Coat. Technol.,* Vol 39/40, 1989, p 315

Experimental Techniques for Microstructural Characterization

It is not possible to determine all the structural features of a material using any one analysis technique. Therefore, many techniques that can be used to provide information about specific microstructural features have been developed. It is important to know what factors are important in any application before undertaking a program of structural analysis.

For coatings, many of the techniques are applicable, but somewhat more care must be taken in preparing representative samples, because the volume of material to be investigated is relatively small. Table 1 identifies the most important microstructural features and defines what techniques can be used to assess them. However, other, more unusual techniques can also provide the same information.

Table 1 Techniques for microstructural analysis

Coating property	Technique
Phase composition	X-ray or electron diffraction
Phase distribution	Metallographic sections, SEM, TEM, optical microscopy
Grain size	X-ray diffraction, SEM, TEM (plus image analysis)
Grain shape	SEM, TEM (plus image analysis)
Preferred orientation	X-ray diffraction, TEM
Surface morphology	SEM

Porosity	TEM, mercury intrusion porosimetry, metallographic section (plus image analysis)

Note: SEM, scanning electron microscopy; TEM, transmission electron microscopy

Brief descriptions of some of the most frequently used techniques are described below, as are some of the factors that need to be considered when applying them to coated systems.

Metallography. Most standard metallographic preparation techniques can be applied to coatings, and polished cross sections are commonly used to determine coating thickness and uniformity. Samples are generally cut from a coated component using a low-deformation saw and are mounted in a resin medium prior to polishing. Components should be rigidly clamped and sectioned so that the abrasive wheel enters from the coating side. For most coating-substrate combinations, a hot mounting medium is preferred, but for temperature-sensitive or porous coatings, better results are obtained when a cold-setting resin is used. The section should then be ground back until a flat surface is produced. When dealing with coated samples, it is often observed that some chipping of the coating occurs next to the saw cut. It is therefore essential to grind the section well back to remove any damage prior to polishing. For thin, hard coatings, a large grit size should be avoided during grinding, because it can result in coating detachment (Ref 15). The preferred direction of grinding is from the substrate into the coating because this maintains the best edge sharpness.

After grinding, the section can be prepared using metallographic polishing techniques similar to those used for bulk materials. However, for porous plasma-sprayed coatings, better results can be achieved using more advanced metallographic techniques, as described in Ref 16. The twofold aim of the polishing process is to remove the damage introduced during grinding and to produce the high surface finish needed for metallography. For thin coatings, it is particularly important to use an edge-retaining mount, because edge rounding of the sample can occur during polishing in cases of differential polishing of the coating and the substrate or of sample tilting. For very thin or fragile coatings, the sample can be encapsulated with a thick protective layer prior to sectioning and mounting in order to prevent damage of the coating during preparation. Porous coatings, such as air plasma-sprayed coatings, are best mounted by vacuum infiltration, because the resin can then penetrate the porosity in the coating and will prevent collapse of the coating around the porosity during polishing (Ref 16).

For measuring the thickness and uniformity of the coating, a simple polished cross section may be sufficient. However, particular care must be taken to ensure that the coating has not been damaged during preparation. The importance of grinding back from the cut surface cannot be emphasized enough. Similarly, the porosity revealed in the coating may be an artifact of the preparation process, because grain pullout often occurs in the final stages of polishing materials that have weak boundaries, such as air plasma-sprayed metals. Although there is no simple technique for avoiding these problems, the measurement of thickness or porosity by other techniques can give some indication of whether the measurements obtained from metallography are consistent. A material-specific preparation technique can then be developed for the coating material and process combination of interest.

When dealing with very thin coatings, more detail can be revealed by using a taper section. A taper angle of 5.7°, for example, will give a 10× magnification in the plane of the section. In this case, the sample is mounted in the resin with one edge supported by a spacer, the height of which is chosen to give the required tilt angle, and then prepared in the same way as a cross section (Ref 15). Figure 4 shows a taper section of a PVD titanium nitride coating on stainless steel with a 400 nm (16 μin.) titanium interlayer that is not visible in the polished cross section, but which can be easily resolved in the taper section. Because of nonuniform polishing, the initially planar interface has become irregular in the taper section. This is almost impossible to avoid in practice.

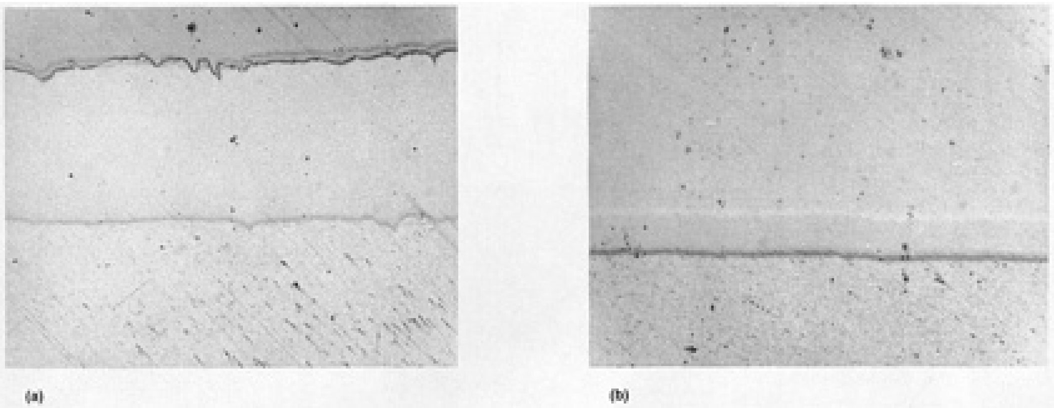


Fig. 4 Micrographs of a PVD titanium nitride coating on stainless steel. (a) Cross section. (b) Taper section showing the presence of a 400 nm (16 μin.) titanium interlayer

The grain structure of the substrate and coating and, sometimes, even the presence of the coating itself can be revealed by etching with an appropriate reagent, as is done for bulk materials. Because it is often difficult to choose an etch that will attack both coating and substrate, a multistage etching process may be needed. It is important to determine whether an etch used for the coating will badly attack the substrate, because that could lead to the observation that there is interfacial porosity, when this is really just an artifact of etch selection. Figure 5 shows the structure of a PVD Fe-Cr-Al-Y coating on stainless steel after 100 h of oxidation at 1000 °C (1830 °F). The structures of both coating and substrate have been revealed by electrolytic etching in CrO_3/H_2O. Image analysis can be used to determine grain size and shape, along with porosity, in a quantitative manner (Ref 16).

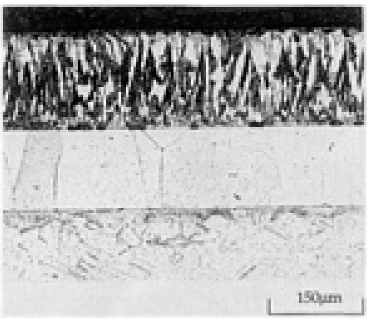


Fig. 5 Polished cross section of a Fe-Cr-Al-Y coating on austenitic stainless steel after 100 h at 1000 °C (1830 °F), electrolytically etched in CrO_3/H_2O to reveal grain structure of coating and substrate

X-ray Diffraction. In most cases, diffraction analysis is used to identify the structure of a deposited film from a list of known possibilities, rather than to identify the structure of a completely unknown or new substance. The analysis is thus essentially limited to the comparison of an experimentally observed diffraction pattern with patterns of substances, the structures of which are already known. This is made considerably easier if the composition of the coating can be determined, because the number of possible structures is then limited. In a typical x-ray diffraction experiment, a monochromatic beam of x-rays, wavelength λ, hits the coated surface from which it is diffracted. The intensity of the diffracted beam is recorded as a function of the diffraction angle, θ. The intensity of the beam will be nonzero only at those diffraction angles at which the Bragg condition is satisfied (Ref 17):

$$\lambda = 2d_{hkl}\sin\theta \quad \textbf{(Eq 1)}$$

where d_{hkl} is the spacing of the lattice planes with Miller indices *hkl*. All elements or compounds consist of atomic arrays with a unique combination of geometry and spacing. The smallest repeatable unit that completely defines the structure is

called the unit cell, and the spacing of these unit cells is defined by one or more lattice parameters (depending on crystal structure). The position of the diffraction maxima gives information about the size and shape of the unit cell, whereas the width of the maxima can be used to evaluate the size, orientation, and strain in grains of polycrystalline materials.

The intensity of the diffracted beam depends on several factors:

- Structure of the material
- Volume of irradiated material
- Diffraction geometry
- Sample alignment

For a more detailed discussion of the x-ray diffraction technique, readers are referred to Ref 17.

Once an experimental diffraction pattern has been obtained, the position and intensities of the peaks can be easily measured. It is then possible to calculate the intensities and positions for all candidate structures and compare these to the measurements to determine the structure of the film. However, a much easier way is to rely on powder diffraction standards (Ref 18), which represent a collection of experimentally determined relative intensity values for a large number of substances. These are available in book, microfilm, or card form, and can also be retrieved from disks or data bases. A typical card, for example, contains information on the structure of the material as well as the relative density data (Fig. 6). Information is available for both stoichiometric and nonstoichiometric compounds.

6-0642 MAJOR CORRECTION

d	2.12	2.44	1.50	2.44	$(TiN)^8E$
I/I_1	100	75	55	75	Titanium Nitride (Osbornite)

Rad. Cu I 1.5405 Filter Ni
Dia. Cut off CoIL
I/I_1 Diffractometer
Ref. Beattle and VerSnyder, Trans. ASM 45, 397 (1953)

Sys. Cubic S.G. Fm3m
9ϕ. 4.240 b_ϕ c_ϕ A C
α β γ Z4
Ref. I bid.

Sys. Cubic
δ_α nωβ ε_γ Sign
2V Dx 5.4 mp Color: Yellow
Ref. I bid.

Contains trace of Zr

d Å	I/I_1	hkl	d Å	I/I_1	hkl
2.44	75	111			
2.12	100	200			
1.496	55	220			
1.277	25	311			
1.223	16	222			
1.059	8	400			
0.972	12	331			
.948	20	420			
.865	20	422			
.816	----	333,511			

Fig. 6 Powder diffraction standard card for stoichiometric titanium nitride

The data on peak positions for titanium nitride (from Fig. 6) are represented as vertical lines in Fig. 7, which also shows an experimental diffraction pattern obtained for a titanium nitride film produced by sputter ion plating. It is clear that the observed peaks line up with the standard peak positions, but the measured pattern is slightly shifted to higher angles because of the presence of residual stress within the coating. The intensities, however, differ considerably from the values of the card shown in Fig. 6 because of the preferred orientation of the film. To fully assess the preferred orientation, it is necessary to compare the intensity of the measured line with that of the standard. A texture coefficient, T^*, can be defined as:

$$T^*(h'k'l') = \frac{I_{h'i'l'} / I^0_{h'k'l'}}{l/n \sum_0^n (I_{hkl} / I^0_{hkl}} \qquad \textbf{(Eq 2)}$$

In this equation, h' k' l' are the Miller indices of the plane of interest, I is the measured intensity, and I^0 is the intensity of the standard, which is randomly oriented. A value of unity corresponds to a random texture, and values greater than this show an increasing level of preferred orientation. For the data presented in Fig. 7, a {111} preferred orientation is observed, because $T^*_{\{111\}} = 4$.

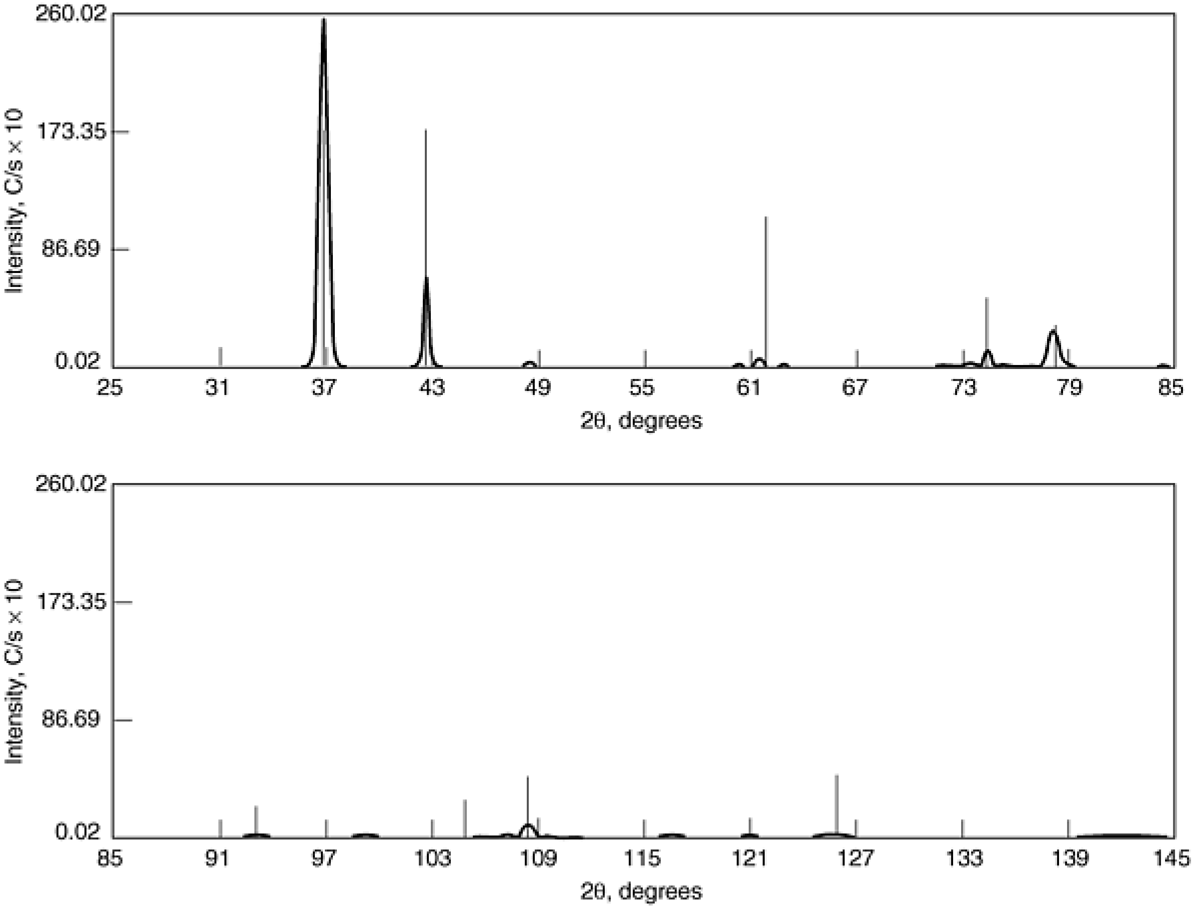


Fig. 7 Measured x-ray diffraction pattern for sputter ion plated titanium nitride. Vertical lines represent data peak positions for titanium nitride from Fig. 6. Film shows a [111] preferred orientation. C/s, counts per second

Once the phase composition of the coating has been identified, lattice parameter measurements can be undertaken. This is particularly important if measurements of residual stress are to be made or if there is a need to assess either the stoichiometry of a material or the composition of a solid solution. Because the accuracy of measurement increases as the Bragg angle increases, high angle reflections of sufficient intensity should be used for stress measurements. For the accurate measurement of peak position, it is necessary to fit a function to the peak profile (Ref 19). It is often assumed that a Gaussian profile provides a good description of peak shape, but, in many cases, a Pearson 7 function will provide a better fit. If the film is under stress, then measurements of the lattice parameter from a single reflection can be misleading, because of anisotropy constants. It is therefore important to use an extrapolation function, such as the Nelson-Riley or cosθ cotθ function, to improve reliability (Fig. 8). In this operation, the lattice parameter determined for a number of reflections is plotted against cosθcotθ, and a line through the points is extrapolated to θ= 0° to determine a_0. The deviations of some reflections from the line that are due to pseudo macrostresses can be revealed by this approach (Ref 19), which has the added advantage of minimizing alignment errors.

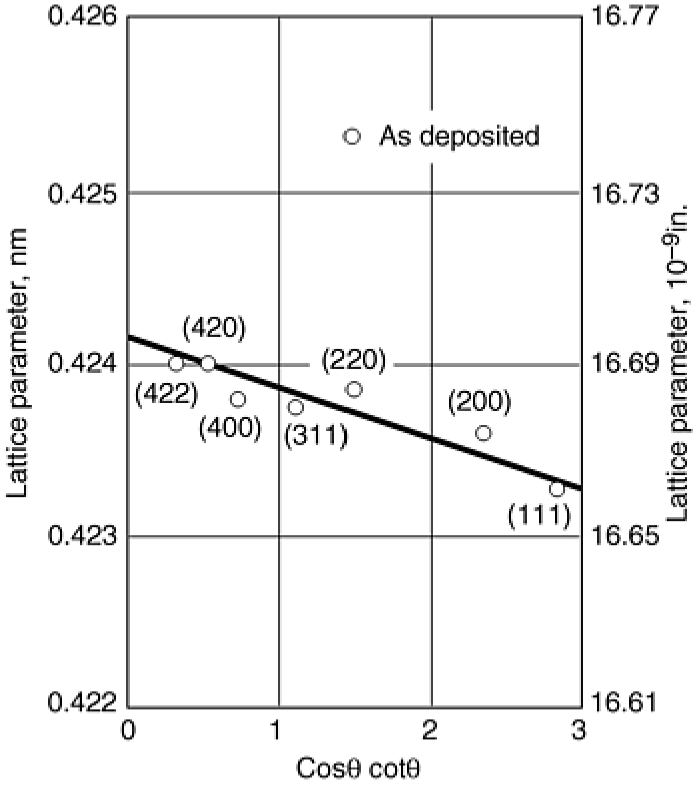


Fig. 8 Variation of lattice parameter with cosθcotθ for sputtered titanium nitride in order to extrapolate a lattice parameter, a_0, corrected for measurement errors

The width of a diffraction line is determined by the grain size and strain in a material, as well as by instrumental factors. A typical diffractometer will have an angular resolution of approximately 0.01°, which means that line broadening can be observed if the grain size *D* is lower than approximately 1 μm (40 μin.). This is easily achievable by various coating techniques, and x-ray diffraction can be used to give a measure of grain size for these technologies, averaged over the penetration depth of the x-ray (Ref 20).

If βis the full width at half-maximum intensity of the diffraction peak (for the case of a Cauchy peak shape, α_2 stripped and corrected for instrumental broadening), then (Ref 19):

$$\frac{\beta \cos\theta}{\lambda} = \frac{1}{D} + \frac{4\varepsilon \sin\theta}{\lambda} \quad \textbf{(Eq 3)}$$

where ε is the average strain in the material. Thus, by plotting βcosθ/λ against sinθ/λ, which is the so-called Hall-Williamson plot (Ref 21), it is possible to determine both *D* and ε. Figure 9 compares the Hall-Williamson plots for titanium nitride coatings produced by several deposition technologies. The broadening is dominated by strain, because the intercept is close to zero, implying a grain size greater than 1 μm (40 μin.).

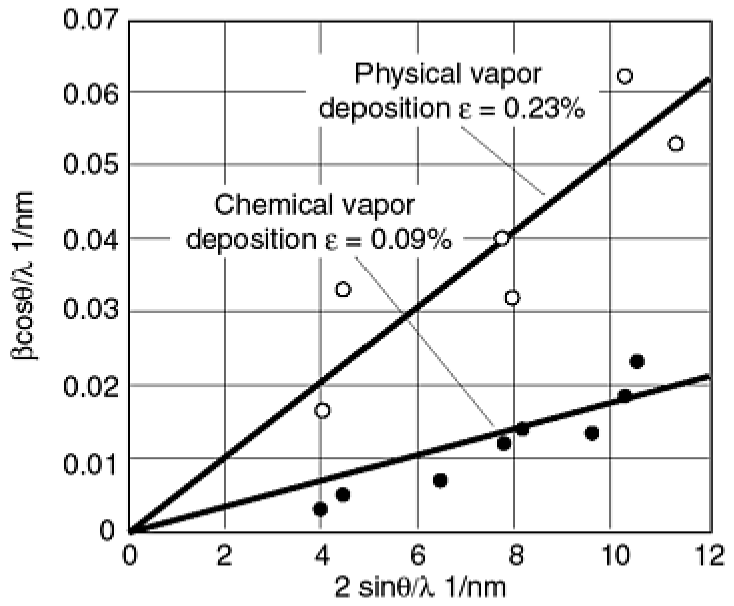


Fig. 9 Hall-Williamson plots for physical and chemical vapor deposited titanium nitride, showing increased strain in the physical vapor deposited films

Electron Microscopies. Perhaps the most useful techniques for characterizing thin films are scanning electron microscopy and transmission electron microscopy, because they can be used to investigate morphology, crystal structure, grain structure, and porosity. Both techniques depend on good sample preparation. Samples are relatively easy to produce for the former technique, but they are time-consuming and often difficult to prepare for the latter technique.

Scanning Electron Microscope (SEM). Numerous signals are available for SEM imaging (Ref 22). When coupled with energy-dispersive x-ray spectroscopy (EDS), the SEM can be used to obtain a wide range of information about surface topography, composition, crystallography, and electronic properties (Table 2). For example, the SEM can be used to assess the grain size, packing density, and porosity of a coating if a fracture cross section is imaged. The chamber of many SEMs is large enough that many components can be imaged nondestructively, and the surface topography induced by surface treatment, together with damage to the coating (after deposition or after service) can be determined.

Table 2 Scanning electron microscope imaging modes

Mode	Detected emission	Best resolution	Information available
Emission	Secondary electrons	5-15 nm (0.2-0.6 μin.)	Topographic
Reflection	Primary electrons (back scattered)	50-250 nm (2-10 μin.)	Topographic, atomic number
Leakage	Specimen current	>1 μm (>40 μin.)	Topographic, defects in some materials
X-ray	X-ray fluorescence	>1 μm (>40 μin.)	Chemical analysis (*Z* >5)
Cathodoluminescence	Luminescence	>1 μm (>40 μin.)	For some materials, quantitative chemical analysis or defect imaging

Crystallographic	Electron channeling	0.05° from 1 μm (40 μin.)	Lattice parameter selected area and defect density

In a typical SEM, an electron beam from a tip or filament is accelerated by the anode (typically, by 5 to 30 kV) and focused by two magnetic lenses to a fine spot on the sample. At the same time, the beam is scanned in the *x* and *y* direction. The electrons that are emitted from the sample are then either collected by a back-scattered electron detector, or, more generally, by a detector for secondary electrons. After amplification, the signal is fed to a cathode-ray tube, which is deflected in the same manner as the microscope electron beam. The magnification of the image is fixed by the *x*-*y* deflection coils.

The primary electron beam generates a tear-drop-shape interaction volume with the specimen. Elastically reflected electrons emerge from the surface with energies close to those of the primary beam. The proportion of back-scattered electrons depends on the material. As the atomic number of the element increases, the back-scattering coefficient increases and such atomic number contrast can be used to distinguish between phases in coatings and substrates. However, back-scattered electron emission is highly directional, and strong topographic contrast is visible for rough surfaces, depending on the position of the detector.

Secondary electrons leave from the near-surface region of the sample when energies are less than approximately 50 eV and show no such directional effect, because they are collected by a positively biased detector from all points on the sample. Their emission intensity is not strongly materials dependent. The secondary electron image clearly shows topographic features, such as cracks in electroplated coatings (Fig. 3). However, it should be realized that these images should not be interpreted like reflected light micrographs, because shadows are not generally caused by topography effects.

The primary electron beam can excite core electrons in the sample, which relax by the emission of an x-ray, as is characteristic of the excited atom. Such x-rays typically escape from 0.5 μm or greater depths. X-ray analysis can be achieved by energy-dispersive or wavelength-dispersive spectroscopies (EDS or WDS, respectively). The EDS system generally uses a lithium-doped silicon detector in conjunction with a beryllium window for analysis of elements with atomic number, Z, greater than 9 (i.e., neon and heavier atoms), although the range can be reduced to $Z = 5$ (boron) with a windowless detector. The WDS method uses a range of crystals with different lattice parameters that can be rotated to focus x-rays from elements where $Z > 6$ into a detector. The EDS system is faster than WDS but has poorer energy resolution. Both EDS and WDS can be quantitative methods of evaluating elemental composition if care is taken in correcting for instrumental, chemical, and physical factors. This is a standard feature in most commercial analysis systems.

Fracture sections provide a very good means for assessing the structure of thin PVD coatings. Figure 2 shows fracture sections through PVD tungsten coatings deposited under unbiased conditions (zone 1), with an applied bias voltage of -150 V (zone T). The columnar structure is clearly visible for both coatings, but the columnar packing density increases with applied substrate bias (i.e., energy of ion bombardment). Because each column consists of an array of grains, a true measure of grain size is not generally possible using the SEM, but an indication of relative grain size may be possible from the column dimensions. The coatings are deposited onto a ferritic steel substrate that was cut through from the back side with a saw until it reached approximately 1 mm (0.04 in.) below the coating. The sample was then immersed in liquid nitrogen to cool below the substrate ductile-brittle transition temperature. After 10 min, the sample was removed and half placed in a vise. Then, the free end was struck with a hammer to fracture the sample in two. The coated side was struck so that the section was not put into compression during fracture, in order to avoid excessive coating damage. The cracks started in the saw cut and ran through the coating without damaging it. Similar results can be achieved for coatings on brittle substrates, such as silicon wafers, by using a diamond scribe to initiate fracture on the back of the substrate.

Insulating substrates or coatings will become charged in the electron beam, which quickly reduces image quality and occasionally damages the material. Charging can be avoided by depositing a thin carbon or gold film on the specimen surface. However, this will reduce the accuracy of any subsequent microanalysis and should only be used if necessary. Alternatively, a low accelerating voltage can be used for the primary beam, because when voltages are less than 3 kV, the sum of the secondary and back-scattered electrons generated can equal the number of primary electrons, and no charging occurs. Such low-voltage SEMs have the added advantage of better resolution, but their poorer signal-to-noise ratio means that some image processing may be necessary to obtain the best results.

Relatively poor resolution can also be encountered with magnetic coatings or substrates. For high-resolution work, it is recommended that a nonmagnetic substrate, such as silicon or stainless steel, be used wherever possible.

Transmission electron microscope (TEM) studies require very thin specimens (5-500 nm, or 0.2-20 μin.), depending on the material. These specimens of foil must be prepared from the bulk of the coating or substrate. With such foils, it is possible to visualize structures on the nanometer level, and when specialized techniques are used, it is even possible to see the presence of single-atom columns and to locate dislocations in the crystal (Ref 23). Grain boundaries and interfaces can also be studied using this technique. When the crystallites range in size from micrometers to nanometers, the TEM can be used for electron diffraction studies to identify phase composition, as well (Ref 24).

The preparation of TEM samples is a skilled operation, and considerable effect is often required to develop the technique for a specific coating-substrate system. Plan-view TEM samples are by far the easiest to produce and consist of sections of the coating parallel to the interface (Fig. 10). In general, plan-view sample preparation takes place in two stages. The first is mechanical thinning, in which a parallel slice of material is cut from the coating and machined to a 3 mm (0.12 in.) disk using a punch or ultrasonic drill. The disk is then polished to approximately 0.1 to 0.2 mm (0.04 to 0.08 in.) in thickness. Finally, the center of the disk is further reduced in thickness by dimpling, that is, grinding with a spherical abrasive tool, which leaves a depression in the center that can be 20 μm (800 μin.) thick.

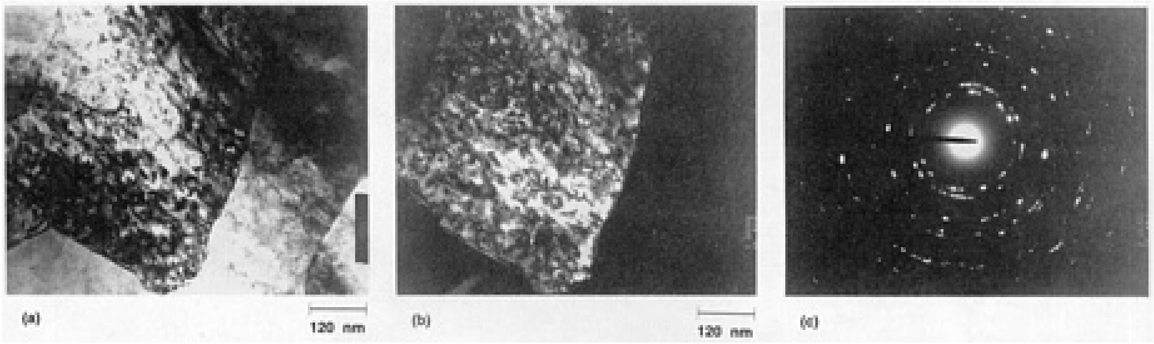


Fig. 10 Plan-view transmission electron microscope images of sputtered titanium nitride coatings. (a) Bright-field image. (b) Dark-field image obtained by putting an aperture over two bright {200} diffraction spots. (c) Corresponding diffraction pattern

The second stage involves final thinning to perforation, which occurs by either electropolishing, using a fine jet of etchant, or ion beam milling, using an argon ion beam of approximately 3 kV, which is directed at the surface at a low angle (5-20°). For metals and semiconductors, the electropolishing route is preferred, whereas for ceramic materials, ion beam milling is usually necessary. Depending on whether the area of interest in the coating is near the substrate interface or further out in the film, thinning of the sample will occur on the film side or the substrate side, respectively, before final perforation is achieved by thinning from both sides. Using this approach, a section can be produced from any level within the coating, but it is difficult to ascertain how far from the interface any plan-view sample lies.

Another method used to produce foils is to deposit a sufficiently thin coating onto a soluble substrate, such as aluminum (soluble in sodium hydroxide) or sodium chloride (soluble in water). After dissolution of the substrate, the film is transferred to a copper grid for imaging. However, in some cases, the film will collapse when the substrate is removed, leaving a fine powder, which can be captured on a copper grid in order to study individual grains (or columns, for PVD coatings) in more detail, but which gives no information about columnar packing.

More information can be obtained from cross-sectional TEM samples, which are considerably more difficult to produce. Usually, the sample is cut in two and joined, coating side to coating side, with a good epoxy adhesive. The assembly is then cut into thin slices and prepared in a similar manner to plan-view samples. However, the differential thinning rates of coating, substrate, and adhesive mean that it is often difficult to prevent the sample from collapsing during thinning. A number of workers have used this technique to study the interfacial regions of hard coatings in some detail (Ref 25, 26).

A TEM consists of an electron gun (typically, 100 to 400 kV for analytical configurations) and an assembly of lenses, all enclosed in a column evacuated to about 1.3 × 10^{-3} Pa (10^{-5} torr). The optical arrangement is similar to that of a light

microscope, but additional stages of magnification are used. Condenser lenses collimate the electron beam, which passes through the specimen, and an objective lens is then used to form a first image in the object plane of the first projector lens. This image is magnified about 40 times. A small area from this image is then projected as an intermediate image, magnified about 40 times by the first projector lens. A small area of this image is then projected onto a fluorescent screen or photographic plate by another projector lens. The image is formed from the intensity distribution of the electrons leaving the bottom surface of the specimen. A total magnification ranging from 10,000 to 1,000,000 is achievable.

In addition to imaging, the TEM can be used for diffraction patterns. The diffraction pattern is formed at the back focal plane of the objective lens, and can be imaged by adjusting the projector lens excitation, which is an automatic function for most modern TEMs. The resolution of the TEM increases with electron-beam energy, and is approximately 0.19 nm (0.008 μin.) at 400 kV.

Contrast in the images is generated in two different ways. For amplitude-contrast imaging, an aperture is used to select either the primary transmitted electron beam (bright field) or one of the diffracted beams (dark field). The aperture is placed in the back focal plane of the objective lens, and the beam is focused to form an image with a further lens. Dark-field imaging is particularly useful when several phases are present. The formation of a dark-field image using a diffracted beam from one of the several phases present highlights the locations in the sample where that phase can be found. Microcracks, grain boundaries, stacking faults, and other defects can also be identified using dark-field imaging techniques (Ref 27).

For phase-contrast imaging, the primary and diffracted beams are allowed to interfere with one another. Local phase shifts of the electron waves are created by voids, defects, heavier atoms, and other phenomena. Phase contrast is the principle underlying lattice imaging (Ref 23). In addition, phase-contrast imaging under defocus conditions is used to identify voids or density variations (Ref 14, 28).

The combination of selected-area diffraction with imaging makes the TEM a very powerful tool. Phase identification and morphological characteristics can be achieved on the same areas of a sample. State-of-the-art analytical TEMs can focus the beam to a spot that is only several nanometers in diameter. The use of an x-ray detector on the column allows the analysis of chemical composition with nanometer-range spatial resolution. However, it should be realized that only a very small volume of material is sampled, because of the high magnifications used and the thin samples needed for imaging. Many microstructural variations occur on a larger scale. Therefore, x-ray diffraction is a more appropriate analytical technique for the study of large-scale structural features such as these, because it samples larger volumes of the sample.

Porosimetry. Porosity can be measured by the mercury intrusion porosimetry (MIP) technique, tests that use corrosive gases to decorate defects, density bottle methods, or optical or electron micrographs. These methods measure different types of porosity, namely open porosity for MIP and gas methods, closed porosity for the density bottle methods and total porosity (including sample preparation artifacts) for the microscopy measurements. No technique is particularly suitable when the porosity levels are low or the pores very small. In these cases, only electron micrographs can be used, and these sample a rather small volume of material.

MIP is very suitable for measuring the intersplat porosity for plasma-sprayed coatings. The determination of pore size distribution by MIP is based on the physical principle that mercury will not penetrate fine pores until sufficient pressure is applied to force its entry. The relationship between the applied pressure, *P*, and the pore radius into which mercury will intrude, *r*, is:

$$Pr = -2\gamma\cos\theta \qquad \textbf{(Eq 4)}$$

where γ is the surface tension of mercury and θ is the contact angle between mercury and the pore wall. Varying the externally applied pressure results in changes in the intruded volume that can be related to pore-size distribution. The method assumes an ideal model in which the specimen pore structure is represented by a labyrinth of interconnected cylindrical pores of sequentially diminishing size. Most natural materials diverge from this. Completely closed pores will not be assessed, and pores accessed through a narrow neck will have their size underestimated. However, as a method of quality-control testing or to compare materials produced by different processes, this is a valuable technique. It cannot be used for materials with which mercury forms an amalgam.

The visibility of porosity can be enhanced by filling pores with a colored mount or metal. For instance, if a plasma-sprayed alumina coating is deposited onto a metal substrate, then copper can be electroplated into the pores, which will

make them extremely easy to identify in polished cross sections. This minimizes the effects of grain pullout on the accuracy of porosity measurements.

References cited in this section

14. D.S. Rickerby and S.J. Bull, *Surf. Coat. Technol.,* Vol 39/40, 1989, p 315
15. A. Schulz, H.R. Stock, H. Vetters, and P. Mayr, *Pract. Met.,* Vol 27, 1990, p 269
16. G.A. Blann, D.J. Diaz, and J.A. Nelson, *Adv. Mater. Proc.,* Vol 12, 1989, p 31
17. B.D. Cullity, *Elements of X-ray Diffraction,* Addison-Wesley, 1978
18. Joint Committee of Powder Diffraction Standards, *Powder Diffraction File,* International Center for Diffraction Data
19. D.S. Rickerby, A.M. Jones, and B.A. Bellamy, *Surf. Coat. Technol.,* Vol 37, 1989, p 111
20. H.P. Klug and L.E. Alexander, *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials,* Wiley-Interscience, 1974, p 618-708
21. G.E. Williamson and W.H. Hall, *Acta Metall.,* Vol 1, 1953, p 22
22. D.E. Newbury, D.C. Joy, P. Echlin, C.E. Fiori, and J.I. Goldstein, *Advanced Scanning Electron Microscopy and X-ray Microanalysis,* Plenum Press, 1986
23. A. Bourret, J. Desseaux, and A. Renault, *Philos. Mag.,* Vol A45, 1982, p 1
24. G. Thomas and M.J. Goringe, *Transmission Electron Microscopy of Materials,* Wiley, 1979
25. I. Petrov, L. Hultman, U. Helmersson, J.-E. Sundgren, and J.E. Greene, *Thin Solid Films,* Vol 169, 1989, p 299
26. J. Echigoya, Z.-T. Liu, A. Imanura, and S. Takatsu, *Thin Solid Films,* Vol 198, 1991, p 293
27. A.R. Pelton, B.W. Dabrowski, L.P. Lehman, C. Ernsberger, A.E. Miller, and J.F. Mansfield, *Ultramicroscopy,* Vol 29, 1989, p 50
28. M. Ruhle and M. Wilkens, *Proc. 5th Evr. Conf. Electron Microscopy* (Manchester), Institute of Physics, 1972, p 416

Property/Technique Synopsis

As already noted, any single technique cannot provide all the information needed to completely categorize a coating material. For phase identification, x-ray diffraction is the primary technique used, although electron diffraction can also be used. The volume of material sampled by the x-ray technique is much larger, and a more representative picture of the complete coating phase composition is produced. However, very thin coatings or phases with very small volume fractions may be difficult to detect with x-rays, in which case electron diffraction would be preferred.

Coating thickness and surface morphology can be determined from fracture or polished cross sections using either light or scanning electron microscopy. Some estimates of grain size or porosity can also be made in these cases, if an appropriate sample preparation method is used. Etching may be necessary before polished cross sections can reveal grain or phase boundaries. For coatings that are less than 10 μm (400 μin.), scanning electron microscopy is necessary to determine the structure in cross section. For films that are considerably less than 1 μm (40 μin.) in thickness, only transmission electron microscopy is capable of giving cross-sectional images that can be used to determine grain size, phase distribution, or porosity. This is particularly true when interfacial structures are to be examined.

The importance of good specimen preparation for all structural analysis techniques cannot be overemphasized. In many cases, apparently featureless fracture or polished cross sections have been taken to indicate amorphous or single-phase coating. Subsequent etching or diffraction analysis has shown the presence of grain or phase boundaries.

It is also important to correlate the structure of coatings with their composition, which can vary through the coating thickness. The article "Surface and Interface Analysis of Coatings and Thin Films" in this Section of the Volume provides information on coating analysis.

Surface and Interface Analysis of Coatings and Thin Films

S. Hofmann, Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft, Stuttgart, Germany

Introduction

SURFACE AND INTERFACE ANALYSIS TECHNIQUES have been among the paramount characterization methods since the beginning of modern, scientifically based thin film and coatings technology in the seventies, and their use very often has led to substantial progress in new fabrication techniques and devices (Ref 1, 2). This is obvious because the structure and composition of surfaces and interfaces is decisive for many properties of thin films, such as chemical reactivity, friction and wear, film adhesion, and electronic and diffusional properties. Of course, any of the large variety of physical characterization methods is more or less surface sensitive, but this article refers mainly to the "classical" methods of surface chemical analysis, namely electron spectroscopies (Ref 3) and ion spectroscopies (Ref 4), of which the most important techniques are Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS or ESCA, electron spectroscopy for chemical analysis), and secondary ion (and neutral) mass spectroscopy (SIMS and SNMS) (Ref 5, 6). Glow discharge optical emission spectroscopy (GDOES) or glow discharge mass spectroscopy (GDMS), ion scattering spectroscopy (ISS), and Rutherford backscattering spectroscopy (RBS) are becoming of increasing importance, as is total reflection x-ray fluorescence spectroscopy (TRXF) (Ref 7) in special applications. All these techniques were emerging in the late 1960s and early 1970s (Ref 5) and have been developed since then into often sophisticated instruments for local microanalysis down to the nanometer scale (Ref 3, 4, 6). A survey of the most important surface analysis techniques and their relative frequency of application is shown in Fig. 1.

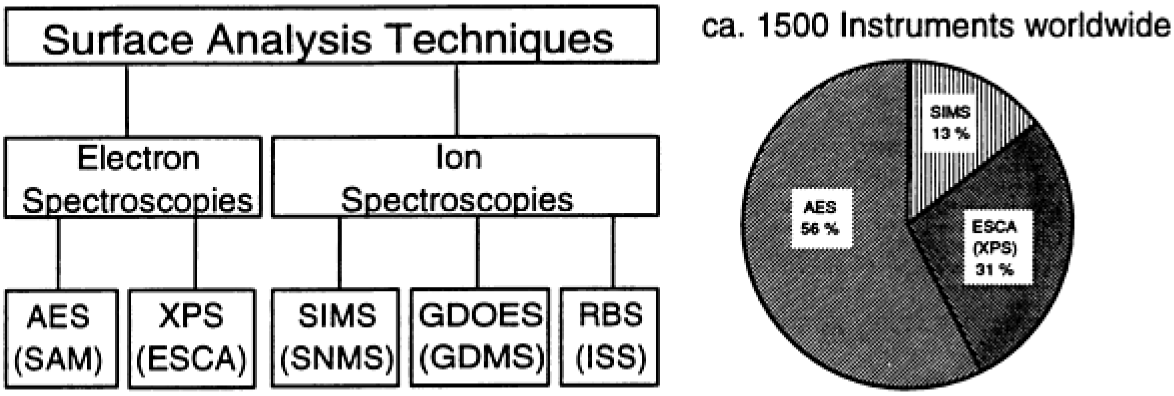


Fig. 1 Survey of the most important surface analysis techniques. AES (SAM), Auger electron spectroscopy (scanning Auger microscopy). XPS (ESCA), x-ray photoelectron spectroscopy (electron spectroscopy for chemical analysis). SIMS (SNMS), secondary ion mass spectroscopy (secondary neutral mass spectroscopy). GDOES (GDMS), glow discharge optical emission spectroscopy (glow discharge mass spectroscopy). RBS (ISS), Rutherford backscattering spectroscopy (ion scattering spectroscopy). Source: Ref 3

Coatings and thin films can be studied with surface analysis methods because their inherently small depth allows characterization of surface composition, interface composition, and the in-depth distribution of composition. This provides an indispensable method for the control of fabrication parameters as well as for the study of property/composition relationships. The full potential of surface analysis is further enhanced if the methods are applied in combination with other characterization methods including phase and structural identification (x-ray diffraction, transmission electron microscopy, and scanning tunneling microscopy) and stereochemistry (infrared and Raman spectroscopy). Recent trends are the development of increased spatial resolution (e.g., toward the 10 nm region and below in AES and SIMS) and improved databases and evaluation software for quantitative analysis.

With the exception of RBS, any of the above-mentioned surface analysis methods involves the use of an ion sputtering facility, which allows destructive depth profiling. Therefore, these methods can also be used for chemical analysis of the "bulk" of thin films and for the characterization of interfaces. Nondestructive depth profiling can be performed with RBS up to a few micrometers in depth, and with angle-resolved XPS up to about 5 nm thickness. Another method of interface analysis is based on brittle fracture or cleavage of the sample along internal interfaces, which exposes two surfaces to be studied by surface analysis. Following are the most important phenomena and structures that can be studied by the above-mentioned methods, the majority of which are relevant for coatings and thin films:

Surfaces, studied directly

- Segregation
- Diffusion
- Contamination
- Adsorption
- Oxidation
- Catalysis
- Friction and wear

Interfaces, studied by fracture and/or profiling

- Segregation
- Diffusion
- Embrittlement
- Intercrystalline corrosion
- Sintering
- Adhesion
- Composites

Thin films, studied by depth profiling

- Interdiffusion
- Ion implantation
- Reaction layers (oxides, passivation layers, etc.)
- Evaporation layers
- Protective coatings
- Microelectronic devices

From the more than 50 different existing techniques in surface analysis (Ref 6), this article only considers the main methods that have broad applicability and for which commercially available instruments exist (AES, XPS, SIMS, SNMS, GDOES, ISS, and RBS). They are characterized by the ability to provide quantitative analysis of all elements (except hydrogen and helium in AES and XPS) and intrinsic information depth in the nanometer range or below.

The latter point is the important difference to (spatially resolved) bulk analysis methods such as x-ray analysis in the electron microprobe. It should be mentioned that high-resolution, analytical scanning transmission electron microscopy (STEM) can also be used for surface and interface analysis (see the article "Microstructure/Characterization of Coatings and Thin Films" in this Volume).

A survey of the lateral and in-depth dimensions of the analyzed volume of typical microanalytical techniques is given in Fig. 2. For surface analyzing techniques with depth resolution below 5 nm, the depth of information is an intrinsic, physical parameter determined by the mean escape depth of photoelectrons or Auger electrons or that of the sputtered particles (SIMS, SNMS). In contrast, the lateral resolution depends mainly on instrumental capabilities, such as primary beam diameter or optical imaging facility.

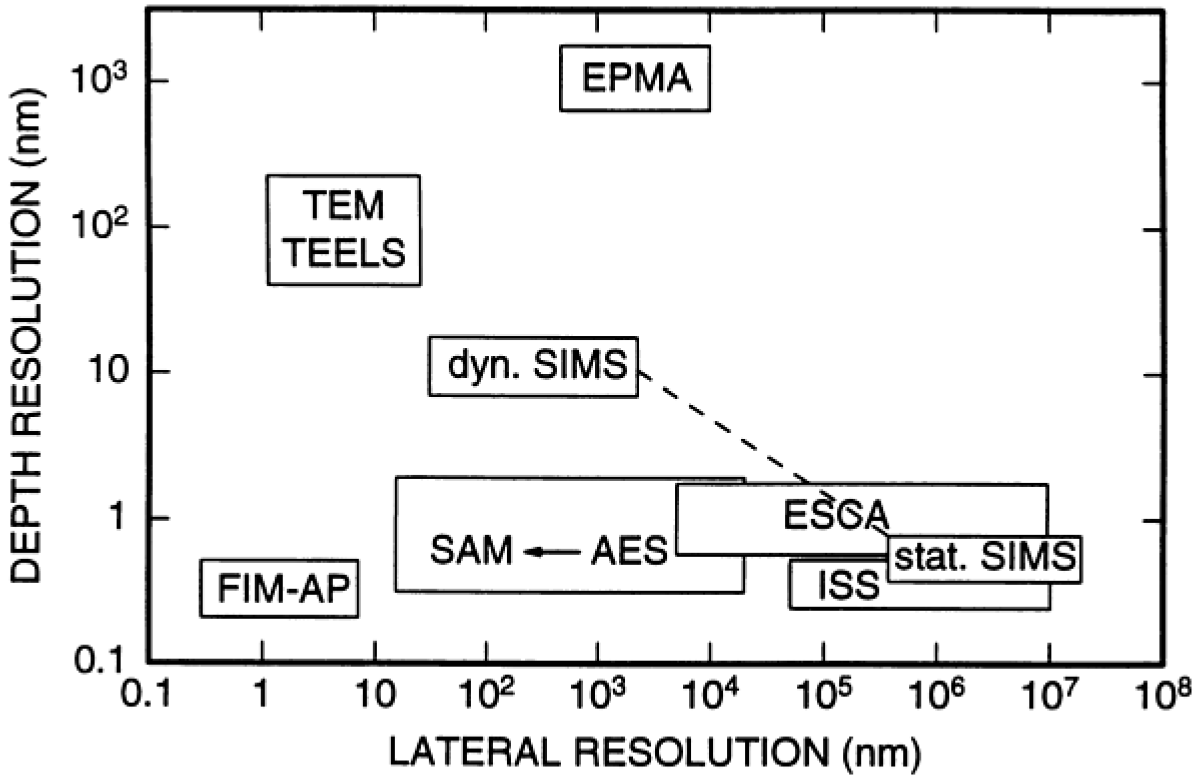


Fig. 2 Depth of information (depth resolution) and lateral resolution of surface and microanalysis techniques. AES, Auger electron spectroscopy. EPMA, electron probe microanalysis. ESCA, electron spectroscopy for chemical analysis. FIM-AP, field ion microscopy - atom probe. ISS, ion scattering spectroscopy. SAM, scanning Auger microscopy. SIMS, secondary ion mass spectroscopy. TEELS, transmission electron energy loss spectroscopy. TEM, transmission electron microscopy.

The principal components of an analytical surface analysis instrument are schematically shown in Fig. 3. They are: an excitation source (electrons, ions, or x-rays), an auxiliary ion gun for depth profiling, and a spectrometer (energy or mass) with particle detector, data acquisition, and processing facility. Together with the sample, the main components are in an ultrahigh vacuum chamber (UHV, $\leq 10^{-9}$ mbar). Therefore they can often be used for process control, as in modern molecular beam epitaxy or physical and chemical vapor deposition methods (Ref 7, 8) which work under UHV base pressure conditions (Ref 7). The principles of the main analysis methods are outlined in the following sections of this article. (For a quick survey and comparison of their most important features, see Table 1.)

Table 1 Comparison of surface and thin-film analysis techniques

Parameter	**Technique**					
	AES	**XPS**	**ISS**	**RBS**	**SIMS**	**GDOES**
Excitation	Electrons	X-rays	Ions	Ions	Ions	Ions
Emission	Electrons	Electrons	Ions (*E*)	Ions (*E*)	Ions (*m*/*e*)	*h*ν (optical)
Typical depth of information, nm	1	1	0.3	1-1000	0.6	10

Lateral resolution	15 nm -30 µm	5 µm -10 mm	1 mm	1 mm	50 nm -10 mm	10 mm
Detection limit	0.1 at.%	0.1 at.%	0.1 at.%	0.1 at.%	1 ppb -10 ppm	1 ppm
Detection of:						
Elements	All except H, He	All except H, He	All except H	H only with ERD	All	All
Isotopes	No	No	Yes	Yes	Yes	No
Chemical state	Yes	Yes	No	No	Yes	No
Imaging/mapping	Yes	Limited	No	No	Yes	No
Depth profile:						
Nondestructive	No	Yes (<5 nm)	No	Yes	No	No
Destructive	+ Sputtering	+ Sputtering	+ Sputtering	No	Yes	Yes
Main usage	Element surface and thin-film analysis	Chemical state analysis	Topmost layer analysis	Nondestructive thin-film analysis	Dopant profiles	Rapid thin-film analysis

AES, Auger electron spectroscopy; ERD, elastic recoil detection; GDOES, glow discharge optical emission spectroscopy; ISS, ion scattering spectroscopy; RBS, Rutherford backscattering spectroscopy; SIMS, secondary ion mass spectroscopy; XPS, x-ray photoelectron spectroscopy

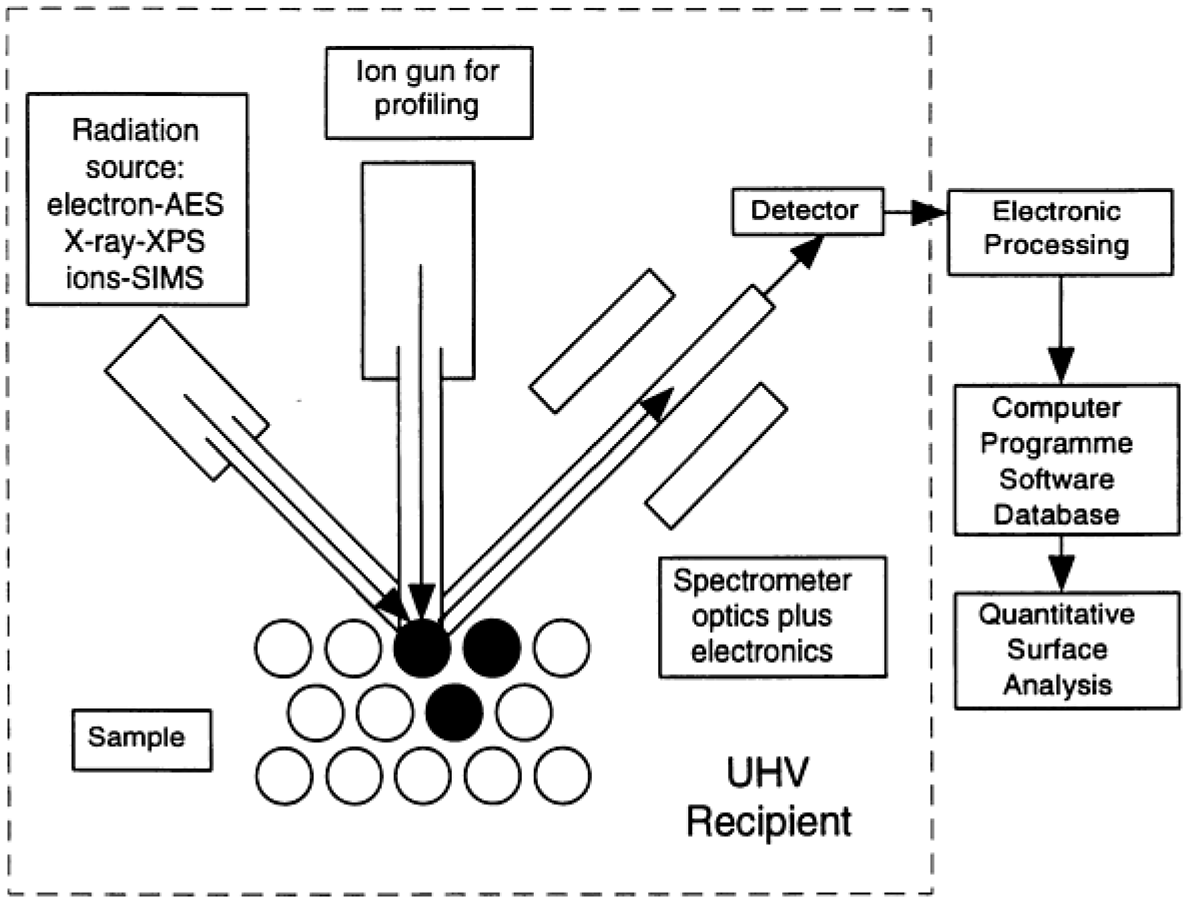


Fig. 3 Principal components of a surface analysis instrument. AES, Auger electron spectroscopy. SIMS, secondary ion mass spectroscopy. UHV, ultrahigh vacuum chamber. XPS, x-ray photoelectron spectroscopy. Source: Ref 3

References

1. A. Benninghoven, in *Thin Solid Films,* No. 31, 1976, p 3
2. S. Hofmann and A. Zalar, in *Thin Solid Films,* No. 39, 1976, p 219
3. D. Briggs and M.P. Seah, Ed., *Practical Surface Analysis, Vol 1: Auger- and X-ray Photoelectron Spectroscopy,* 2nd ed., Wiley, 1990
4. D. Briggs and M.P. Seah, Ed., *Practical Surface Analysis, Vol 2: Ion Spectroscopy,* Wiley, 1991
5. A.W. Czanderna, Ed., *Methods of Surface Analysis,* Elsevier, 1975
6. J.E. Riviere, *Surface Analysis Techniques,* Clarendon, 1990
7. A. Prange, in *Spectrochim. Acta,* Vol 44B, 1989, p 437
8. A.W. Denier van der Gon, R.M. Tromp, and M.C. Reuter, in *Thin Solid Films,* No. 236, 1993, p 140

Electron Spectroscopies (AES and XPS)

AES and XPS determine the energies of electrons emitted from a surface. Those with specific energies usually are photoelectrons or Auger electrons. For detailed information, the reader is referred to Ref 3, 5, and 6. Principles for basic understanding are briefly characterized in the following and illustrated by some examples.

X-ray Photoelectron Spectroscopy. Irradiation of the sample with x-rays of energy $h\nu$ (e.g., characteristic radiation of AlKα: $h\nu$ = 1486.6 eV; or MgKα: $h\nu$ = 1253.6 eV, often combined with a monochromator for narrower line width) causes emission of photoelectrons with kinetic energy E_{kin} according to:

$$E_{\mathrm{kin}} = h\nu - E_{\mathrm{B}} - j_{\mathrm{A}} \quad \textbf{(Eq 1)}$$

where E_B is the binding energy of the respective electron level and j_A is the work function of the electron energy analyzer (Fig. 3). Because hu is the energy of the x-ray source used, the binding energy can be determined directly in most usual instruments if j_A and the analyzed energy E_{kin} are empirically calibrated with standard samples. Tables of binding energies are available (Ref 9).

The terminology of XPS follows that of atomic physics. Each electronic level is characterized by its orbital number *n* (= 1, 2, 3, 4 . . .), the orbital momentum *m* (= *s, p, d, f*), and the total spin quantum number *I* (= 1/2, 3/2, 5/2 . . .).

Chemical Effects and Compound Analysis. In general, chemical bonding changes the electron binding energy of valence band and core levels, which for core levels is recognized in XPS by a distinct "chemical shift" of the elemental peak with respect to the pure element (Ref 3). An example is shown in Fig. 4 for the 2*p* 3/2 and 2*p* 1/2 doublet of the Ti-2*p* XPS spectrum of a native oxide layer on a titanium nitride (TiN) coating (Ref 10). If the characteristic binding energies are known from measurements of standard samples or, often less precisely, from data banks (e.g., the National Institute of Standards and Technology the XPS database in Ref 9), the relative amount of a compound can be directly determined by peak fitting of peaks at the respective energies and subsequent determination of the Ti-2*p* 3/2, 1/2 respective peak areas. This was done for the Ti-2*p* 3/2, 1/2 doublet in Fig. 4, which is decomposed into two doublets, one for TiO_2 and the other for TiN. Comparison of the peak areas in this case gives $X_{TiO_2}/X_{TiN} = 0.49$. With the emission angle θ= 45° and an electron attenuation length of $\lambda_0 = 1.2$ nm, this value corresponds to a 1.8 nm thick TiO_2 layer on TiN.

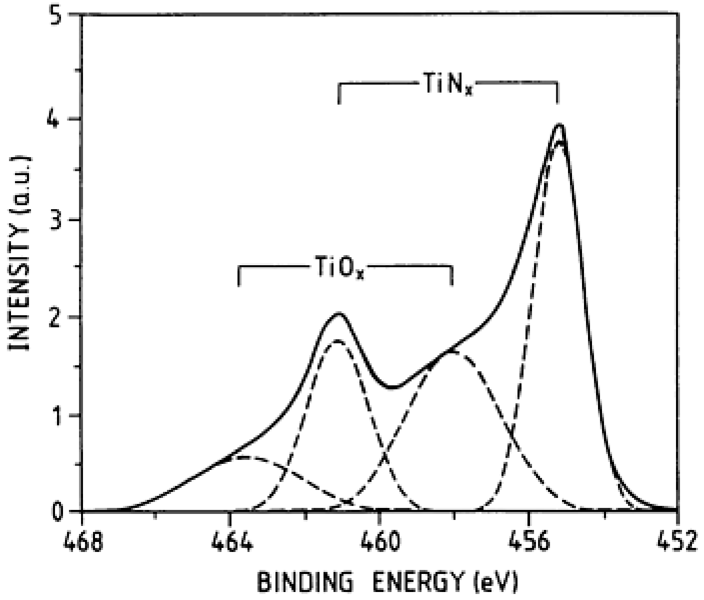


Fig. 4 X-ray photoelectron spectroscopy of the Ti-2*p* 1/2, 3/2 doublet in TiN and TiO_2 obtained with a thin oxide layer on TiN. Source: Ref 10

Usually, the chemical shift of compounds such as nitrides and oxides is of the order of a few electron volts (see Fig. 4) (Ref 3, 9). In many compounds, different valency states have a characteristic shift of the core level. For example, the Ta-4*f* doublet in Ta_2O_5 shows a shift of the binding energy of 5 eV from Ta^0 to Ta^{5+}, whereas for TaO a shift of 2 eV (corresponding to Ta^{2+}) is obtained (Ref 11).

Auger Electron Spectroscopy. The most important method for chemical microanalyses of a surface is electron-beam-excited AES, which is based on the Auger effect (Ref 3, 5, 6). It is a radiationless transition, competing with x-ray fluorescence when an atom is ionized (e.g., by electron impact) in an inner shell (e.g., *K*-shell). The generated electron vacancy can be filled by an electron from an outer shell (e.g., *L*-shell), and the energy gain of this transition causes the

emission of another electron from the outer shell. According to the net energy of the described Auger transition involving K, L_1, L_2 levels, the kinetic energy of the emitted Auger electron is given by:

$$E_{kin}\,(KL_1L_2) = E_K - EL_1 - EL_2 - \Delta E - j_A \qquad \textbf{(Eq 2)}$$

where E_K, EL_1, and EL_2 are the respective electron binding energies, ΔE is a small correction term for the relaxation of the twofold ionized state, and j_A is the work function of the analyzer.

Equation 2 gives a characteristic kinetic energy--independent of the excitation energy--for any specific Auger transition of an element and therefore is the basis of qualitative analysis. Because three electron levels are involved, hydrogen and helium cannot be detected. For elements with higher atomic number, transitions such as *LMM*-, *MNN*-, and so on are used for Auger analysis. In general, the derivative spectrum $d[N(E) \cdot E]/dE$ is recorded as shown in Fig. 5 for TiN (Ref 10).

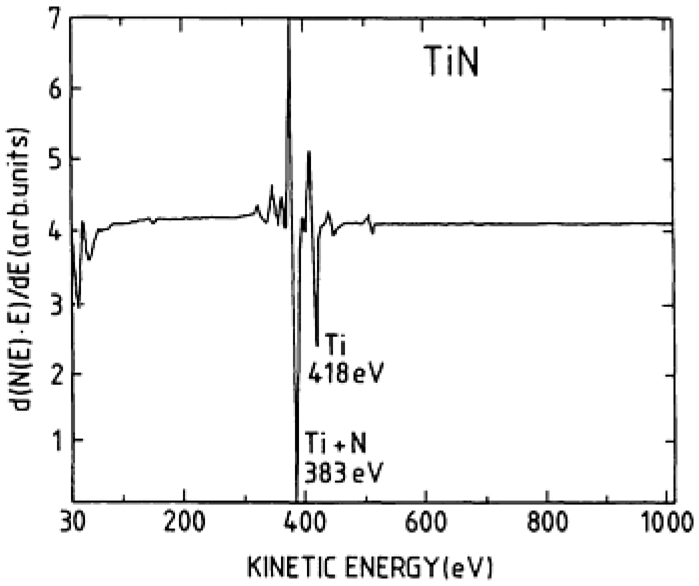
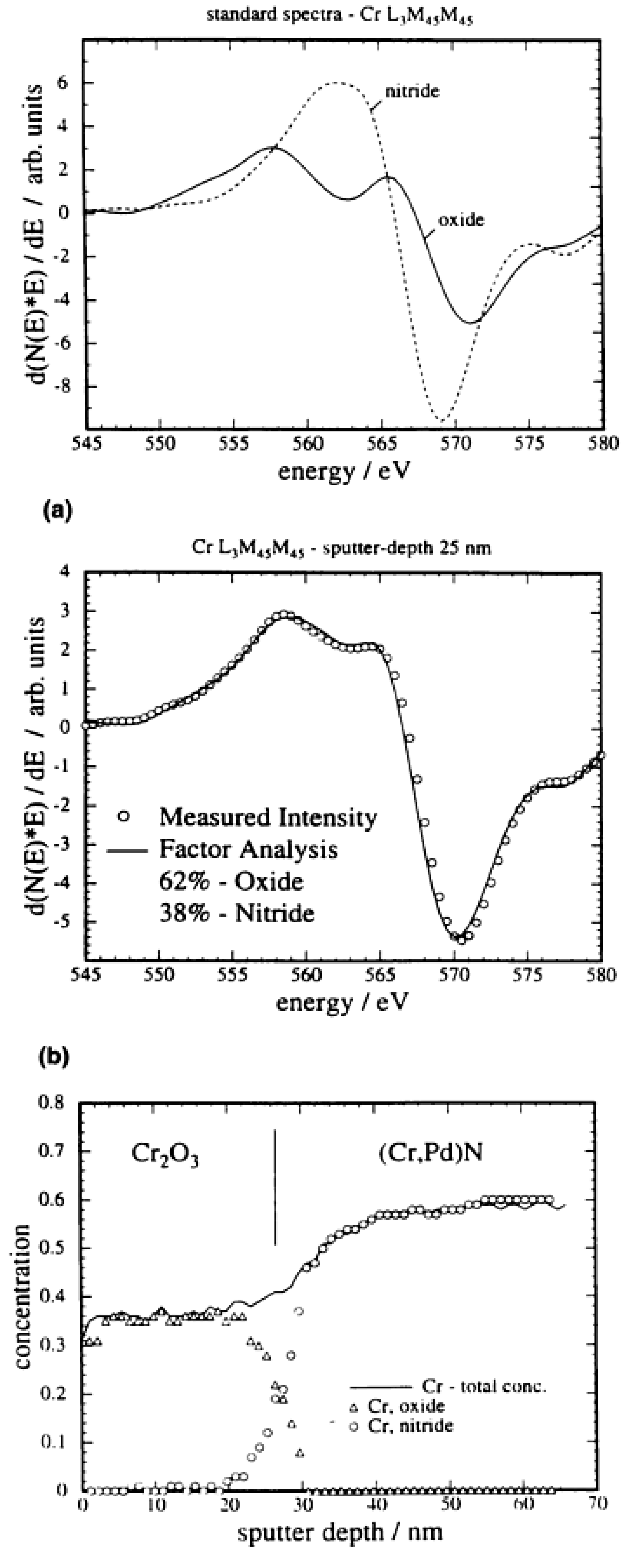


Fig. 5 Auger electron spectroscopy of a TiN coating in the derivative mode. At 383 eV, one of the major titanium peaks overlaps with the nitrogen (381 eV) peak. Source: Ref 10

Chemical Effects and Compound Analysis. Because of the three electron levels involved in AES, the chemical bonding effect is much more complex than in XPS and is most often recognized as a peak shape change that impedes elemental quantification (Ref 3). However, the knowledge of standard spectra of the relevant factors (or principal components) allows the decomposition of a measured depth profile into quantitative contributions, as shown in Fig. 6 for Cr_2O_3 and CrN in an oxidized (Cr,Pd)N coating (Ref 12).



(a) (b) (c)

Fig. 6 Factor analysis in Auger electron spectroscopy depth profiling of an oxidized (Cr,Pd)N coating. (a)

Standard spectra of the components chromium nitride and chromium oxide. (b) Comparison of measured and synthesized spectra. (c) Depth profile of the principal components. Source: Ref 12

Applying the mathematical method of factor analysis (Ref 13) to a series of spectra, for example in a depth profile (Ref 14, 15) enables the assessment of the number of principal components and a test of the validity of the otherwise obtained standard spectra, as well as the determination of one unknown component *n* if *n*-1 components are known. For more details of this powerful method, the reader is referred to Ref 13, 14, and 15 (see also the section "Thin Film and Interface Analysis" in this article).

Information Depth. Whenever an Auger electron or photoelectron is generated, its characteristic energy can be analyzed outside the sample only if it leaves the surface without any inelastic scattering event by which it loses some amount of energy and contributes then only to the lower-energy background of the spectrum. The probability of inelastic scattering increases exponentially with the traveled distance and is described by the inelastic mean free path λ_0 or, more precisely, attenuation length, which additionally includes elastic scattering (Ref 16). Depending on electron energy and material, the attenuation length is typically between 0.4 and 3 nm and increases with the kinetic energy. Although physical theories for predictions of λ_0 have recently been developed (Ref 17), the semiempirical relation of Seah and Dench (Ref 18) is still useful and gives the right order of magnitude for elements as well as for many inorganic compounds for the energy range of 30 to 3000 eV:

$$l_o = \left[\frac{534}{E^2} + 0.41.(a.E)^{1/2}\right].a \qquad \textbf{(Eq 3)}$$

where λ_0 is in nanometers, E is the kinetic electron energy in electron volts, and a is the mean atomic distance in nanometers. The atomic mass number, M, the density, ρ, and Avogadro's number, N_0, determine $a = [M/(\rho \cdot N_0)]^{1/3}$. Values of λ_0 are typically between 0.4 nm ($E \approx 100$ eV) and 2 nm ($E \approx 1500$ eV), meaning that 63% of the measured intensity of Auger electrons or photoelectrons stems from a surface layer with the thickness λ_0 for emission perpendicular to the surface (θ = 0). This fact is the reason for the surface-specific information of the electron spectroscopies. If the emission angle θ increases, the electron escape depth λ is smaller than λ_0 and given by $\lambda = \lambda_0 \cdot \cos\theta$(Ref 18).

Quantification Principles of Electron Spectroscopies. The signal intensity, given by the number of Auger electrons or photoelectrons in an elemental peak, is a measure of the number of atoms of this element in the analyzed volume and therefore of its concentration. Usually, the signal intensity is given by the area under the measured peak [$N(E)$] after background subtraction (Ref 3). Whereas background subtraction is generally used in XPS, the much larger electron background in AES causes relatively large errors. Therefore it is still customary to use the Auger peak-to-peak height in the differentiated [$d[N(E) \cdot E]/dE$] spectrum in AES to characterize the elemental signal intensity I_i, as shown in Fig. 5 for the Auger spectrum of TiN (Ref 10). For both AES and XPS we may write:

$$I_i = k_0 \cdot (1 + r_B) \cdot S_i \cdot X_i \cdot l_0^2 \cdot \cos\theta \qquad \textbf{(Eq 4)}$$

where k_0 is an instrumental constant given by the analyzed area, excitation intensity (primary current or x-ray intensity), and the total analyzer transmission; r_B is the backscattering factor in AES, mainly dependent on the atomic number, and is typically between 0.1 and 1.5 (however, $r_B = 0$ for XPS); S_i is the relative elemental sensitivity factor (generally defined with respect to pure silver in AES and with respect to pure carbon in XPS); X_i is the mole fraction in the analyzed volume (analyzed area times l_0^2); l_0^2 is the inelastic mean free path for the peak energy of element *i* or, more precisely, the attenuation length (Ref 16, 17), and θ is the angle of emission of the detected electrons with the normal to the sample surface.

For a complete spectrum with I_i the intensity of the most intense peak of every detected element *i*, k_0, and θ are constant. Assuming that r_B (in AES) and λ_i are approximately constant, it follows from Eq 4 that:

$$X_i = \frac{I_i / S_i}{\sum_{j=1}^{n} (I_j / S_j)} \qquad \textbf{(Eq 5)}$$

which gives the mole fraction X_i for the chosen element i of a total of n elements. Note that Eq 5 is only a first-order approximation, because the matrix dependence of l_0^2, and of r_B in AES, are neglected. This expected deviation can be taken into account by a correction factor F_{AB} of element A in matrix B, by which every I_A/S_A has to be multiplied in Eq 3 (Ref 3, 10, 19):

$$F_{AB} = \frac{(1+r_B^A).l_0^A}{(1+r_B^A).l_0^A} \quad \textbf{(Eq 5a)}$$

where l_0^A and l_0^B are the electron attenuation lengths and r_B^A and r_B^B are the AES electron backscattering coefficients of the pure element A and of element A in matrix B, respectively. The F_{AB} correction factor depends on the difference, mainly with respect to density and mean atomic number, of matrix and pure element. In favorable cases, F_{AB} is of the order of a few percent; for strong differences, F_{AB} can be between 0.5 and 2 (Ref 3). According to Eq 5a, these values are a measure of the error margin contained in quantification of homogeneous samples using Eq 5.

Depth-Dependent Composition. Homogeneous composition in electron spectroscopies means constant composition within about 5λ from the surface, because the intensities contributing to the signal decay exponentially with depth z, that is, $I_i = I_i^0 \exp(-z/\lambda)$. For $z = 5\lambda$, I_i is about 0.7% of I_i^0 of a pure element at the surface and is therefore approximately at the limit of detection for most elements. Because λ_0 is between 0.4 and 2 nm, the above condition means a required homogeneity in a range between 2 and 10 nm. This is the maximum information depth or the intrinsic sampling depth in AES and XPS.

For example, if λ_0 is 2 nm ($\lambda_0 = \lambda$ for emission perpendicular to the surface, $\theta = 0$) in an AB composition and the first monolayer d = 0.25 nm composed of pure A ($X_A = 1$) with the rest being pure B, then $I_A/I_A^0 = 1 - \exp(-0.25/2) = 0.12$ and $I_A/I_B^0 = \exp(-0.25/2) = 0.88$, which corresponds to $X_A = 0.12$ homogeneously distributed in a region of ≥10 nm. From the measured intensity alone, both possibilities or intermediate cases are indistinguishable. If λ_0 is 0.4 nm, $X_A = 0.46$ is obtained. Figure 7 shows the relation between the ratio $\overline{X}_A(5 \cdot \lambda)/X_A(d)$, of the measured $\overline{X}_A(5 \cdot \lambda)$ and the true $X_A(d)$ homogeneously distributed within a layer of thickness d. It is easily recognized from Fig. 7 that because of matrix effects with respect to the elemental standard, changing λ changes the sampling depth and therefore the sensitivity factor, as outlined above (Ref 19).

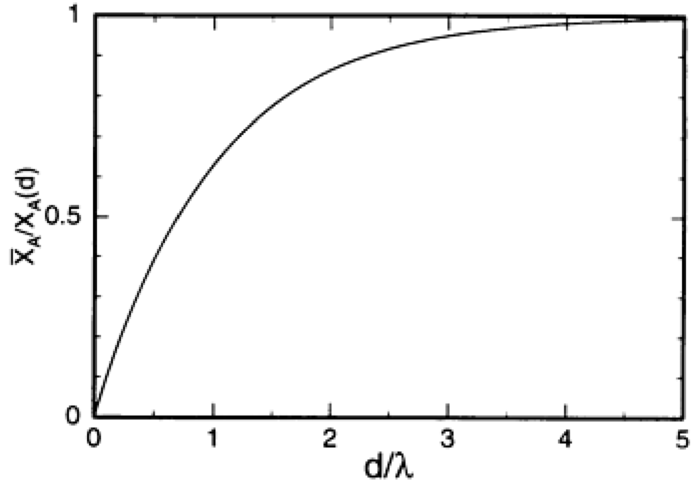


Fig. 7 Ratio of the average concentration $\overline{X}_A$, assuming a constant $\overline{X}_A$ with depth of an A-B alloy, to the concentration $X_A(d)$ of a thin layer of thickness d of A on a substrate B

Because the relative change in λ with composition should be the same for any elemental peak, the sensitivity factor, S_A/S_B, which is decisive for correct quantification of homogeneous samples, should not change with changing composition (except for r_B in AES, Eq 5a). Therefore, any matrix has a characteristic set of elemental sensitivity factors that can be best evaluated by the use of standards (Ref 3, 4, 19, 20).

Microanalysis and Lateral Resolution. The technique of scanning a focused electron beam and simultaneous plotting the peak-to-background intensity of an elemental signal using scanning Auger microscopy (SAM) allows elemental mapping (Ref 21). A secondary electron image of an electronic thin-film device is shown in Fig. 8(a), whereas Fig. 8(b, c, d) show the silicon, aluminum, and fluorine maps. In this case, the device was etched by a fluorine-containing reactive gas. It is clearly recognized that fluorine remained only at the aluminum contact layers and not on the silicon structures (Ref 22).

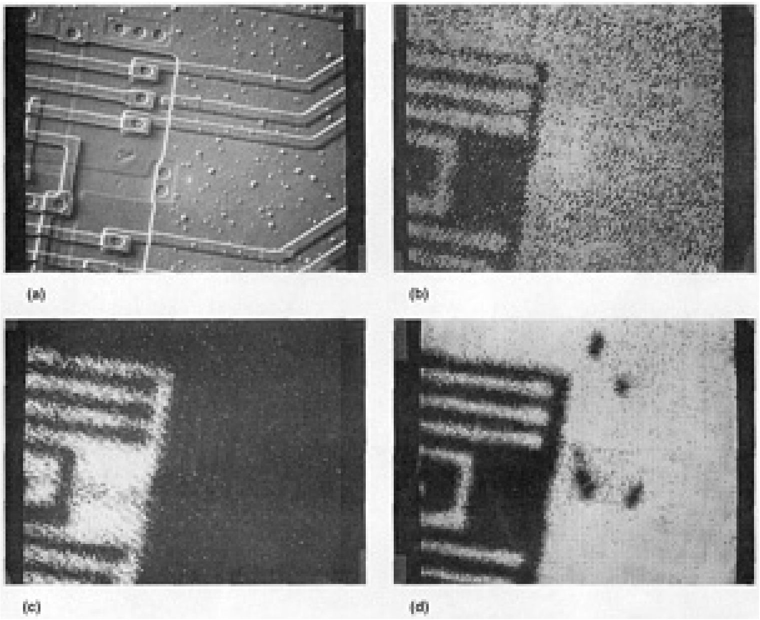


Fig. 8 Integrated circuit after cleaning treatment with a fluorine-containing compound analyzed with Auger electron spectroscopy/scanning Auger microscopy. (a) Secondary electron image. (b) Chemical map of aluminum. (c) Chemical map of silicon. (d) Chemical map of fluorine. Note that fluorine is removed by electron-stimulated desorption from focusing spots of the electron beam. Source: Ref 22

A lateral resolution in SAM of about 0.1 μm can be routinely obtained. Modern instruments with field emission cathodes provide primary beam diameters of 15 nm at 1 nA beam current, suitable for the analysis of microelectronics devices. Limitations in quantification and detrimental effects such as beam heating are discussed in Ref 22.

XPS offers somewhat less spatial resolution than SAM, about 70 to 5 μm. Small-spot XPS can be performed either by excitation of a restricted sample area (e.g., a focused x-ray beam by a bent monochromator crystal) or by an electron optical lens in front of the analyzer, which selects a limited area of the sample for analysis (Ref 23). Imaging XPS uses monochromatic electrons and a multichannel parallel detection device to generate an elemental image (Ref 23).

Limitations and Special Problems. High-spatial-resolution AES of small particles, protrusions, or precipitates in micrometer dimensions is difficult to analyze quantitatively because of distortions by backscattered primary electrons that excite Auger electrons from the surrounding material. The achievable resolution is limited by the amount of current in a small-diameter beam that is necessary for a sufficient signal-to-noise ratio and by the temperature increase that is due to the high current density (up to 10^3 A/cm^2), which may cause diffusion and even evaporation processes in thin films on substrates with low thermal conductivity (Ref 21, 22). Furthermore, electron-stimulated desorption may lead to decomposition of compounds at the surface. For both cases of sample damage, lowering the current density (e.g., by enlarging the beam diameter or scanning the electron beam over a certain area) is a remedy, but at the cost of decreasing spatial resolution. The usually much lower power density greatly reduces this problem in XPS.

Charging of insulating materials is a severe problem in both AES and XPS. However, whereas negative charging of the sample in AES is difficult to overcome in practical analysis, even though a number of special techniques can help (Ref 24, 25), XPS causes positive surface charging, which can often be successfully compensated by low-energy electron flooding with an auxiliary electron source (Ref 26).

References cited in this section

3. D. Briggs and M.P. Seah, Ed., *Practical Surface Analysis, Vol 1: Auger- and X-ray Photoelectron Spectroscopy,* 2nd ed., Wiley, 1990
4. D. Briggs and M.P. Seah, Ed., *Practical Surface Analysis, Vol 2: Ion Spectroscopy,* Wiley, 1991
5. A.W. Czanderna, Ed., *Methods of Surface Analysis,* Elsevier, 1975
6. J.E. Riviere, *Surface Analysis Techniques,* Clarendon, 1990
9. *X-ray Photoelectron Database,* National Institute of Standards and Technology, 1990
10. S. Hofmann, in *J. Vac. Sci. Technol.,* Vol A4, 1986, p 2789
11. S. Hofmann and J.M. Sanz, in *J. Trace and Microprobe Techniques,* Vol 1, 1982-83, p 213
12. E. Huber and S. Hofmann, Oxidation Behavior of Chromium Based Nitride Coatings, *Thin Solid Films,* in press
13. E.R. Malinowski and D.G. Howery, *Factor Analysis in Chemistry,* Wiley, 1980
14. S. Hofmann and J. Steffen, in *Surf. Interface Anal.,* Vol 14, 1989, p 59
15. H. Bubert and A. Mucha, in *Surf. Interface Anal.,* Vol 19, 1992, p 187
16. A. Jablonski and C.J. Powell, in *Surf. Interface Anal.,* Vol 20, 1993, p 771
17. S. Tanuma, C.J. Powell, and D.R. Penn, in *Surf. Interface Anal.,* Vol 17, 1991
18. M.P. Seah and W. Dench, in *Surf. Interface Anal.,* Vol 1, 1979, p 2
19. H.A. Jehn, E. Grallath, I. LeR. Strydom, and S. Hofmann, in *Surf. Interface Anal.,* Vol 16, 1990, p 540
20. A.J. Perry, C. Strandberg, W.D. Sproul, S. Hofmann, C. Ernsberger, J. Nickersen, and L. Chollet, in *Thin Solid Films,* No. 153, 1987, p 169
21. S. Hofmann, in *Mikrochim. Acta,* Vol 1, 1987, p 321
22. S. Hofmann, in *Mikrochim. Acta Suppl.,*Vol 114/115, p 21
23. R.L. Chaney, in *Surf. Interface Anal.,* Vol 9, 1986, p 345
24. S. Ichimura, H.E. Bauer, H. Seiler, and S. Hofmann, in *Surf. Interface Anal.,* Vol 14, 1989, p 250
25. S. Hofmann, in *J. Electron Spectr. Rel. Phen.,* Vol 59, 1992, p 15
26. C.P. Hunt, C.T.H. Stoddart, and M.P. Seah, in *Surf. Interface Anal.,* Vol 3, 1981, p 157

Ion Spectroscopies

When ions are used as a probe, there are several possibilities for surface chemical analysis: the characteristic energy loss of scattered primary ions (ISS, RBS), the mass of secondary (sputtered) particles (SIMS, SNMS, GDMS), or their optical emission (GDOES). Primary ion energy spectroscopy is performed either at low energy (<10 keV) (Ref 27) or at high energy (>300 keV) (Ref 28). The term *low-energy ion scattering* (LEIS) is often used synonymously with ISS. The term *high-energy ion scattering* (HEIS) is akin to RBS. SIMS (Ref 29) and SNMS (Ref 30) or GDMS (Ref 31) are based on mass spectrometric detection of the sputtered species, while GDOES (Ref 32) measures optical emission lines characteristic for specific elements.

Energy Analysis of Scattered Primary Ions

Ion Scattering Spectroscopy. The principle of ISS is the collisional elastic momentum and energy transfer of a primary ion of mass m_1 and energy E_0 (1 to 5 keV) with an atom of mass m_2 in the topmost layer of the sample (Ref 27). For a given scattering angle, the energy E_1 of the backscattered primary ion (generally He^+) is a unique function of the ratio m_2/m_1. For example, at 90° scattering angle the relation

$$E_1 = E_0 \cdot \left(1 - \frac{m_1}{m_2}\right) / \left(1 + \frac{m_1}{m_2}\right) \quad \textbf{(Eq 6)}$$

is valid and shows how the energy scale (E_1) can be calibrated in a mass scale (m_2). The single-collision binary scattering described by Eq 6 occurs only at the surface. Therefore ISS is unique in determining the composition of only the topmost surface layer. However, the limitations in sensitivity and mass resolution at higher masses (see Eq 6), along with its difficult quantification, have confined ISS to more fundamental research.

Rutherford backscattering spectroscopy is one of the techniques first applied to thin-film analysis (Ref 28). The reason is that due to their high energy (>300 keV, up to several MeV), the primary ions penetrate between several 100 nm and some 10 μm of a solid until they lose their energy and are stopped. Along their way, a considerable fraction undergoes Rutherford backscattering, provided that the nuclei in the target have a higher mass than the primary ions. (These are usually He^+ ions, so hydrogen and helium cannot be detected by RBS.) However, forward ejection of these atoms, that is, elastic recoil detection, can be applied to detect hydrogen (Ref 33). The backscattered primary ions lose a specific amount of energy, which is determined by both the mass m_2 of the scattering atomic nuclei in the sample and by the well-known energy loss that occurs mainly through electronic interaction, which is proportional to the totally traveled distance z and the loss rate dE/dz. The measured energy $E_1/(m_2, z)$ of the primary ion (m_1) after backscattering is given by the following two terms:

$$E_1(m_2, z) = f(m_2, E_0) - z \cdot f(m_2, E_0, dE/dz) \qquad \textbf{(Eq 7)}$$

Because of the second term, the width of the peak due to scattering at m_2 is a measure of the thickness of the respective material, and its intensity is proportional to the (areal) concentration. It is obvious that the achievable depth resolution depends on the energy resolution of the analyzer. Thin-film analysis with high depth resolution is enabled by modern electrostatic energy analyzers. An example is shown in Fig. 9, where the measured and calculated intensity-energy relations for a 10.4 nm thick niobium layer on sapphire is depicted (Ref 34). The notch of the measured profile is due to a native niobium oxide layer of about 2 nm thickness. The main advantages of RBS are that it is a nondestructive and quantitative method. The main disadvantages are the relatively large analyzed spot (typically 1 mm diameter), the necessity of expensive particle accelerators, and the lack of chemical information. For a summary of the typical features of RBS in comparison with other methods, see Table 1.

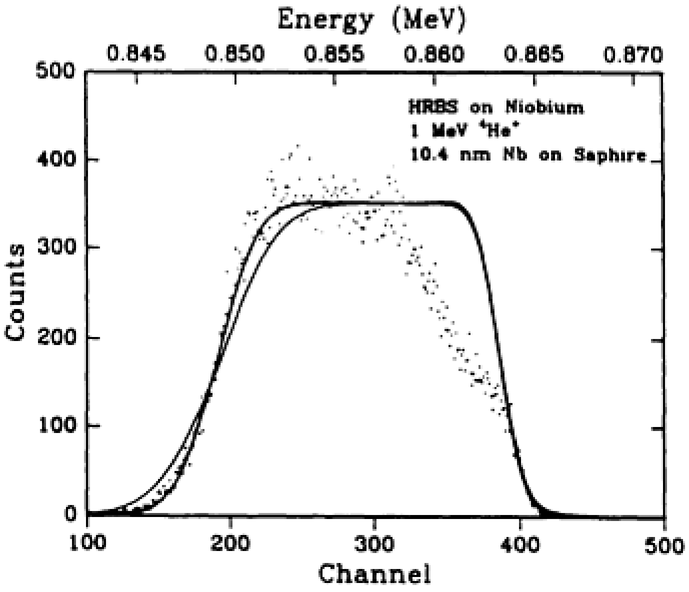


Fig. 9 High-resolution Rutherford backscattering spectroscopy of a 10.4 nm niobium layer on sapphire (calculated solid lines) that was oxidized in air (shoulder in the experimental points distribution). 1 MeV $^4He^+$. Source: Ref 34

Detection of Sputtered Particles

Secondary ion mass spectroscopy (SIMS) is probably the first technique used for depth profiling (Ref 29). A primary ion beam of about 0.5 to 15 keV energy causes sputter erosion of the surface by emission of neutrals and ions. The ejected secondary ions are separated in a mass spectrometer (electric quadrupole or magnetic sector or, in time-of-flight SIMS, by flight time measurements of pulse-accelerated secondary ions). The precision of identification of atomic

and molecular species depends on the mass resolution, ($m/\Delta m$), which typically is 500 to 2000 for quadrupole, up to 10,000 for magnetic sector, and up to 15,000 for time-of-flight spectrometers. The basic equation for quantitative SIMS can be written as (Ref 29):

$$I_I^{\pm} = I_0^{\pm} \cdot T_i \cdot Y_i \cdot b_i^{\pm} \cdot X_i \qquad \textbf{(Eq 8)}$$

where the measured count rate at mass *i* of the positive or negative secondary ions, $I_I^{\pm}$, is determined by the primary ion intensity $I_0^{\pm}$, the total instrumental transmission T_i, the sputter yield Y_i (atoms/ion), the ionization probability $b_i^{\pm}$ (≤ 1) of the sputtered particles (*i*), and their mole fraction X_i in the sample.

The main advantages of SIMS are its:

- Ability to detect all elements, including hydrogen
- Ability to detect elements in the parts-per-billion range
- Ability to perform microanalysis and imaging in the submicrometer range
- High dynamic range of up to 8 orders of magnitude in concentration

Besides its intrinsic destructiveness, the main disadvantage of SIMS is its difficult quantification. The strong matrix dependence of the ionization probability $b_i^{\pm}$ (up to 5 orders of magnitude) is the main reason for the notorious difficulty of quantifying SIMS in a multicomponent matrix with varying composition. Because the sputter yield Y_i is much less matrix dependent, ionization of practically all sputtered neutrals (i.e., $b_i^{\pm}$ approaching unity) would drastically reduce the matrix effect. Indeed, this is done in the so-called SNMS method, where the sputtered neutrals are ionized by a low voltage of plasma or an electron beam ("positonization") (Ref 30). The simplest way to achieve enhanced ionization is a direct-current glow discharge on the sample surface, which at the same time generates sputtered particles and ionizes them (GDMS method) (Ref 31).

A similar method that also uses a direct-current glow discharge is GDOES (Ref 32), where the excitation of optical emission is used as a means to analyze the sputtered species. As in GDMS, the main advantages are the high sputter rate due to the high current density and therefore the speed of thin-film depth profile analysis and high sensitivity. However, lack of spatial resolution and a generally lower depth resolution than with SIMS and SNMS are disadvantageous.

Table 1 compares the most important surface and thin-film analysis methods: AES, XPS, SIMS, and ISS, together with the generally non-UHV methods for thin-film analysis, RBS and GDOES.

References cited in this section

27. J.W. Rabalais, in *Surf. Sci.,* Vol 299/300, 1994, p 219

28. L.C. Feldmann, in *Surf. Sci.,* Vol 299/300, 1994, p 233

29. A. Benninghoven, F.G. Rüdenauer, and H.W. Werner, *Secondary Ion Mass Spectrometry,* Wiley, 1987

30. A. Wucher and H. Oechsner, in *Fresenius Z. Anal. Chem.,* Vol 333, 1989, p 470

31. N. Jakubowski and D. Stuewer, in *J. Anal. At. Spectr.,* Vol 7, 1992, p 1951

32. A. Bengtson, A. Eklund, M. Lundholm, and A. Sarie, in *J. Anal. At. Spectr.,* Vol 5, 1990, p 563

33. A. Turos and O. Meyer, in *Nucl. Inst. Meth. Phys. Res.,* Vol B4, 1984, p 92

34. Th. Enders, M. Rilli, and H.D. Carstanjen, in *Nucl. Inst. Meth. Phys. Res.,* Vol B64, 1992, p 817

Surface Analysis Applications

Surface Adsorbates and Contamination. The most obvious application of surface analysis methods is the study and control of the surface composition prior to further treatment, as in the production of thin-film structures in microelectronics (Ref 35) (see Fig. 8). Trace elements on flat, larger surfaces, for example silicon wafers, can be investigated with total reflection x-ray fluorescence spectroscopy at glancing incidence angle (Ref 7) with high

sensitivity. Different chemical species can be observed. For example, the detection of residues after etching of a silicon surface with a (CHF_3 + O_2) plasma in semiconductor fabrication is enabled by the carbon 1*s* XPS spectrum, which allows the recognition of different peaks attributable to several compounds. Further Ar^+ ion etching removes the fluorine-containing compounds (Ref 35). Any kind of surface contamination can be detected. For example, friction and wear often is accompanied by transfer of materials from one part to the other, which can be monitored by surface analysis.

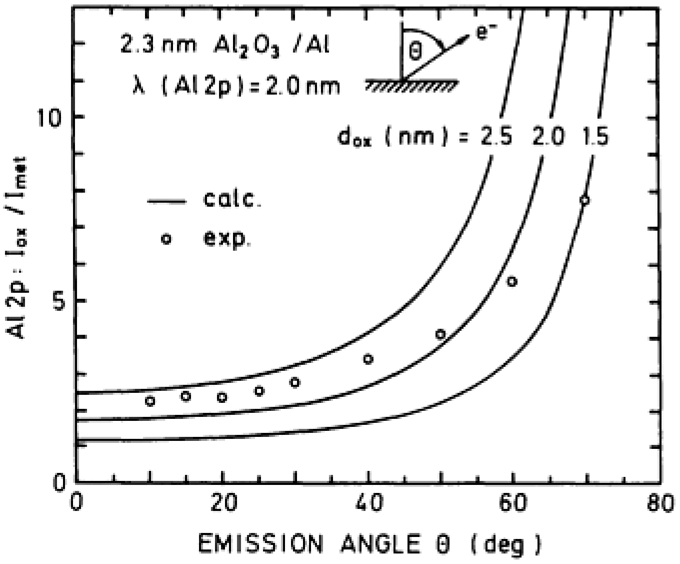
Thin Film and Interface Analysis. Analysis of internal interfaces with surface analysis methods can be principally performed in either of two ways: in-situ fracture of a sample along the interface (e.g., coating-substrate) and subsequent surface analysis of one or both parts (Ref 36, 37, 38), or by depth profiling through the interface (Ref 39, 40). A special method is angle lapping of the sample and taking a line scan across the interfacial region (Ref 3).

Coating-substrate interfaces are often prone to accumulation of impurities (e.g., by segregation or oxidation) that lead to a change in adhesive properties. These can be disclosed by a scratch test, by which a part of the interface is exposed due to peeling of the coating. For example, sulfur segregation was shown to have a detrimental effect on the adhesion of thin films, as determined by an in-situ scratch test in an AES instrument (Ref 41).

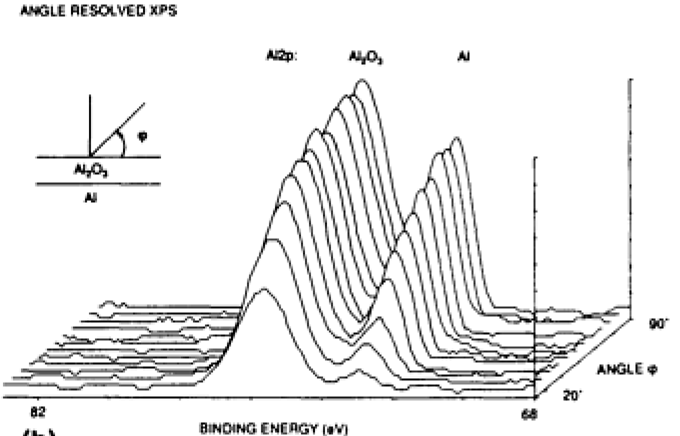
Whereas sputter depth profiling is a destructive method, nondestructive methods make use of the known energy-range relation of ions (RBS) or electrons (AES, XPS) in solids. A particularly important nondestructive method to disclose the in-depth distribution of composition is angular resolved XPS, which is, however, restricted to a probing depth of 2 to 3 times the electron attenuation length (i.e., to <5 nm for conventional XPS). By tilting the sample around an axis perpendicular to the analyzer axis and away from the latter, relatively more and more intensity from the species in the top layer is obtained as compared to deeper layers. An example is given in Fig. 10 for the determination of the thickness of an oxide layer (Al_2O_3) on aluminum. The peak area I_{ox} of the Al-2*p* peak indicating Al_2O_3 (75.7 eV) increases relative to that of pure aluminum (72.3 eV, I_{met}) with increasing takeoff angle φ. The thickness *d* of the Al_2O_3 layer is given by (Ref 42, 43, 44):

$$d = \lambda \cdot \sin \varphi \cdot \ln(1 + k \cdot I_{ox}/I_{met}) \qquad \textbf{(Eq 9)}$$

where λ is the electron attenuation length (2.0 nm) and *k* is a sensitivity correction factor of the order of unity. Figure 10(b) shows a plot of the ratio I_{ox}/I_{met} from Fig. 10(a) as a function of the emission angle $\theta = 90° - \varphi$. Using a more general formulation of the angular dependence $I(\varphi)$ being a Laplace transform of $I(1/\lambda)$, more detailed layer profiles can be revealed, as shown by Bussing and Holloway (Ref 45) for the altered layer of sputtered Ga-As surfaces. Recently, multilayer samples were successfully studied by using grazing incidence XPS, which combines the low penetration depth of x-rays at $\varphi < 3°$ incidence angle to the surface (and its variation with φ) with all the XPS features (Ref 46).



(a)



(b)

Fig. 10 Angle-resolved x-ray photoelectron spectroscopy spectrum of a 2.3 nm thick Al_2O_3 layer on aluminum. (a) Al-2*p* peak as a function of the takeoff angle *j*. (b) Ratio of the peak areas of Al_2O_3 and aluminum as a function of the emission angle θ= 90° - *j*. Source: Ref 47

Most common and straightforward is depth profiling by ion sputtering in combination with a surface analysis method. This technique discloses the elemental distribution as a function of the sputtered depth, including the composition of interfaces. Important is the attainment of a high depth resolution (Ref 3, 39, 47), which can be achieved by a rastered beam of Ar^+ ions with less than 3 keV energy, a small analyzed area, and a high angle of incidence (e.g., 70°) of the ion beam (Ref 39). Sample rotation during profiling has been shown to give optimum results with respect to high depth resolution (Ref 40, 48). With this technique, a depth resolution of Δz = 6 nm was achieved for Ni-Cr multilayer thin films (even at a sputtered depth of about 0.5 μm) employing AES and SIMS profiling in a study involving four laboratories (Ref 48).

SIMS depth profiling is particularly useful for determining dopant profiles (e.g., implantation profiles) in semiconductors or detecting impurity segregation at interfaces. The profile obtained from less than a monolayer ("delta layer") of aluminum in Ga-As is shown in Fig. 11 (Ref 49, 50), demonstrating the advantageous sensitivity and high depth resolution of SIMS. Other examples of thin-film depth analyses are given in previous sections of this article.

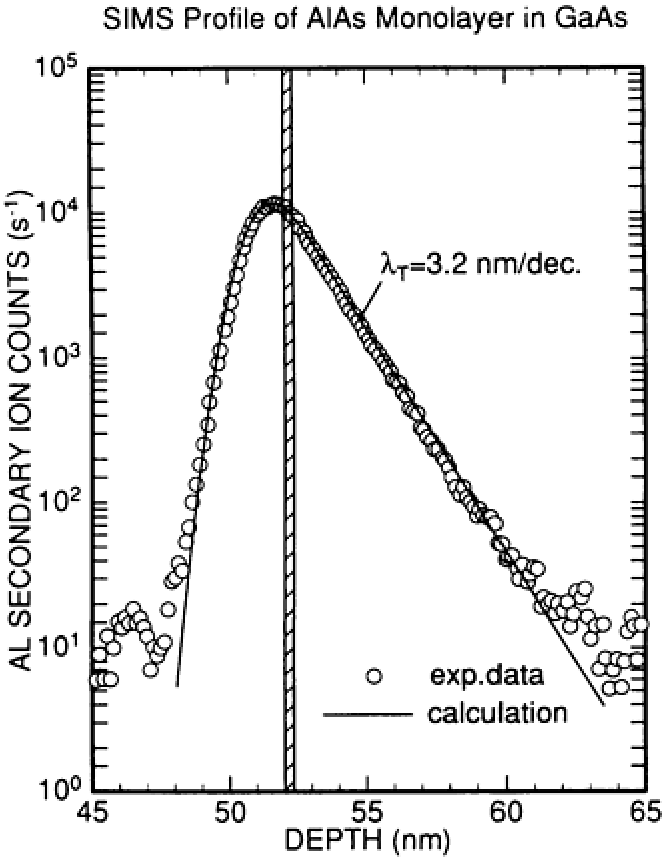
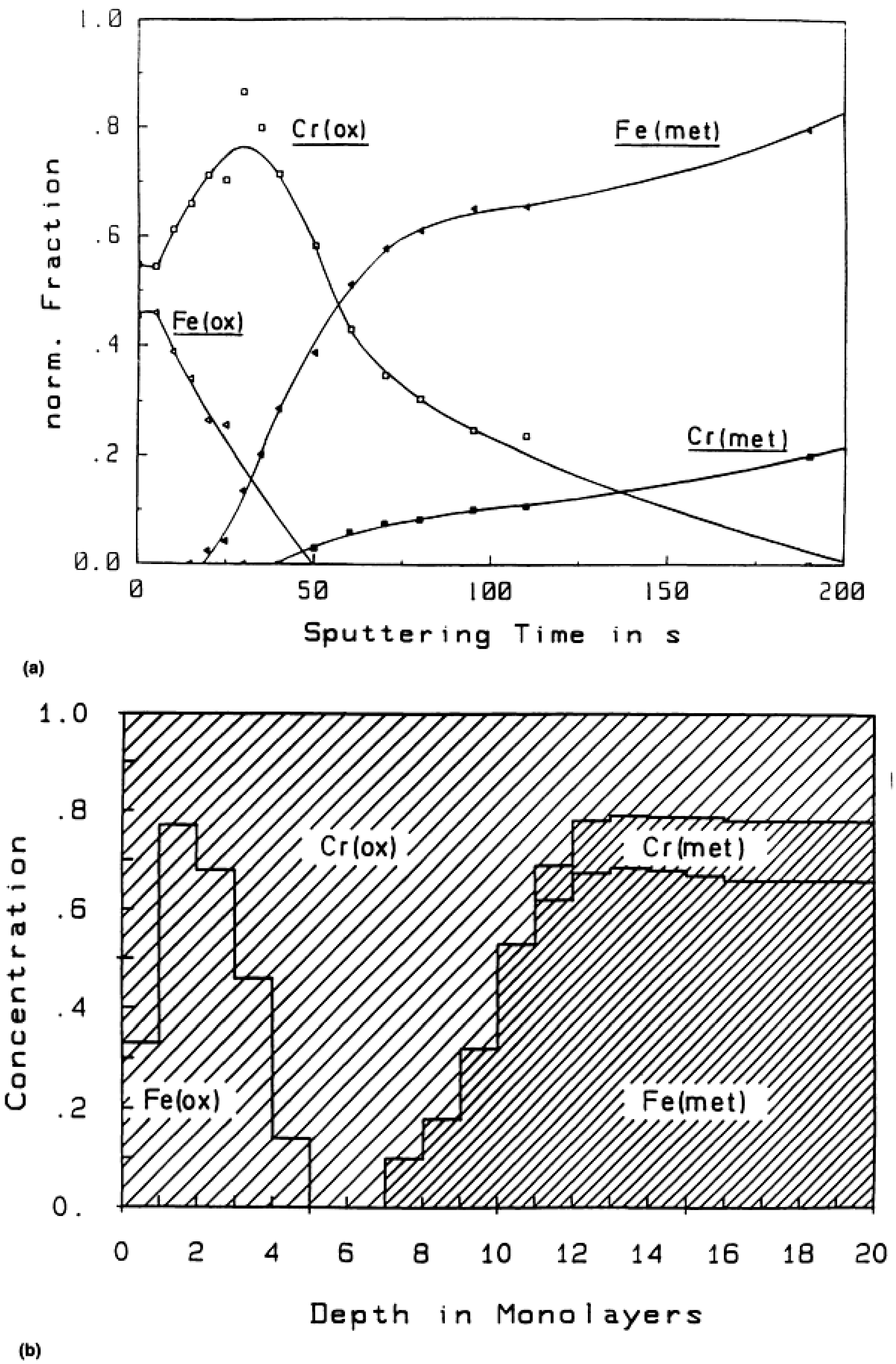


Fig. 11 Secondary ion mass spectroscopy depth profile of an AlAs monolayer doping in GaAs. Comparison between measured points (circles) (Ref 49) and calculations (solid line). Source: Ref 50

The result of chemical reactions at the gas-solid or liquid-solid interface often are specific layer structures, and further reaction behavior depends on their chemical composition. Passive layers on stainless steels (Ref 51) and oxide layers on different alloys and nitride coatings (Ref 52) have frequently been studied. An example of the composition of a passive layer on an Fe-Cr alloy is shown in Fig. 12. Figure 12(a) shows the AES depth profile obtained by using factor analysis and least-squares fitting of the four different standard spectra of metallic and oxidized iron and chromium (Ref 53). Figure 12(b) gives the result of a "convolution" procedure employed in order to calculate the original depth distribution (Fig. 12b) from the measured profile (Fig. 12a). Profile broadening schemes are used to account for the effects of sputtering and information depth influences on the assumed profile in Fig. 12(b) until an optimal fit with the profile in Fig. 12(a) is obtained (Ref 34, 39).



(a)

(b)

Fig. 12 Depth profile of the chemical composition of a passive layer on an Fe-18at.%Cr alloy. (a) Normalized fractions of the standard components Cr_{met}, Cr_{ox}, Fe_{met}, and Fe_{ox} in the Auger spectra as a function of the

sputtering time. (b) Concentrations of the alloy elements in metallic and oxidic states after fitting all fractions of the respective components with a sequential-layer sputtering model. Source: Ref 53

High-resolution AES (i.e., scanning Auger microscopy) is another way to obtain the in-depth composition at interfaces by line scanning the focused electron beam (of ≤ 1 μm diameter) across the rim of the crater generated by sputter profiling (Ref 39, 54). An example of such a "crater edge profile" is shown in Fig. 13 for a TiN coating on a high-speed steel interface characterized by the iron Auger intensity (Ref 55). It is clearly seen, by comparison of the traces of the oxygen signal and the titanium signal, that oxygen varies with titanium and not with iron. This means that only titanium oxide, no iron oxide, is contained in the interface.

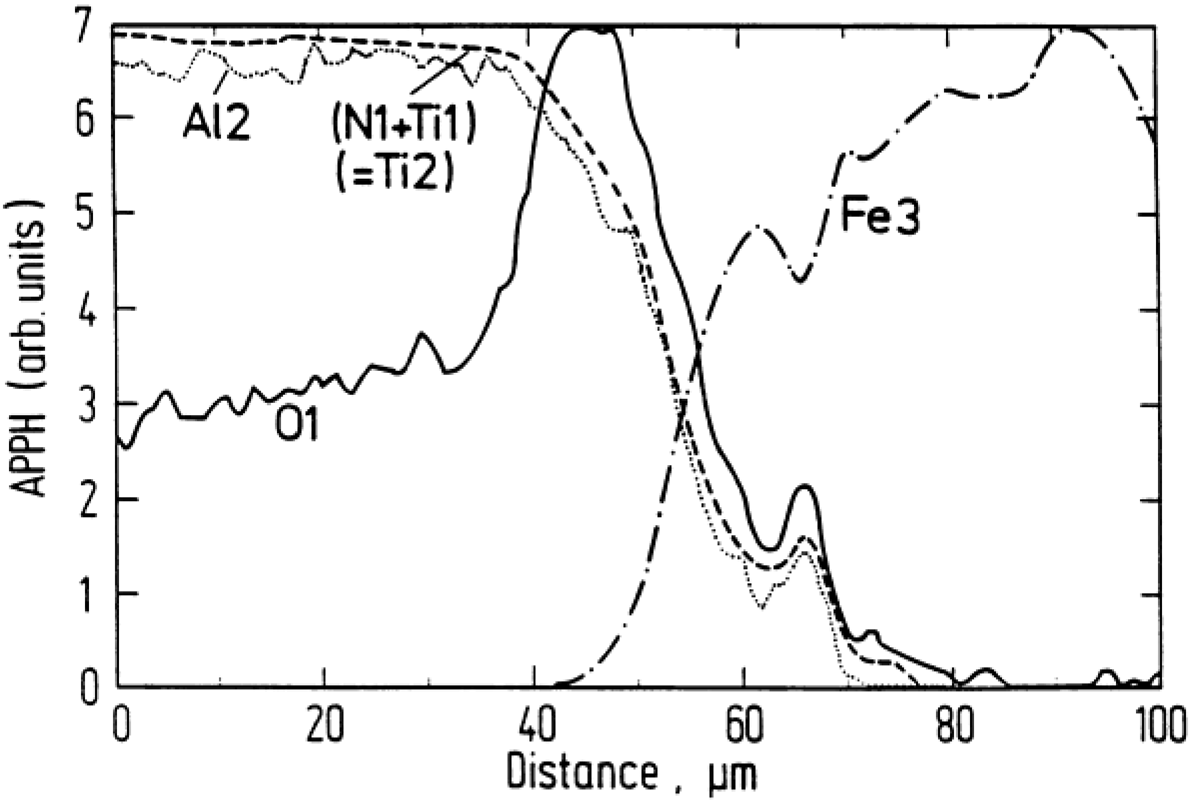
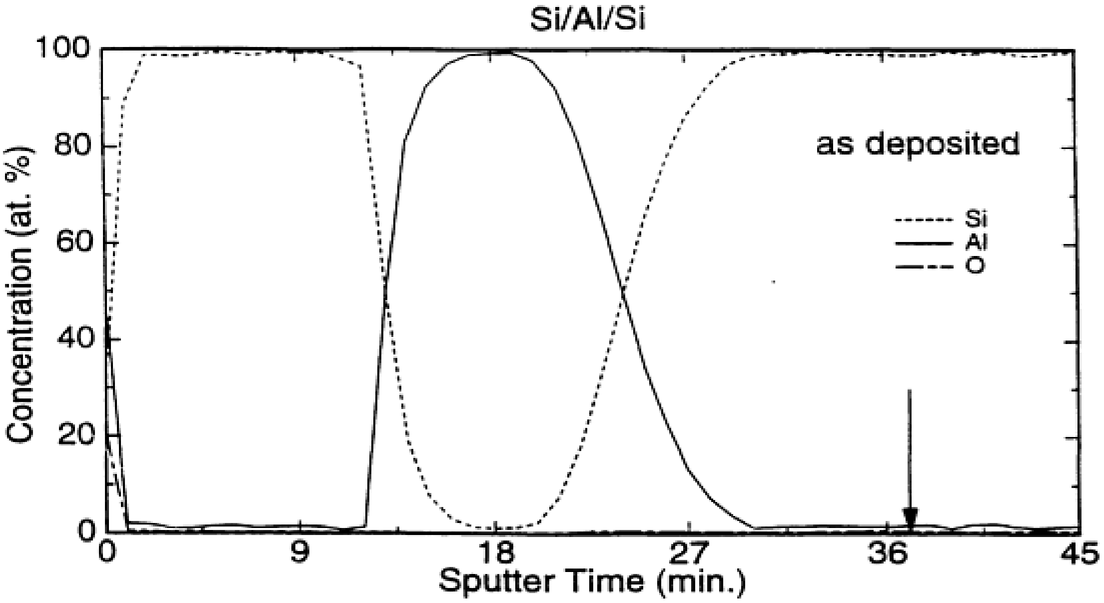


Fig. 13 Oxide layer at the interface between an (Al,Ti)N coating and a high-speed steel substrate (Fe), disclosed by using crater edge profiling with scanning Auger microscopy. Source: Ref 54

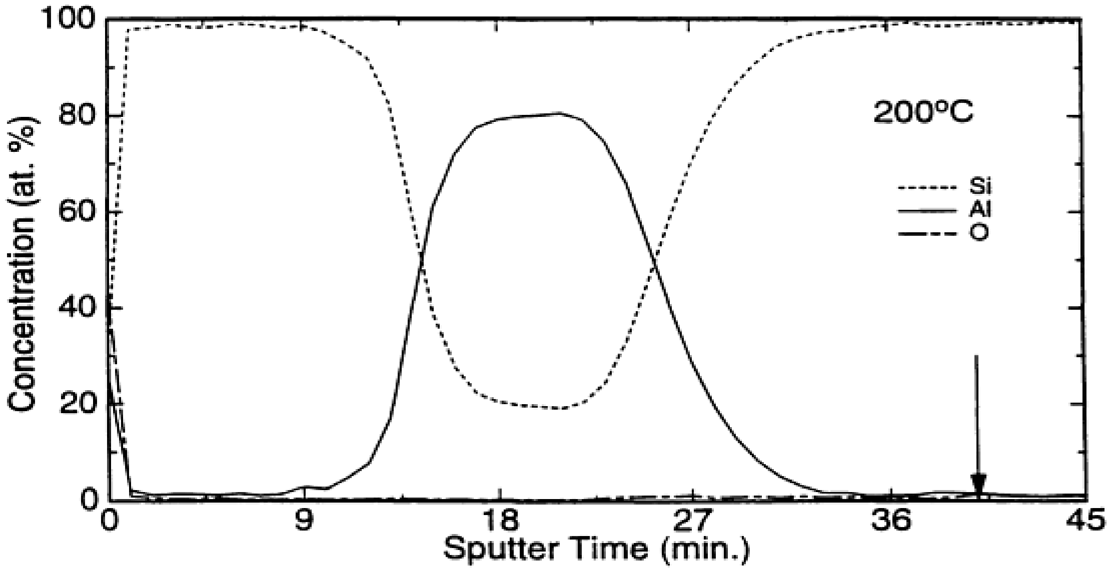
The chemical shift in XPS can be used to disclose different chemical bonding states at interfaces. For example, the two phases ZrO_2 and ZrN were found at the interface ZrN-Fe of a ZrN coating on a high-speed steel substrate (Ref 54). Another example is that different SiO_x suboxides in the interface of ultrathin SiO_2 layers on silicon were disclosed by high-resolution XPS (Ref 56).

Reactions at interfaces can be directly studied by AES and XPS depth profiling. An example is shown in Fig. 14 for a thin-film structure of Si-Ni-Si (each layer about 50 nm thick) sputter deposited on a Si(111) substrate (Ref 57). Figure 14(a) shows the Auger depth profile for the as-deposited sample. Although the apparent interface width increases with depth, the small peak of oxygen at a sputtering time of about 9 min indicates the native SiO_2 layer of about 2 nm thickness on the silicon substrate. The shape of the profile after thermal treatment, with a linear temperature increase up to 205 °C at a heating rate of 40 °C/min, shows that mainly nickel was migrating into the adjacent silicon layers and that mainly a Si_2Ni phase was formed, which was confirmed by selected area diffraction in TEM (Ref 57). Evaluating the increase of the measured interface width, $\Delta z = z\,(0.84\,I_0) - z\,(0.16 \cdot I_0)$, with increasing temperature, T, and time, t, $\Delta z(T) - \Delta z(T_0) \approx 2 \cdot (D \cdot t)^{1/2}$, allows determination of the interdiffusion constant, in this case $D = D_0 \cdot \exp(-Q/kT)$ with $D_0 = 2.5 \cdot 10^{-2}$ m^2/s and the activation energy $Q = 0.5$ eV (Ref 57). The error in this evaluation is mainly due to a change of the sputtering rate with composition (about +50% from pure nickel to pure silicon).



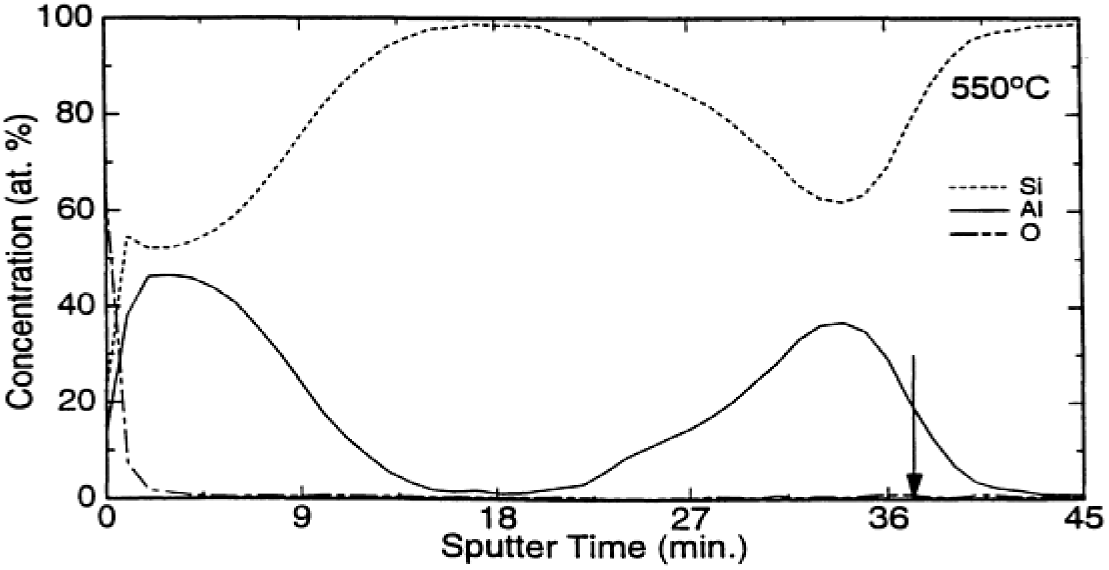
Si/Al/Si
as deposited
Si
Al
O
Concentration (at. %)
Sputter Time (min.)

(a)



200°C
Si
Al
O
Concentration (at. %)
Sputter Time (min.)

(b)



550°C
Si
Al
O
Concentration (at. %)
Sputter Time (min.)

(c)

Fig. 14 Sandwich layer of 30 nm aluminum between two silicon layers, deposited on a silicon substrate, studied with Auger electron spectroscopy depth profiling. (a) As-deposited. (b) After heating to 200 °C. (c) After heating to 550 °C. Source: Ref 57

References cited in this section

3. D. Briggs and M.P. Seah, Ed., *Practical Surface Analysis, Vol 1: Auger- and X-ray Photoelectron Spectroscopy,* 2nd ed., Wiley, 1990
7. A. Prange, in *Spectrochim. Acta,* Vol 44B, 1989, p 437
34. Th. Enders, M. Rilli, and H.D. Carstanjen, in *Nucl. Inst. Meth. Phys. Res.,* Vol B64, 1992, p 817
35. B.O. Kolbesen and W. Pamler, in *Fresenius Z. Anal. Chem.,* Vol 333, 1989, p 561
36. S. Hofmann, in *Scanning Microscopy,* Vol 1 (No. 3), 1987, p 989
37. P. Lejcek and S. Hofmann, in *Surf. Sci.,* Vol 307-309, 1994, p 798
38. D. Müller, Y.R. Cho, and E. Fromm, in *Thin Solid Films,* No. 236, 1993, p 253
39. S. Hofmann, in *Progr. Surf. Sci.,* Vol 36, 1991, p 35
40. E.-H. Cirlin, in *Thin Solid Films,* No. 220, 1992, p 197
41. M. Hecht, in *Thin Solid Films,* No. 190, 1989, p 321
42. M.F. Ebel, in *Surf. Interface Anal.,* Vol 3, 1981, p 333
43. P. Marcus, and C. Hinnen, I. Olefjord, in *Surf. Interface Anal.,* Vol 20, 1993, p 923
44. S. Hofmann, in *Advances in X-ray Anal.,* Vol 35, 1992, p 883
45. T.D. Bussing and P.H. Holloway, *J. Vac. Sci. Technol.,* Vol A3, 1985, p 1973
46. M.J. Chester and T. Jach, in *Phys. Rev.,* Vol B48, 1993, p 262
47. S. Hofmann, Depth Profiling in Corrosion Research, *Proc. of the Symp. on the Application of Surface Analysis Methods to Environmental Materials Interactions,* D.R. Baer, C.R. Clayton, and G.D. Davis, Ed., The Electrochemical Society, Inc., 1991, p 366-393
48. S. Hofmann, A. Zalar, E.-H. Cirlin, J.J. Vajo, H.J. Mathieu, and P. Panjan, in *Surf. Interface Anal.,* Vol 20, 1993, p 621
49. J.J. Vajo, E.-H. Cirlin, P.C. Wilson, and T.C. Hasenberg, in *SIMS-8,* A. Benninghoven et al., Ed., Wiley, 1992, p 355
50. S. Hofmann, in *Appl. Surf. Sci.,* Vol 70/71, 1993, p 9
51. H. Knote, S. Hofmann, and H. Fischmeister, in *Fres. Z. Anal. Chem.,* Vol 329, 1987, p 292
52. S. Hofmann, in *Thin Solid Films,* No. 193/194, 1990, p 648
53. J. Steffen and S. Hofmann, in *Fresenius Z. Anal. Chem.,* Vol 333, 1989, p 408
54. H.A. Jehn, S. Hofmann, and W.-D. Münz, in *Thin Solid Films,* Vol 153, 1987, p 45
55. H.A. Jehn, E. Fromm, and S. Hofmann, in *Vuoto,* Vol 22, 1992, p 19
56. T. Hattori, in *Thin Solid Films,* Vol 206, 1991, p 1
57. A. Zalar, S. Hofmann, E. Pimentel, and P. Panjan, Interfacial Reactions in Dynamically Heated Si/Me/Si Sandwich Layers, *Thin Solid Films, in press*

Introduction

WEAR AND EROSION TESTS have traditionally been used by materials engineers and scientists to optimize materials selection or development for a given application. Standardization, repeatability, convenience, short testing time, and simple measuring and ranking techniques are desirable in these tests. Currently, more demanding and complex methods

of wear testing are being used by mechanical and reliability engineers to determine wear parameters that can project performance and establish the influence of various factors on these parameters.

Wear is closely related to friction and lubrication. The study of these three subjects is known as *tribology*. The apparatus used for one tribological test can frequently be used for another, but friction, wear, and lubrication are distinct phenomena, and test procedures and interpretations vary. For example, a lubricant test evaluates the ability of a lubricant to withstand temperature, speed, or load and still provide protection against wear. The degree or amount of wear is a measure of lubricant response. In contrast, the area of interest in a wear test, which can be conducted lubricated or dry, is the wear response of the material.

No general-purpose wear test exists that can establish a unique wear parameter or rating of a material. Consequently, a general discussion of wear testing must encompass overall methodology. This article presents a brief review of wear testing methods. Detailed information about significant wear mechanisms, tribological phenomena, and test methods appear in *Friction, Lubrication, and Wear Technology*, Volume 18 of the *ASM Handbook*, and in the article "Wear Testing" in *Mechanical Testing*, Volume 8 of the *ASM Handbook.*

Acknowledgements

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Wear and Erosion Test Equipment

In the 1960s the American Society for Lubrication Engineers (ASLE) listed more than 200 types of wear tests and equipment in use (Ref 1), and the list has since grown. This wide variety is the result of a desire to ensure appropriate controls, make tests convenient, and simulate the wear conditions of the intended application.

The equipment described in Ref 2 includes apparatuses specifically designed for laboratory use. Although many of these test configurations are one-of-a-kind machines, others are available as commercial units.

Standards related to wear and erosion testing are listed in Ref 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15. These standards do not suggest adequate test methods for wear or erosion resistance, but they relate to the testing of metals, plastics, refractory materials, and organic coatings. Reference 12 describes an abrasion tester that is essentially an air-blast erosion rig. Reference 13 describes an erosion tester that is similar but different in detail. References 14 and 15 describe air-blast erosion test rigs for coatings.

References 16, 17, 18, 19, 20, 21, 22, and 23 give design details of the three most commonly used erosion test rigs: air-blast rigs (Ref 16, 17, 18, 19), whirling arm rigs (Ref 20, 21, 22), and wind tunnel rigs (Ref 23). Reference 24 contains a general discussion of these erosion test methods.

References cited in this section

1. R. Benzing et al., *Friction and Wear Devices,* American Society for Lubrication Engineers, 1976
2. "Standard Practice for Ranking Resistance of Materials to Sliding Wear Using Block-on-Ring Wear Test," G 77, ASTM
3. R. Bayer, Ed., *Selection and Use of Wear Tests for Metals,* STP 615, ASTM, 1976
4. E. Rabinowicz, *Friction and Wear of Materials,* John Wiley & Sons, 1966
5. R.G. Bayer, Understanding the Fundamentals of Wear, *Mach. Design,* Dec 1972, p 73-76
6. R. Bayer, Ed., *Wear Tests for Plastics: Selection and Use,* STP 701, ASTM, 1979
7. F. Borik, Testing for Abrasive Wear, *Selection and Use of Wear Tests for Metals,* R.G. Bayer, Ed., STP 615, ASTM, 1976, p 30-44
8. R.G. Bayer and T.C. Ku, *Handbook of Analytical Design Procedures for Wear,* Plenum Press, 1964
9. "Standard Practice for Conducting Dry Sand/Rubber Wheel Abrasion Test," G 65,ASTM

10. "Standard Test Method for Wear Testing with a Crossed-Cylinder Apparatus," G 83, ASTM
11. "Standard Practice for Jaw Crusher Gouging Abrasion Test," G 81, ASTM
12. "Test Method for Abrasion Resistance of Refractory Materials at Room Temperature," C 704, ASTM
13. "Determination of Resistance to Abrasion," British Standard 1902, Part 1A, Appendix C, 1966
14. "Test Method for Abrasion Resistance of Organic Coatings by the Air Blast Abrasion Test," D 658, ASTM
15. "Method for the Determination of Resistance to Abrasion," British Standard 1615, Appendix D, 1958
16. C.E. Smeltzer et al., Report 70-36, USAAV Labs, 1970
17. G.L. Sheldon, "Erosion of Brittle Materials," Ph.D. thesis, University of California at Berkeley
18. D. McFadden, "Erosion of Ductile Metals by Solid Particles," M.S. thesis, University of California at Berkeley (Lawrence Berkeley Laboratory Report 6279)
19. "Standard Practice for Conducting Erosion Tests by Solid Particle Impingement Using Gas Jets," G 76, ASTM
20. J.E. Goodwin, "Rig Development and Investigation of Velocity Effect on Sand Erosion," Note NT698, National Gas Turbine Establishment (U.K.), 1968
21. G.P. Tilly et al., in *Proc. Inst. Mech. Eng.,* Vol 184 (No. 15), 1969, p 279-292
22. D.G. Rickerby and N.H. Macmillan, in *Wear,* Vol 60, 1980, p 369-382
23. G. Grant and W. Tabakoff, Report 73-28, University of Cincinnati, Department of Aerospace Engineering, 1972
24. I.M. Hutchings, *Monograph on the Erosion of Materials by Solid Particle Impact,* Publication 10, Materials Technology Institute of the Chemical Process Industries (now affiliated with the National Association of Corrosion Engineers), 1983

Elements of a Wear Test

General elements of a wear test are simulation, acceleration, specimen preparation, control, measurement, and reporting. Simulation is the most critical, but no element of the application should be overlooked. Wear and wear phenomena can be influenced by load, environment, geometry, motion, the wearing mediums and counterface, and other factors.

Simulation ensures that the behavior experienced in the test is the same as in the application. Given the complexity of wear and the current incomplete understanding of wear and its phenomena, test development is subject to trial and error and is dependent on the capability of the developer. The ideal test exactly duplicates a wear situation. Generally, this is not practical, but any modifications in the test procedure should be carefully evaluated to obtain the most useful wear data.

General knowledge and experience can aid in assessing the differences between test and application, but correlations between test and application should also be studied. The most helpful correlation in developing a test is comparison of the worn surface and wear debris produced in the test to those produced in the application. For example, the morphology of the scar, the presence or absence of oxidized surface layers, changes in the microstructure of the material, and wear debris size, shape, and composition can be compared. If major features of the wear scar and debris are different, valid simulation is unlikely. Wear mechanisms frequently result in characteristic wear particles.

Measurement. Common direct measures of wear are mass or weight loss, volume loss or displacement, and scar width, depth, or other geometrical measures. Examples of indirect measures are the time required to wear through a coating, the load required to cause severe wear, and the load required to change surface reflectance. The selection of variables to measure wear is often based on convenience, the nature of the wear specimens, available techniques, and the amount of wear.

Material wear behavior can be compared by determining a wear curve or measuring wear at a single point in the test. Wear behavior frequently is complex, and a wear curve provides more information and allows evaluation of more complex behavior than single-point measurement. For example, the wear behaviors of two materials in the same test are plotted as functions of the number of sliding cycles (Fig. 1).

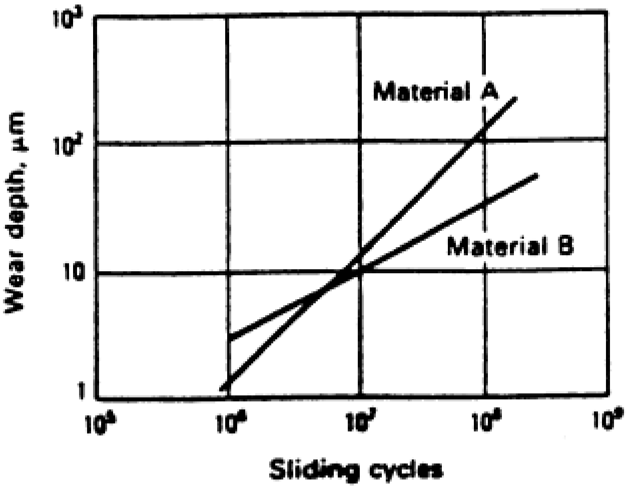


Fig. 1 Wear behavior of two materials in the same test

Reporting. Wear is a system response. When wear data are reported, a description of the wearing system must be supplied, including apparatus, geometry of contact, type of motion, load, speed, environmental condition, condition of wearing mediums, description of materials, description of lubricant and lubrication, description of wear-in period, and unusual observations, such as evidence of transfer.

Surface Engineering of Cast Irons

J.R. Davis, Davis & Associates

Introduction

THE TERM "CAST IRON," like the term "steel," identifies a large family of ferrous alloys. Cast irons primarily are alloys of iron that contain more than 2% carbon and from 1 to 3% silicon. Wide variations in properties can be achieved by varying the balance between carbon and silicon, by alloying with various metallic or nonmetallic elements, and by varying melting, casting, and heat-treating practices.

Cast iron is produced by adding excess amounts of carbon to an austenite structure. During solidification, a portion of this carbon separates from the melt as either iron carbide or graphite. The form that the excess carbon takes is determined by the rate of cooling. If the cooling is rapid, the carbon will solidify as iron carbide. If the cooling is slow, the carbon will solidify as graphite. The type of carbon present and its shape will determine the type and, in particular, the properties of the cast iron.

Following a brief review of the classification and characteristics of cast irons, this article will review the processes used to clean iron castings as well as surface treatments used to extend casting life when resistance to corrosion, wear, and erosion is required. Additional information on the cleaning and coating processes described herein can be found in the cited articles appearing elsewhere in this Volume.

Classification of Cast Irons

There are six basic types of cast irons and several varieties of each. The types of iron are classified as to how the excess carbon occurs in the microstructure. The correspondence between commercial and microstructural classification, as well as the final processing stage in obtaining common cast irons, is given in Table 1.

Table 1 Classification of cast iron by commercial designation, microstructure, and fracture

Commercial designation	Carbon-rich phase	Matrix[(a)]	Fracture	Final structure after
Gray iron	Lamellar graphite	P	Gray	Solidification
Ductile iron	Spheroidal graphite	F,P,A	Silver-gray	Solidification or heat treatment
Compacted graphite iron	Compacted vermicular graphite	F,P	Gray	Solidification
White iron	Fe_3C	P,M	White	Solidification and heat treatment[(b)]
Mottled iron	Lamellar Gr + Fe_3C	P	Mottled	Solidification
Malleable iron	Temper graphite	F,P	Silver-gray	Heat treatment
Austempered ductile iron	Spheroidal graphite	At	Silver-gray	Heat treatment

(a) F, ferrite; P, pearlite; A, austenite; M, martensite; At, austempered (bainite).

(b) White irons are not usually heat treated, except for stress relief and to continue austenite transformation.

White iron is essentially free of graphite, and most of the carbon content is present as separate grains of hard Fe_3C. White iron exhibits a white, crystalline fracture surface because fracture occurs along the iron carbide plates. White cast iron contains 2.0 to 3.6% C and 0.5 to 2.0% Si with high-alloy grades containing as much as 7% Ni, 28% Cr, and 3.5% Mo.

White cast irons have high compressive strength and good retentions of strength and hardness at elevated temperature, but they are most often used for their excellent resistance to wear and abrasion. The massive carbides in the microstructure are chiefly responsible for these properties.

Malleable iron contains compact nodules of graphite flakes. These are called "temper carbon" because they form during an extended annealing of white iron of a suitable composition. Malleable cast iron contains 2.2 to 2.9% C and 0.9 to 1.9% Si. Tensile strengths can range from 275 MPa (40 ksi) to 725 MPa (105 ksi).

Gray iron, the most commonly used cast iron, contains carbon in the form of graphite flakes. Gray iron exhibits a gray fracture surface because fracture occurs along the graphite plates (flakes). Gray irons usually contain 2.5 to 4.0% C, 1 to 3% Si, and 0.1 to 1.2% Mn. Tensile strengths range from 140 to 415 MPa (20 to 60 ksi) with higher strengths possible in high-alloy gray irons.

Gray cast iron has several unique properties that are derived from the existence of flake graphite in the microstructure. Gray iron can be machined easily at hardnesses conducive to good wear resistance. It resists galling under boundary-lubrication conditions (conditions wherein the flow of lubricant is insufficient to maintain a full fluid film). It has outstanding properties for applications involving vibrational damping or moderate thermal shock.

Ductile iron, also known as spheroidal graphite or nodular iron, contains spherulitic graphite in which the graphite flakes form into balls as do cabbage leaves. Ductile iron is so named because in the as-cast form it exhibits measurable ductility. Ductile iron typically contains 3 to 4% C, 1.8 to 2.8% Si, and 0.1 to 1.0% Mn. Alloying additions are sometimes made to ductile irons to improve heat and corrosion resistance. These alloyed grades may contain 1 to 6% Si, 0.7 to 2.4% Mn, 18 to 36% Ni, and up to 5.5% Cr.

The chief advantage of ductile iron over gray iron is its combination of high strength and ductility--up to 18% minimum elongation for ferritic ductile iron with a tensile strength of 415 MPa (60 ksi) as opposed to only about 0.6% elongation for a gray iron of comparable strength. Martensitic ductile irons with tensile strengths of about 830 MPa (120 ksi) exhibit at least 2% elongation.

Austempered Ductile Iron. If ductile iron is austenitized and quenched in a salt bath or a hot oil transformation bath at a temperature of 320 to 550 °C (610 to 1020 °F) and held at this temperature, transformation to a structure containing mainly bainite with a minor proportion of austenite takes place (Fig. 1). Irons that are transformed in this manner are referred to as austempered ductile irons. Austempering generates a range of structures, depending on the time of transformation and the temperature of the transformation bath. The properties are characterized by very high strength, some ductility and toughness, and often an ability to work harden, giving appreciably higher wear resistance than that of other ductile irons. Austempered ductile irons exhibit in excess of 5% elongation at tensile strengths exceeding 1000 MPa (145 ksi).

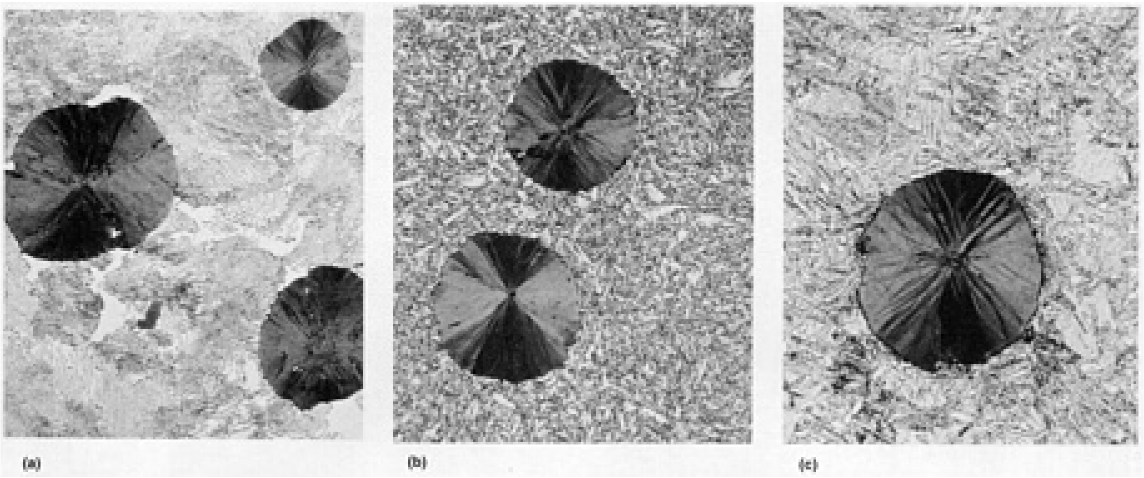


Fig. 1 Comparison of ductile iron microstructures. (a) Microstructure of normalized ductile iron showing pearlite matrix. (b) Microstructure (tempered martensite) of hardened-and-tempered ductile iron. (c) Microstructure of austempered ductile iron showing matrix of upper bainite and retained austenite. All etched in picral. 500×

Compacted graphite (CG), or vermicular graphite, irons have structures and properties that are in between those of gray irons and ductile irons. The graphite forms interconnected flakes as in a gray iron, but the flakes are shorter and thicker. The CG irons contain 2.5 to 4.0% C, 1.0 to 3.0% Si, with manganese contents varying between 0.1 and 0.6%, depending on whether a ferritic or pearlitic structure is desired.

High-alloy iron contains over three percent alloy content and is commercially classified separately. As indicated above, high-alloy irons may be a type of white iron, gray iron, or ductile iron. The matrix may be ferritic, pearlitic, martensitic, or austenitic, depending upon which alloying element dominates the composition. Table 2 lists approximate ranges of alloy content for various types of alloy cast irons used for abrasion-resistant, corrosion-resistant, and heat-resistant applications.

Table 2 Ranges of alloy content for various types of alloy cast irons

Description	Composition, wt%[(a)]									Matrix structure, as-cast[(c)]
	TC[(b)]	Mn	P	S	Si	Ni	Cr	Mo	Cu	
Abrasion-resistant white irons										

Low-carbon white iron[d]	2.2-2.8	0.2-0.6	0.15	0.15	1.0-1.6	1.5	1.0	0.5	[e]	CP
High-carbon, low-silicon white iron	2.8-3.6	0.3-2.0	0.30	0.15	0.3-1.0	2.5	3.0	1.0	[e]	CP
Martensitic nickel-chromium iron	2.5-3.7	1.3	0.30	0.15	0.8	2.7-5.0	1.1-4.0	1.0	. . .	M,A
Martensitic nickel, high-chromium iron	2.5-3.6	1.3	0.10	0.15	1.0-2.2	5-7	7-11	1.0	. . .	M,A
Martensitic chromium-molybdenum iron	2.0-3.6	0.5-1.5	0.10	0.06	1.0	1.5	11-23	0.5-3.5	1.2	M,A
High-chromium iron	2.3-3.0	0.5-1.5	0.10	0.06	1.0	1.5	23-28	1.5	1.2	M
Corrosion-resistant irons										
High-silicon iron[f]	0.4-1.1	1.5	0.15	0.15	14-17	. . .	5.0	1.0	0.5	F
High-chromium iron	1.2-4.0	0.3-1.5	0.15	0.15	0.5-3.0	5.0	12-35	4.0	3.0	M,A
Nickel-chromium gray iron[g]	3.0	0.5-1.5	0.08	0.12	1.0-2.8	13.5-36	1.5-6.0	1.0	7.5	A
Nickel-chromium ductile iron[h]	3.0	0.7-4.5	0.08	0.12	1.0-3.0	18-36	1.0-5.5	1.0	. . .	A
Heat-resistant gray irons										
Medium-silicon iron[i]	1.6-2.5	0.4-0.8	0.30	0.10	4.0-7.0	. . .	. . .	. . .	. . .	F
Nickel-chromium iron[g]	1.8-3.0	0.4-1.5	0.15	0.15	1.0-2.75	13.5-36	1.8-6.0	1.0	7.5	A
Nickel-chromium-silicon iron[j]	1.8-2.6	0.4-1.0	0.10	0.10	5.0-6.0	13-43	1.8-5.5	1.0	10.0	A
High-aluminum iron	1.3-2.0	0.4-1.0	0.15	0.15	1.3-6.0	. . .	20-25 Al	. . .	. . .	F

Heat-resistant ductile irons										
Medium-silicon ductile iron	2.8-3.8	0.2-0.6	0.08	0.12	2.5-6.0	1.5	. . .	2.0	. . .	F
Nickel-chromium ductile iron[h]	3.0	0.7-2.4	0.08	0.12	1.75-5.5	18-36	1.75-3.5	1.0	. . .	A
Heat-resistant white irons										
Ferritic grade	1-2.5	0.3-1.5	. . .	. . .	0.5-2.5	. . .	30-35	. . .	. . .	F
Austenitic grade	1-2.0	0.3-1.5	. . .	. . .	0.5-2.5	10-15	15-30	. . .	. . .	A

(a) Where a single value is given rather than a range, that value is a maximum limit.

(b) Total carbon.

(c) CP, coarse pearlite; M, martensite; A, austenite; F, ferrite.

(d) Can be produced from a malleable-iron base composition.

(e) Copper can replace all or part of the nickel.

(f) Such as Duriron, Durichlor 51, Superchlor.

(g) Such as Ni-Resist austenitic iron (ASTM A 436).

(h) Such as Ni-Resist austenitic ductile iron (ASTM A 439).

(i) Such as Silal.

(j) Such as Nicrosilal

Cleaning of Castings

Cleaning of the surface is the most important prerequisite of any coating process. Suitable levels of cleanliness and surface roughness are established by various mechanical and nonmechanical methods. Foundries deliver castings that have been shot or grit blasted (see the discussion on blast cleaning below). Supplementary nonmechanical cleaning may be needed to reach interior passages or to remove heat-treating scale or machining oil.

The choice of cleaning process depends not only on the types of soils to be removed but also on the characteristics of the coating to be applied. The cleaning process must leave the surface in a condition that is compatible with the coating process. For example, if a casting is to be treated with phosphate and then painted, the cleaning process must remove all oils and oxide scale because these inhibit good phosphating.

If castings are heat treated before they are coated, the choice of heat treatment conditions can influence the properties of the coating, particularly a metallic or conversion coating. In most cases, heat treatment should be done in an atmosphere that is not oxidizing. Oxides and silicates formed during heat treating must be removed before most coating processes.

Mechanical Cleaning and Finishing

Mechanical cleaning and finishing methods most commonly employed for processing iron castings include abrasive blast cleaning (the most commonly used method for cleaning cast irons), abrasive waterjet cleaning and finishing, vibratory finishing, barrel finishing, and shot peening.

Blast cleaning of castings is a process in which abrasive particles are propelled at high velocity to impact the casting surface and thereby forcefully remove surface contaminants. The contaminants are usually adhering mold sand, burned-in sand, heat treat scale, and the like.

The usual methods of imparting high velocity to abrasive particles are by the use of either centrifugal wheels (Fig. 2) or compressed air nozzles. Centrifugal wheels are the most widely used method because of their ability to propel large volumes of abrasive efficiently. For example, a 56 kW (75 hp) centrifugal wheel can accelerate steel shot to 73 m/s (240 ft/s) at 55,800 kg/h (123,000 lb/h) flow. To do the same with 13 mm ($\frac{1}{2}$ in.) direct pressure venturi nozzles at 45 kg (100 lb)/min per nozzle would require approximately 20 nozzles and an air flow of 0.120 m^3/s/nozzle (260 ft^3/min/nozzle) × 20, or a total of 2.45 m^3/s (5200 ft^3/min) at 550 kPa (80 psi). Approximately 700 kW (940 hp) at the air compressor would be required to supply this amount of air, which gives a 700 kW/56 kW = 12.5 to 1 (940 hp/75 hp = 12.5 to 1) efficiency advantage for the centrifugal wheel.

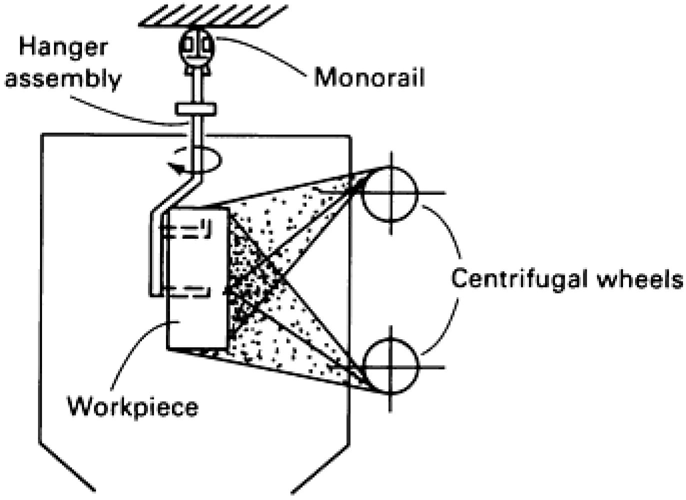


Fig. 2 Front view of a typical rotating hanger blast cleaning assembly. The workpiece is rotated 360° as it is held in position on the monorail track to provide full coverage by the blast pattern produced by the centrifugal wheels.

Even though the nozzle blast is not as efficient overall as the wheel blast, in some applications it may be more efficient because the blast stream can be more efficiently applied, when, for example, blasting into small holes to clean the interior areas of a casting. Other reasons for using a nozzle blast are requirements for:

- Low production
- Portability

- Suitability for very hard abrasives, such as aluminum oxide

More detailed information on the selection and design of blast cleaning equipment can be found in Ref 1 and the article "Mechanical Cleaning Systems" in this Volume.

In the past, chilled iron grit and malleable abrasives were used. Today, however, practically all the shot and grit used is high-carbon cast steel that is heat treated and drawn to give a desired tempered martensite microstructure and hardness. The hardness range of the most commonly used shot and grit is HRC 40 to 50. Harder shot and grit are also produced, with a range of HRC 55 to 65. For faster cleaning or special surface finish requirements, hard abrasive is not often used; but when it is, the wear on machine parts is high, and the abrasive breakdown rate is more rapid. This is especially true of hard grit. Table 3 lists commercially available shot and grit sizes.

Table 3 Society of Automotive Engineers shot and grit size specifications for abrasive blast cleaning

	High-limit screen			**Nominal screen**			**Low-limit screen**	
	Maximum % retained	**Screen number and aperture (in.)**	**Maximum % retained**	**Screen number and aperture (in.)**	**Minimum % retained**	**Screen number and aperture (in.)**	**Minimum % retained**	**Screen number and aperture (in.)**
Shot number								
S-780	1	7 (0.111)	. . .	. . .	85	10 (0.0787)	97	12 (0.0661)
S-660	1	8 (0.0937)	. . .	. . .	85	12 (0.0661)	97	14 (0.0555)
S-550	1	10 (0.0787)	. . .	. . .	85	14 (0.0555)	97	16 (0.0469)
S-460	1	10 (0.0787)	5	12 (0.0661)	85	16 (0.0469)	96	18 (0.0394)
S-390	1	12 (0.0661)	5	14 (0.0555)	85	18 (0.0394)	96	20 (0.0331)
S-330	1	14 (0.0555)	5	16 (0.0469)	85	20 (0.0331)	96	25 (0.0280)
S-280	1	16 (0.0469)	5	18 (0.0394)	85	25 (0.0280)	96	30 (0.0232)
S-230	1	18 (0.0394)	10	20 (0.0331)	85	30 (0.0232)	97	35 (0.0197)
S-170	1	20 (0.0331)	10	25 (0.0280)	85	40 (0.0165)	97	45 (0.0138)

S-110	All pass	30 (0.0232)	10	35 (0.0197)	80	50 (0.0117)	90	80 (0.0070)
S-70	All pass	40 (0.0165)	10	45 (0.0138)	80	80 (0.0070)	90	120 (0.0049)
Grit number								
G-10	1	7 (0.111)	. . .	. . .	80	10 (0.0787)	90	12 (0.0661)
G-12	1	8 (0.0937)	. . .	. . .	80	12 (0.0661)	90	14 (0.0555)
G-14	1	10 (0.0787)	. . .	. . .	80	14 (0.0555)	90	16 (0.0469)
G-16	1	12 (0.0661)	. . .	. . .	75	16 (0.0469)	85	18 (0.0394)
G-18	1	14 (0.0555)	. . .	. . .	75	18 (0.0394)	85	25 (0.0280)
G-25	1	16 (0.0469)	. . .	. . .	70	25 (0.0280)	80	40 (0.0165)
G-40	1	18 (0.0394)	. . .	. . .	70	40 (0.0165)	80	50 (0.0117)
G-50	1	25 (0.0280)	. . .	. . .	65	50 (0.0117)	75	80 (0.0070)
G-80	All pass	40 (0.0165)	. . .	. . .	65	80 (0.0070)	75	120 (0.0049)
G-120	All pass	50 (0.0117)	. . .	. . .	60	120 (0.0049)	70	200 (0.0029)
G-200	All pass	80 (0.0070)	. . .	. . .	55	200 (0.0029)	65	325 (0.0017)

Making a choice between shot and grit depends on the surface contaminants or the surface texture required. Grit is used when a chiselling action is required, for example, when removing rust, or perhaps to help remove burned-in sand or provide a good bonding surface for painting, plating, or enameling. Hard grit is used to clean the surface of bathtubs prior to enameling, where a definite tooth is required on the casting surface to provide for better adhesion of the enamel. In some cleaning applications, a shot and grit mixture may be used.

Abrasive Waterjet Cleaning. Although most often used as a cutting or machining process, the abrasive waterjet process has been tested for its use in degating and defining castings, as well as burn-in removal from castings. High-pressure waterjets (without abrasives) have also been tested for cleaning hydraulic passageways in castings. Using this process, coherent fluid jet is formed by forcing high-pressure 200 to 400 abrasive-laden water through a tiny sapphire orifice. The accelerated jet exiting the nozzle travels at more than twice the speed of sound and impinges on the workpiece. Results from a study from a foundry producing castings used in lawn, garden, and farm equipment are given in Ref 2. Detailed information on the use of abrasive waterjets for cutting metals and nonmetals can be found in Ref 3 and 4.

A vibratory finishing machine is an open-topped tub or bowl mounted on springs, usually lined with polyurethane. Parts and media are loaded in a fashion similar to that of a tumbling barrel (see the discussion on barrel finishing which immediately follows). With a vibratory machine, the container can be almost completely filled. Vibratory action is created either by a vibratory motor attached to the bottom of the container, by a shaft or shafts with eccentric loads driven by a standard motor, or by a system of electromagnets operating at 50 or 60 Hz. The action of media against components takes place throughout the load, so that process cycles are substantially shorter than conventional tumbling in barrels.

Vibratory finishing is used to clean the internal passages of cast iron cylinder heads and engine blocks. The internal passages of such components are rather intricate and it is usually difficult to reach all surface areas from any externally propelled form of cleaning. High pressure water, air blast, and shot blasting all would clean the internal surface areas that were located near an external opening; however, most of the internal passageways are hidden from this method of cleaning. Therefore, the vibratory media cleaner was introduced to clean these passages (Ref 5).

The media enters the internal passageways of the castings under the vibration of the vibratory machine and literally scrubs the surface walls of the internal cavities. The in-and-out movement of the media also carries core wash and sand from the internal passages of the castings, allowing removal of the material and providing a clean casting. Additional information on vibratory finishing can be found in the article "Mechanical Cleaning Systems" in this Volume.

Barrel Finishing. The rotary barrel, or tumbling barrel, utilizes the sliding movement of an upper layer of workload in the tumbling barrel, as shown in Fig. 3. The barrel is normally loaded about 60% full with a mixture of parts, media, compound, and water. As the barrel rotates, the load moves upward to a turnover point; then the force of gravity overcomes the tendency of the mass to stick together, and the top layer slides toward the lower area of the barrel. The rotation of the barrel causes the abrasive medium to scour the casting surfaces. Scale, sand, and even fins can be affectively removed during tumbling. Additional information on barrel finishing can be found in the article "Mechanical Cleaning Systems" in this Volume.

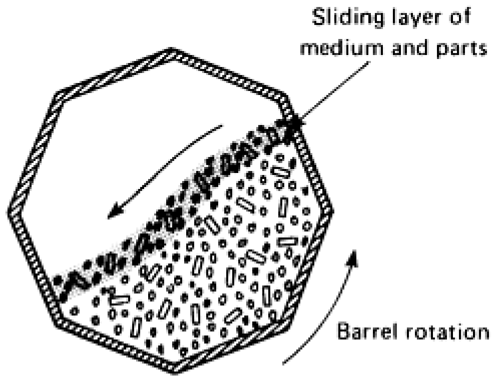


Fig. 3 Action of media and parts within a rotating barrel

Shot peening is a method of cold working in which compressive stresses are induced in the exposed surface layers of cast iron parts by the impingement of a stream of steel shot, directed at the surface at high velocity under controlled conditions. It differs from blast cleaning in primary purpose and in the extent to which it is controlled to yield accurate and reproducible results. Although shot peening cleans the surface being peened, this function is incidental. The major purpose of shot peening is to increase fatigue strength.

Both the benefits in improved fatigue strength and increased surface hardness have been shown in studies on shot peened austempered ductile iron gears (Ref 6). In cases where severe grinding operations are performed on a gear, resultant surface tensile stresses can have a negative impact on part endurance. Peening after the grinding operation can increase the endurance limit even above the original gentle grind design condition, as shown in Fig. 4.

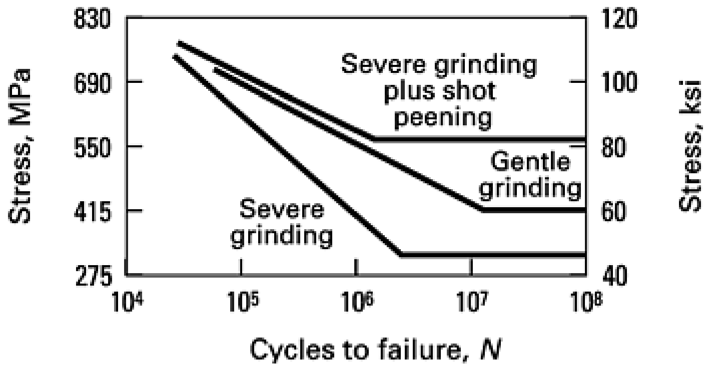


Fig. 4 Effect of shot peening on the fatigue strength of a ground component. A part designed for a gentle grinding operation could be salvaged by shot peening after a severe grinding operation. Source: Ref 6

When fatigue problems occur, one of the solutions is to eliminate stress risers in the part by polishing or other surface refining process. Though the stress riser in the material tends to be reduced, any subsequent scarring of the surface in application can greatly reduce any benefits of the polishing operation. Costs to produce a surface finish finer than a 125 rms will usually increase substantially.

Instead of polishing the surface, shot peening will produce a compressed stress layer below the surface of the material that will prevent crack propagation and increase fatigue strength. Not only can this be used as a salvage technique, but it can be used as a cost reducer by eliminating the need for the added polishing costs.

In cases where uniform casting texturing is required, the controls used in the peening process can impart a finish that is homogenous in appearance. In this situation, the benefits of the compressive stress to produce improved fatigue strength may not be critical, and surface texture selection will most likely determine shot size and application intensity.

To retain the fatigue strength benefits produced by peening, no more than 10% of the depth of compression can be removed by the subsequent machining operation. Shot peening should be performed after heat treating so that the compressive stresses and reduction of fatigue strength are not dissipated as heat treating temperature approaches stress relieving temperature.

Nonmechanical Cleaning

Nonmechanical cleaning methods applicable to cast irons include molten salt bath cleaning, pickling, and chemical cleaning with the latter method including acid cleaning, solvent cleaning, vapor degreasing, and emulsion cleaning. Articles on each of the aforementioned processes can be found in the Section on "Surface Cleaning" in this Volume.

Molten salt baths are excellent for cleaning complex interior passages in castings. In one electrolytic, molten salt cleaning process, the electrode potential is changed so that the salt bath is alternately oxidizing and reducing. Scale and graphite are easily removed with reducing and oxidizing baths, respectively. Molten salt baths are fast compared to other nonmechanical methods, but castings may crack if they are still hot when salt residues are rinsed off with water.

Pickling of cast iron is usually done prior to hot dip coating or electroplating. When pickling is used, the castings are cleaned in solutions containing sulfuric and hydrofluoric acids. The concentration of each acid depends on whether the primary purpose is to remove sand or scale. Increased hydrofluoric acid is needed to remove embedded sand from the casting surface, whereas sulfuric or hydrochloric acids are sufficient for simple scale removal. Table 4 gives the operating conditions for pickling iron castings. Before being pickled, castings must be free of oil, grease, and other contamination. After being removed from the pickling solution, castings are rinsed thoroughly in hot water. Residual heat permits self-drying, but drying may be accelerated by the use of fans. For complex shaped castings, baking ovens may be employed.

Table 4 Operating conditions and solution compositions for pickling cast irons

Operating	Sand	Scale

variable	removal	removal
Sulfuric acid, vol%	5	7
Hydrofluoric acid, vol%	5	3
Water, vol%	90	90
Temperature[(a)], °C (°F)	65-85 (150-185)	50 to over 85 (120 to over 185)
Average immersion time, h	4	4

(a) 50 °C (120 °F) is for slow pickling, 65 to 85 °C (150 to 185 °F) for average pickling speed, and over 85 °C (185 °F) is for fast pickling.

Acid cleaning is a process in which a solution of a mineral acid, organic acid, or acid salt, in combination with a wetting agent and detergent, is used to remove oxide, shop soil, oil, grease, and other contaminants from metal surfaces, with or without the application of heat. The distinction between acid cleaning and acid pickling is a matter of degree, and some overlapping in the use of these terms occurs. Acid pickling is a more severe treatment for the removal of scale from castings, whereas acid cleaning generally refers to the use of acid solutions for final or near-final preparation of metal surfaces before plating, painting, or storage.

Mixtures of 70 wt% phosphoric acid, 5 wt% ethylene glycol monobutyl ether, and 25 wt% water are used for removing grease, oil, drawing compounds, and light rust from iron and steel. This mixture is adaptable to immersion, spray, or wiping methods and leaves a light phosphate coating (100 to 320 mg/m^2, or 10 to 30 mg/ft^2) that provides a paint base or temporary resistance to rusting if the parts are to be stored.

Acid solutions of 40 to 60 vol% hydrochloric or 6 to 8 vol% sulfuric (often containing up to 1% inhibitor) are used at room temperature for removing soil and light rust. Stronger solutions of these acids are used in electrolytic baths for final cleaning of cast irons before electroplating. Various soils, including light rust, may also be removed by combining acid cleaning and barrel finishing.

Other Chemical Cleaning Methods. Organic solvents that were commonly used in the past include naphtha, benzene, methanol, toluene, and carbon tetrachloride. These have been largely replaced by chlorinated solvents, such as those used for vapor degreasing. Solvents effectively remove lubricants, cutting oils, and coolants, but are ineffective against such inorganic compounds such as oxides or salts. Emulsion cleaners are solvents combined with surfactants; they disperse contaminants and solids by emulsification. Emulsion cleaners are most effective against heavy oils, greases, slushes, and solids entrained in hydrocarbon films. They are relatively ineffective against adherent solids such as oxide scale.

After wet cleaning, short-term rust prevention is accomplished by the use of an alkaline rinse. This can be followed by the application of mineral oils, solvents combined with inhibitors and film formers, emulsions of petroleum-base coatings and water, and waxes. A summary of the temporary coatings used for corrosion protection is given in Table 5.

Table 5 Temporary coatings used for corrosion protection

Type	Coating structure	Thickness, μm (mils)	Removal method	Uses

Oil	Non-drying mineral oil viscosity determines coating thickness	5-7 (0.2-0.3)	Seldom required; solvent rinsing, emulsion spray, or vapor degreasing	Finished automotive parts; galvanized irons
Solvent	Petroleum-based inhibitors and film formers dissolved in petroleum solvents	5-50 (0.2-2.0)	Seldom required; solvent rinsing or alkaline washing	External surfaces of machinery parts and tooling. Can be used outdoors
Emulsified	Petroleum-based coating modified to form a stable emulsion with water	5 (0.2)	Removal seldom necessary; solvent rinsing	Same as above, but suggested for indoor use
Wax	Wax layer applied heated or in a volatile solvent	38-75 (1.5-3.0)	Solvent rinsing or alkaline cleaning	Highly finished parts stored for prolonged periods

Source: Ref 7

References cited in this section

1. J.H. Carpenter, Blast Cleaning of Castings, *Casting,* 9th ed., Vol 15, *Metals Handbook,* ASM International, 1988, p 506-520
2. D.L. Malm, Cleaning Castings by High-Pressure Abrasive Water-Jet, *AFS Transactions,* Vol 92, 1984, p 655-660
3. J.G. Sylvia, Abrasive Waterjet Cutting, *Forming and Forging,* 9th ed., Vol 14, *Metals Handbook,* ASM International, 1988, p 743-755
4. C.E. Johnston, Waterjet/Abrasive Waterjet Machining, *Machining,* 9th ed., Vol 16, *Metals Handbook,* ASM International, 1989, p 520-527
5. F.R. Pulice, Developments in Casting Cleaning Technology, *Modern Casting,* August 1986, p 22-24
6. M. Lawerenz, Shot Peening Ductile Iron, *Modern Casting,* February 1990, p 51-53
7. C.F. Walton and T.J. Ajar, Ed., *Iron Castings Handbook,* Iron Casting Society, 1981, p 755-799

Electroplating and Electroless Plating

Cast irons are most commonly plated with chromium, nickel, copper, cadmium, and zinc. In addition, gold, lead, and rhodium are used for specialized applications. Alloy coatings, such as brass, bronze, and tin-base compositions, are used for decorative purposes. As shown in Table 6, each electroplated coating has its own characteristic properties.

Table 6 Properties and characteristics of conventional electroplated metal coatings

Metal	Coating hardness	Appearance	Thickness		Characteristics and uses
			μm	mil	
Cadmium	30-50 HV	Bright white	3-10	0.15-0.5	Pleasing appearance for indoor applications; less likely to darken than zinc; anodic to ferrous substrate
Chromium	900-1100 HV	White--can be varied	0.2-1[(a)] 1-300[(b)]	0.01-0.06[(a)] 0.05-	Excellent resistance to wear, abrasion, and corrosion; low friction and high reflectance

				12.0[b]	
Cobalt	250-300 HK	Gray	2-25	0.1-1.0	High hardness and reflectance
Copper	41-220 HV	Bright pink	4-50	0.2-2.0	High electrical and thermal conductivities; used as undercoat for other electroplates
Lead	5 HB	Gray	12-200[c] 1300[d]	0.5-8.0[c] 50[d]	Resistant to many acids and hot corrosive gases
Nickel	140-500 HV	White	2-40[a] 130-500[c]	0.1-1.5[a] 5-20[c]	Resistant to many chemicals and corrosive atmospheres; often used in conjunction with copper and chromium; can be applied by electroless plating
Rhodium	400-800 HB	Bright white	0.03-25	0.001-1.0	High electrical conductance; brilliant white appearance is tarnish and corrosion resistant
Tin	5 HB	Bright white	4-25	0.015-1.0	Corrosion resistant; hygienic applications for food and dairy equipment; good solderability
Zinc	40-50 HB	Matte gray	2-13[a] 12-50[d]	0.1-0.5[a] 0.5-2.0[d]	Easily applied; high corrosion resistance; anodic to ferrous substrate

Source: Ref 7

(a) Decorative.

(b) Hard.

(c) Wear applications.

(d) Corrosion applications.

Iron castings are electroplated to impart corrosion resistance or to provide a pleasing appearance. Typical applications include many different types of interior hardware, machine parts such as printing cylinders, decorative trim, and casings. Iron castings are also electroplated to enhance their wear resistance; for example, hard chromium plating is applied to the wear surfaces of piston rings (see the discussion below on chromium plating). Areas not requiring a plated surface can be masked or stopped off to prevent coverage. Plating can be applied as a very thin layer for applications requiring only a pleasing appearance or mild corrosion resistance; thicker plating can be applied for more wear resistance, longer corrosion resistance, or to replace lost metal (Table 6).

Electrodeposition is done by making clean iron castings cathodic in an aqueous solution containing a salt of the coating metal and then passing a direct electrical current through the solution. The effective metal content in the plating bath can be replenished by using anodes made of the coating metal to complete the electrical circuit. Variations in the properties of the deposited coating are influenced by the composition, temperature, pH, and agitation of the bath and by current

density. In addition, further variations in the coating can result from the design of the casting, the distance of the casting from the anode, and the preparation of the surface before plating.

This section will review the types of platings applied to cast irons for corrosion or wear resistance. More detailed information on the equipment and plating solutions used for these processes can be found elsewhere in this Volume (see the articles in the Section on "Plating and Electroplating"). Additional information on corrosion and wear characteristics of electroplated coatings can also be found in Volume 13, *Corrosion,* and Volume 18, *Friction, Lubrication, and Wear Technology,* of the *ASM Handbook.*

Chromium Plating. Both hard and decorative chromium electroplates are deposited on cast iron substrates. Commercially, hard chromium is deposited from four types of efficiency etch-free baths. All of the baths contain chromic acid (CrO_3) and sulfate (SO_4^{2-}). The SO_4^{2-} acts as a catalyst. Chromium cannot be electrodeposited from an aqueous CrO_3 solution unless one or more catalysts are present. Depending on which catalysts are present and the plating parameters, between 10 and 45% of the cathodic current will be used to reduce hexavalent chromium (Cr^{6+}) to chromium metal. The properties of the electrodeposits are influenced by the ratio of CrO_3 to the catalysts, plating temperature, and current density. Chromic acid to sulfate ratios vary between 75 to 1 and 120 to 1, plating temperatures range from 45 to 65 °C (110 to 150 °F), and current densities from 10 to 90 A/dm^2 (0.65 to 6 A/in.^{2}).

Hard chromium plating, which is also known as industrial chromium plating, differs from decorative chromium plating in the following ways:

- Hard chromium deposits are intended primarily to increase service life of function parts by increasing their resistance to wear, abrasion, heat, or corrosion. Deposits are also applied to restore dimensions of undersized parts
- Hard chromium normally is deposited to thicknesses ranging from 2.5 to 500 μm (0.1 to 20 mils) and for certain applications to considerably greater thicknesses (up to 6000 μm, or 240 mils) whereas decorative coatings seldom exceed 1.3 μm (0.05 mil)
- With certain exceptions, hard chromium is applied directly to the base metal; decorative chromium is applied over undercoats of nickel or of copper and nickel, and is either buffed or used in the as-plated condition

One of the most prevalent applications for chromium plated cast irons is that of hard plated piston rings. Gray cast iron, with a hardness ranging from 200 to 400 HB, is the most commonly used material for piston rings. Table 7 shows the various types of cast irons used in gasoline engine piston rings. Pearlitic gray iron produced by either centrifugal or sand casting methods has the widest use. In heavy-duty engine applications, alloy cast iron, ductile iron, and malleable iron are used. Harder materials, such as carbon steel or even bearing steels, may also be used.

Table 7 Typical piston ring materials

Type	Approximate specification	Manufacturing method	Range of composition, wt% (balance iron)									Tensile strength		Modulus of elasticity		Hardness HB
			C	Si	Mn	S	P	Ni	Cr	Mo	Other	MPa	ksi	GPa	psi × 10^6	
Gray cast iron	BSS 4K6	Centrifugally cast	3.5 max	1.8-2.5	1.2 max	1.0 max	0.40-0.65	0.4 max	0.5 max	0.4 max	. . .	245	36	117	17	210 min
	BSS 4K6	Sand cast	3.5 max	1.0-1.8	0.6-1.2	0.15 max	0.25-0.60	0.4 max	0.4 max	0.4 max	. . .	245	36	103	15	200-245
	DTD 233A	Centrifugally cast	3.1-3.4	2.1-2.5	0.7-1.0	0.08 max	0.40-0.65	. . .	0.3-0.6	0.5-1.0	. . .	310	45	110	16	255-296
Carbidic/malleable iron	DTD 485A	Individually cast	2.7-3.3	2.0-3.0	0.5-0.9	0.1 max	0.5 max	. . .	0.5-0.85	. . .	V, 0.4 max	585	85	159	23	270-320
	DTD 485A	Centrifugally cast	2.75-3.3	1.8-2.5	0.6-1.0	0.12 max	0.3-0.5	0.3 max	0.65-1.15	0.7-1.0	Al, 0.5 max	400	58	155	22	269-302
Malleable/nodular iron	. . .	Centrifugally cast	3.0-3.3	1.0-1.4	0.6-0.9	0.1 max	0.1 max	0.3 max	0.1-0.5	. . .	. . .	540	78	155	22	200-400
	BS2789 SNG	Sand or centrifugally cast	Varies according to mechanical properties required									570	83	165	24	240-297

Source: Ref 8

Relatively thick coatings (up to 0.2 mm, or 0.008 in.) of plated chromium on the ring periphery provide the best compromise between scuffing, wear, and corrosion resistance and low friction and oxidation resistance at high temperatures. Generally, the use of chromium-plated top rings (with a hardness of 700 to 900 HV) run against cast iron cylinder liners can reduce the ring and liner wear by a factor of 2 to 3 (Ref 8). More detailed information on chromium plating can be found in the articles "Industrial (Hard) Chromium Plating" and "Decorative Chromium Plating" in this Volume.

Electrolytic nickel plating may be categorized as general purpose, special purpose wear-resistant, or bright. General purpose nickel plating is applied for protection against corrosive attack but is also used to build up worn or undersized parts. Wear-resistant nickel plating is used in engineering applications that require abrasion and corrosion resistance as well as surface smoothness. Bright nickel plating is used to provide decorative finishes and is frequently used as a base for a very thin chromium plate. Unless polished occasionally, all nickel plate will tarnish with a yellow cast after long exposure. Severely corrosive atmospheres will turn nickel green. Nickel plating of iron castings does not present any unusual problems, and the cleaning techniques prior to plating often are the same as for low-carbon steel. Three types of general-purpose baths are used for nickel plating: Watts, sulfamate, and fluoborate. A variety of proprietary organic and metallic brighteners, levelers, and antipitting agents are available to tailer the degree of brightness, reflectivity, and hardness desired.

The hardness of nickel deposits can vary from about 150 to 500 HV depending on the plating conditions (current density, solution pH and temperature, and composition). The widest use of electroplated nickel for wear applications is as an undercoat for chromium (Ref 9). If thick deposits are needed, for example, in building up heavily worn parts, it is usually not practical to do so using only chromium plating, because of its low current efficiency and high internal stress. In such cases, most of the deposit thickness is composed of nickel, with chromium constituting only a thin outer layer. For additional information, see the articles "Nickel Plating" and "Nickel Alloy Plating" in this Volume.

Electroless nickel plating is used to deposit nickel without the use of an electric current. The coating is deposited by an autocatalytic chemical reduction of nickel ions by sodium hypophosphite, sodium borohydride, or organic aminoboranes. When sodium hypophosphite is the reducing agent, the deposit generally contains between 3 and 11 wt% phosphorus. The boron contents of electroless nickel range from 0.2 to 4 wt% and from 4 to 7 wt% when the reducing agents are an aminoborane and sodium borohydride, respectively.

The structure of the deposit changes from microcrystalline to amorphous, with increasing alloy content. If the phosphorous content is above about 10 wt%, the coating is amorphous and therefore lacks grain boundaries or other crystalline defects at which corrosion can be initiated. Electroless nickel has some advantage over electrolytic nickel in that its thickness and phosphorus content are uniform over the substrate and independent of substrate geometry.

Electroless nickel can be heat treated to hardnesses comparable to those of electrodeposited chromium. The maximum hardness can be attained in 1 h at about 400 °C (750 °F) or 10 h at 260 °C (500 °F). The hardness of as-plated Ni-P alloys varies from 500 to 650 HV. As-plated Ni-B deposits are generally harder than the Ni-P ones. The ability of electroless nickel deposits to maintain their hardness under elevated-temperature service conditions increases with increasing phosphorus or boron content, but decreases rapidly above 385 °C (725 °F). Nickel-boron coatings tend to better withstand wear at elevated temperatures and are therefore more widely used under these conditions.

Electroless nickel is most frequently used in wear applications in the precipitation-hardened condition. The improved abrasion and wear resistance after heat treating is evident from Fig. 5. Although the greatest hardness was obtained by heat treatment at 400 °C (750 °F), the electroless nickel that was heat treated at 600 °C (1110 °F) showed the least wear. However, the corrosion resistance of as-plated Ni-P coatings, which is one of the main reasons for their use, deteriorates upon heat treating to the maximum hardness, because of cracking. Therefore, under corrosion or corrosive wear applications, the higher hardness should be avoided.

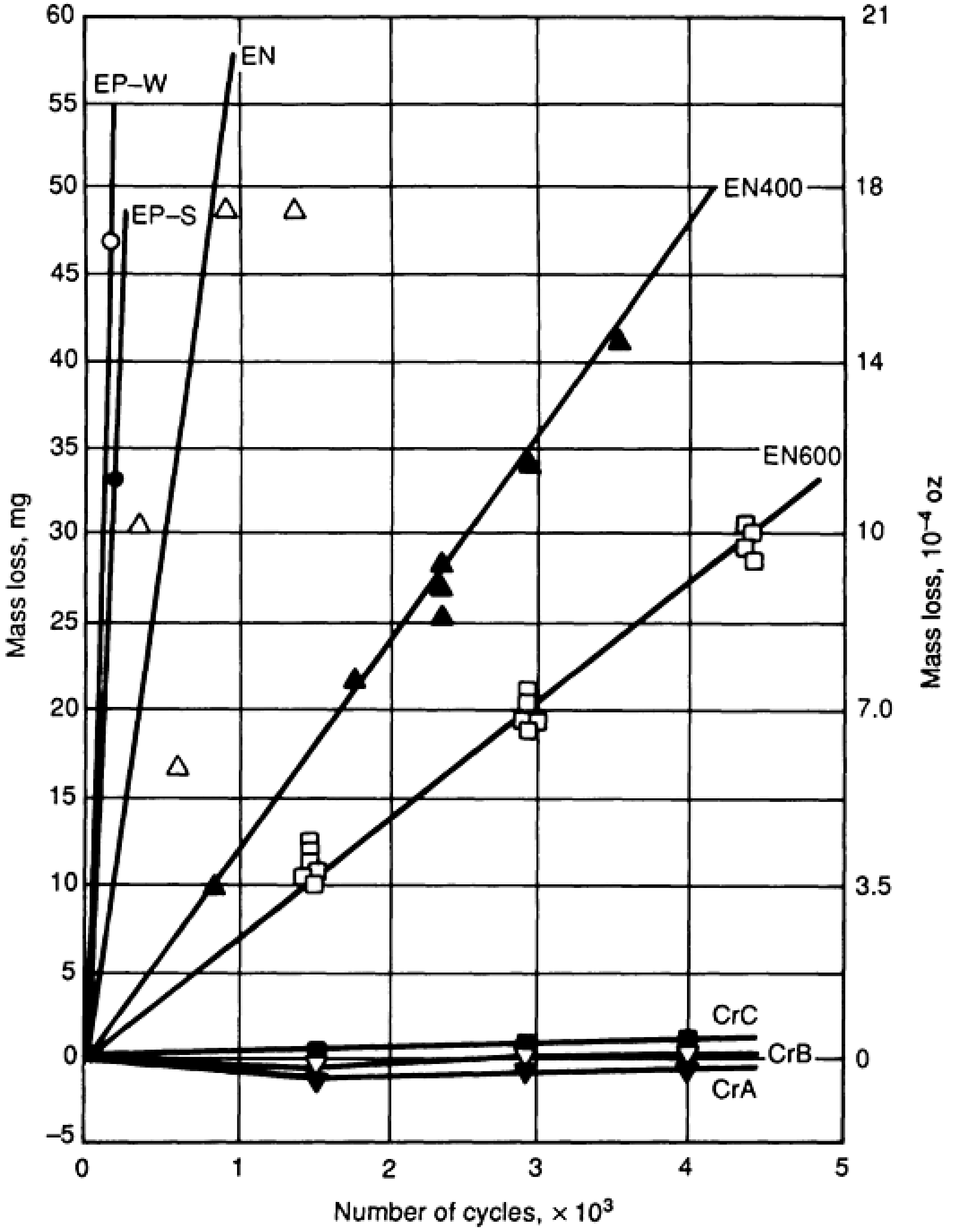


Fig. 5 Effect of number of cycles on wear loss of plated pin versus steel blocks in a Falex test for three chromium deposits (CrA, CrB, and CrC), heat treated electroless nickel deposits (EN400 and EN600), a non-heat-treated electroless nickel deposit (EN), and two electroplated nickel deposits from a sulfamate solution (EP-S) and a Watts solution (EP-W). Source: Ref 9

The widest use of electroless nickel for both corrosion and wear resistance is in complex-shaped cast iron valves that control the flow of either liquids or gases. Another important application for electroless nickel-plated cast irons is printing rolls which must have an especially uniform surface to function properly.

Copper Plating (Ref 7). Electroplated copper usually functions as an underplate for nickel and chromium plating. It provides a desirable base surface because it can be easily deposited in a uniform, pore-free, and ductile condition. Copper underplates also enhance buffing and polishing when multiple-layer plating is used. Copper itself is relatively corrosion resistant, but is subject to tarnishing and staining. It is occasionally used alone for decorative effect, but should be

provided with an overcoat of lacquer. Some use of copper plating is made to facilitate soldering iron to other materials, such as copper tubing.

Anodic Electroplates. Electrodeposits of cadmium and zinc are used extensively to protect cast iron against corrosion. Because these metals are anodic to iron, the underlying ferrous metal is protected at the expense of the electroplate, even if the coating becomes scratched or nicked, exposing the substrate. Cadmium is generally preferred for the protection of cast irons in marine atmospheres and zinc is preferred in industrial environments. Cadmium is much more toxic than zinc, and applications in which its corrosion products may get into the environment should be avoided. The corrosion performance of both cadmium and zinc is greatly enhanced by chromate conversion coatings.

Most cadmium plating is carried out in alkaline cyanide baths prepared by dissolving cadmium oxide (CdO) in a sodium cyanide (NaCN) solution. Sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) are formed by reactions within and are part of this bath. Cadmium balls suspended in steel wire cages serve as the plating anodes. Typical bath compositions suitable for various plating methods and workpieces are summarized in Table 8.

Table 8 Alkaline cyanide cadmium plating baths

Total NaCN-to-Cd ratio	Concentration, g/L (oz/gal)				
	Cd	CdO	NaCN	NaOH	Na_2CO_3
4.0	19.5 (2.6)	22.5 (3.0)	77.9 (10.4)	14.2 (1.9)	30-75 (4-10)
4.1	19.5 (2.6)	22.5 (3.0)	80.1 (10.7)	59.9 (8.0)	30-45 (4-6)
4.5	36 (4.8)	41.2 (5.5)	161.8 (21.6)	25.5 (3.4)	30-45 (4-6)
5.0	20.2 (2.7)	22.5 (3.0)	101.1 (13.5)	14.2 (1.9)	30-60 (4-8)
7.2	19.5 (2.6)	22.5 (3.0)	136.3 (18.2)	14.2 (1.9)	30-45 (4-6)

The choice of a plating bath depends on the size and configuration of the workpiece being plated. Large numbers of small parts are most conveniently barrel plated with solutions of a lower NaCN-to-Cd ratio, while larger parts with intricate and recessed surfaces must be coated by still plating techniques of high throwing power. Automatic plating is normally used for intermediate size products which are arranged on racks and then automatically sequenced through a plating procedure.

Organic or metallic compounds are often added to alkaline cyanide cadmium plating baths to influence the formation of the electrodeposited cadmium crystals and thus the brightness of the coating. They are largely proprietary and, among the organics, include:

- Aldehydes
- Coumarin
- Dextrin
- Furfural
- Gelatin
- Milk
- Molasses
- Sugar

- Some sulfonic acids

Metallic brighteners include nickel, cobalt, molybdenum and selenium compounds.

Best results are achieved by a moderate use of both types. Excessive amounts of the organic brighteners are less harmful in that they ultimately hydrolyze and become harmless. Metallic brighteners should never be used unless technical facilities and competent personnel are available. Baths which are used excessively and which contain large amounts of organic brighteners must be filtered frequently or continuously. Other considerations in bath selection for both cyanide and non-cyanide plating baths can be found in the article "Cadmium Plating" in this Volume.

As shown in Table 9, cadmium is usually applied as a thin coating (less than 25 μm, or 1 mil thick) intended to withstand atmospheric corrosion. It is seldom used as an undercoating for other metals, and its resistance to corrosion by most chemicals is low.

Table 9 Recommended minimum thicknesses and corrosion characteristics for zinc and cadmium coatings electrodeposited on cast iron

Service conditions	Coating thickness		Chromate finish	Time to white corrosion in salt spray, h
	μm	mils		
Electrodeposited zinc				
Mild (indoor atmosphere; minimum wear and abrasion)	5	0.2	None	. . .
			Clear	12-24
			Iridescent	24-72
			Olive drab	72-100
Moderate (mostly dry indoor atmosphere; occasional condensation, wear, and abrasion)	8	0.3	None	. . .
			Clear	12-24
			Iridescent	24-72
			Olive drab	72-100
Severe (exposure to condensation; infrequent wetting by rain; and cleaners)	13	0.5	None	. . .
			Clear	12-24
			Iridescent	24-72

			Olive drab	72-100
Very severe (exposure to bold atmospheric conditions; frequent exposure to moisture, cleaners, and saline solutions; likely damage by abrasion or wear)	25	1	None	. . .
Electrodeposited cadmium				
Mild (see above)	5	0.2	None	. . .
			Clear	12-24
			Iridescent	24-72
			Olive drab	72-100
Moderate (see above)	8	0.3	None	. . .
			Clear	12-24
			Iridescent	24-72
			Olive drab	72-100
Severe (see above)	13	0.5	None	. . .
			Clear	12-24
			Iridescent	24-72
			Olive drab	72-100
Very severe (see above)[(a)]	25	1	None	. . .
			Clear	24
			Iridescent	24-72
			Olive drab	72-100

Thickness specified is after chromate conversion coating, if used.

Source: Ref 11

(a) There are some applications for cadmium coatings in this environment; however, these are normally satisfied by hot-dipped or sprayed coatings.

Zinc, like cadmium, is also anodic to cast iron and therefore offers more protection when applied in thin films of 7 to 15 μm (0.3 to 0.5 mil) than similar thicknesses of nickel and other cathodic coatings. Because it is relatively inexpensive and readily applied in barrel, tank, or continuous plating facilities, zinc is often preferred for coating iron and steel parts when protection from either atmospheric or indoor corrosion is the primary objective. Table 9 lists the recommended minimum thicknesses and corrosion characteristics of zinc electrodeposits.

The adherence of electrodeposited zinc coatings depends on the metal-to-metal bond between the plated coating and the underlying cast iron surface. Therefore, particular attention must be given to the preparation of the surface before plating to obtain a coating in true physical contact with the entire casting surface.

The usual method of removing all rust, scale, and grease from the cast iron surface involves cleaning the surface thoroughly in a hot alkaline bath by soaking the parts for a short period of time. This is often followed by use of an electrolytic alkaline cleaner and a spray alkaline cleaner. An acid dip is then carried out to remove oxides and scale. There must be adequate rinsing between the alkaline/acid baths and the acid/plating baths to avoid contamination of the plating bath by carryover from the cleaning baths.

Zinc plating is done in an acid or an alkaline bath. Although the alkaline-cyanide zinc baths are the most efficient and have the best throwing power, they do create a serious pollution problem. Therefore, more acid zinc baths are being used. Acid bath compositions and operating conditions are described in the article "Zinc Plating" in this Volume.

Various brightening agents may be added to the baths to give a deposit that is more lustrous than that obtained from normal zinc plating baths. The amount of brightening agent requires very careful control, and the bath and the zinc anode must both be kept particularly pure when brighteners are used.

References cited in this section

7. C.F. Walton and T.J. Ajar, Ed., *Iron Castings Handbook,* Iron Casting Society, 1981, p 755-799
8. J.R. Davis, Friction and Wear of Internal Combustion Engine Parts, *Friction, Lubrication, and Wear Technology,* Vol 18, *ASM Handbook,* ASM International, 1992, p 553-562
9. R. Weil and K. Sheppard, Electroplated Coatings, *Friction, Lubrication, and Wear Technology,* Vol 18, *ASM Handbook,* ASM International, 1992, p 834-839
10. H. Morrow, Cadmium Plating, *Metal Finishing,* Vol 89 (No. 1A), 1991, p 175-176, 178
11. J. Mazia and D.S. Lashmore, Electroplated Coatings, *Corrosion,* 9th ed., Vol 13, *Metals Handbook,* ASM International, 1987, p 419-431

Hot Dip Coatings

Hot dip coating consists of immersing the casting in a bath of molten metal. A flux-coated and/or chemically cleaned surface is necessary to achieve satisfactory results. Aluminum, tin, zinc, and their alloys can be applied from a molten bath. Hot dip coatings are preferred because they are thicker than electroplates and because an alloy layer is formed between the coating metal and the iron. This provides additional durability and adhesion. Castings of complex shape are easily coated by these processes, although air may become trapped in blind holes unless the castings are rotated. More detailed information on hot dip coating is available in the articles "Continuous Hot Dip Coatings" and "Batch Hot Dip Galvanized Coatings" in this Volume.

Hot dip zinc coating (galvanizing) is widely used on iron castings, particularly pipe, valves, and fittings. The uniform and adherent coating provides a barrier against corrosive attack and will further protect an iron casting by acting as a sacrificial anode or by undergoing preferential corrosion. Successful galvanizing depends on surface preparation. Pickling followed by dipping in a bath of zinc ammonium chloride or other flux is done prior to dipping in molten zinc. Excess zinc may be drained or centrifuged from the castings before quenching. Quenching improves the brightness of the coating. Iron castings of any type and any composition can be hot dip galvanized.

Hot dip tin coating (hot tinning) provides a protective, decorative, and nontoxic coating for food equipment, a bonding layer for babbitted bearings, or a precoated surface for soldering. Surface preparation is particularly important, and when maximum adherence is desired, such as when tinning is used to prepare a casting for the application of babbitt, electrolytic cleaning in a molten salt is preferred.

For the hot dip lead coating of iron castings, lead-base alloys are preferred over pure lead; with pure lead, bonding is mechanical rather than metallurgical. Tin is the element most widely used to enhance bonding. Lead coatings are noted for their resistance to fumes from sulfuric and sulfurous acids.

The aluminum coating (aluminizing) of iron castings imparts resistance to corrosion and heat. The coating oxidizes rapidly, thus passivating the surface. The resultant aluminum oxide is refractory in nature; it seals the surface and resists degradation at high temperatures. An aluminized surface has limited resistance to sulfur fumes, organic acids, salts, and compounds of nitrate-phosphate chemicals.

Hardfacing and Weld Cladding

Hardfacing can be used when a casting requires an unusually hard and wear-resistant surface and when it is impractical to produce a hard surface in the casting process or by selective heat treatment. Frequently, hardfacing is used to repair worn castings by building up an overlay of new material.

Hardfacing is basically a welding operation in which an alloy is fused to the base metal by oxyfuel welding, arc welding, laser welding, or thermal spray processes. Hardfacing materials include a wide variety of alloys, carbides, and combinations of these materials. Conventional hardfacing materials, also referred to as weld overlays, are normally classified as steels or low-alloy ferrous materials, high-chromium white irons or high-alloy ferrous materials, carbides, nickel-base alloys, or cobalt-base alloys. A few copper-base alloys are sometimes used for hardfacing applications, but for the most part, hardfacing alloys are either iron-, nickel-, or cobalt-base.

Microstructurally, hardfacing alloys generally consist of hard phase precipitates such as borides, carbides, or intermetallics bound in a softer iron-, nickel, or cobalt-base alloy matrix. Carbides are the predominant hard phases in iron- and cobalt-base hardfacing alloys. Carbon contents of iron- and cobalt-base hardfacing alloys generally range up to 4 wt%. Borides, as well as carbides, are the predominant hard phases in nickel-base hardfacing alloys. Combined carbon plus boron contents generally range up to 5 wt%. The specific carbide and/or boride phases that form are determined by matrix alloying additions.

Hardfacing alloys usually are available as bare rod, flux-coated rod, long-length solid wires, long-length tube wires (with and without flux), or powders. The most popular processes, and the forms most commonly associated with each process, are:

Hardfacing process	**Consumable form**
Oxyfuel/oxyacetylene (OFW/OAW)	Bare cast or tubular rod
Shielded metal arc (SMAW)	Coated solid or tubular rod (stick electrode)
Gas-tungsten arc (GTAW)	Bare cast or tubular rod
Gas-metal arc (GMAW)	Tubular or solid wire
Flux-cored open arc	Tubular wire (flux cored)

Submerged arc (SAW)	Tubular or solid wire
Plasma transferred arc (PTA)	Powder
Laser beam	Powder

Detailed information on hardfacing materials, hardfacing alloy selection, and hardfacing process selection can be found in Ref 12. Producers of hardfacing alloys should also be consulted for technical assistance.

A weld clad is a relatively thick layer of filler metal applied to a cast iron base metal for the purpose of providing a corrosion-resistant surface. Weld cladding is normally carried out by arc welding. Materials deposited on cast irons to improve their corrosion performance include copper-base alloys, stainless steels, and nickel-base alloys.

Problems due to dilution of stainless steel or nickel-base filler metals can be minimized by first depositing a buffer layer of low-carbon nickel prior to the application of the cladding alloy. Dilution of the base iron casting into the weld deposit can also be kept to a minimum by:

- Maximizing the amount of metal deposited per unit length. The beads being deposited should be overlapped as much as possible
- Minimizing the amount of heat input in order to reduce the amount of base metal melting. The use of straight-polarity dc current will help decrease the penetration

Caution must be exercised when considering the reduction in penetration or melting of the cast iron substrate. The deposited weld metal must melt part of the casting to adhere properly. A rule of thumb is that a minimum of 5 to 10% dilution is needed for complete fusion.

Reference cited in this section

12. J.R. Davis, Hardfacing, Weld Cladding, and Dissimilar Metal Joining, *Welding, Brazing, and Soldering,* Vol 6, *ASM Handbook,* ASM International, 1993, p 789-829

Thermal Spraying

Thermal spraying comprises a group of processes in which divided molten metallic or nonmetallic material is sprayed onto a prepared substrate to form a coating. The sprayed material is originally in the form of wire, rod, or powder. As the coating materials are fed through the spray unit, they are heated to a molten or plastic state and propelled by a stream of compressed gas onto the substrate. As the particles strike the surface, they flatten and form thin platelets that conform and adhere to the irregularities of the prepared surface and to each other. They cool and accumulate, particle by particle, into a lamellar, castlike structure. In general, the substrate temperature can be kept below approximately 200 °C (400 °F), eliminating metallurgical change of the substrate material. The spray gun generates the necessary heat for melting through combustion of gases, an electric arc, or a plasma. Figure 6 illustrates a general thermal spraying process. Figure 7 illustrates the microstructure that results from the thermal spray process. As shown in this figure, the molten particles spread out and deform (splatter) as they impact the substrate, at first locking onto irregularities on the roughened surface, then interlocking with each other.

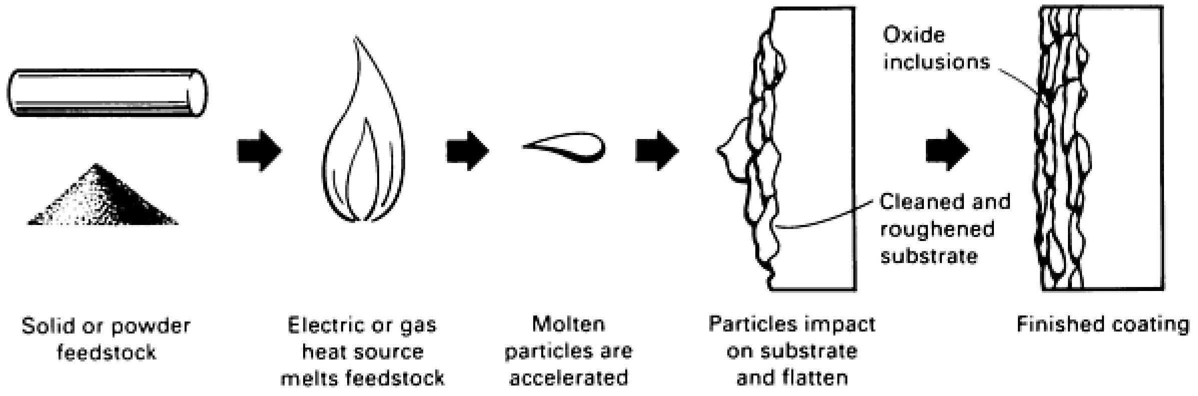


Fig. 6 Schematic of the general thermal spray process. Source: Ref 12

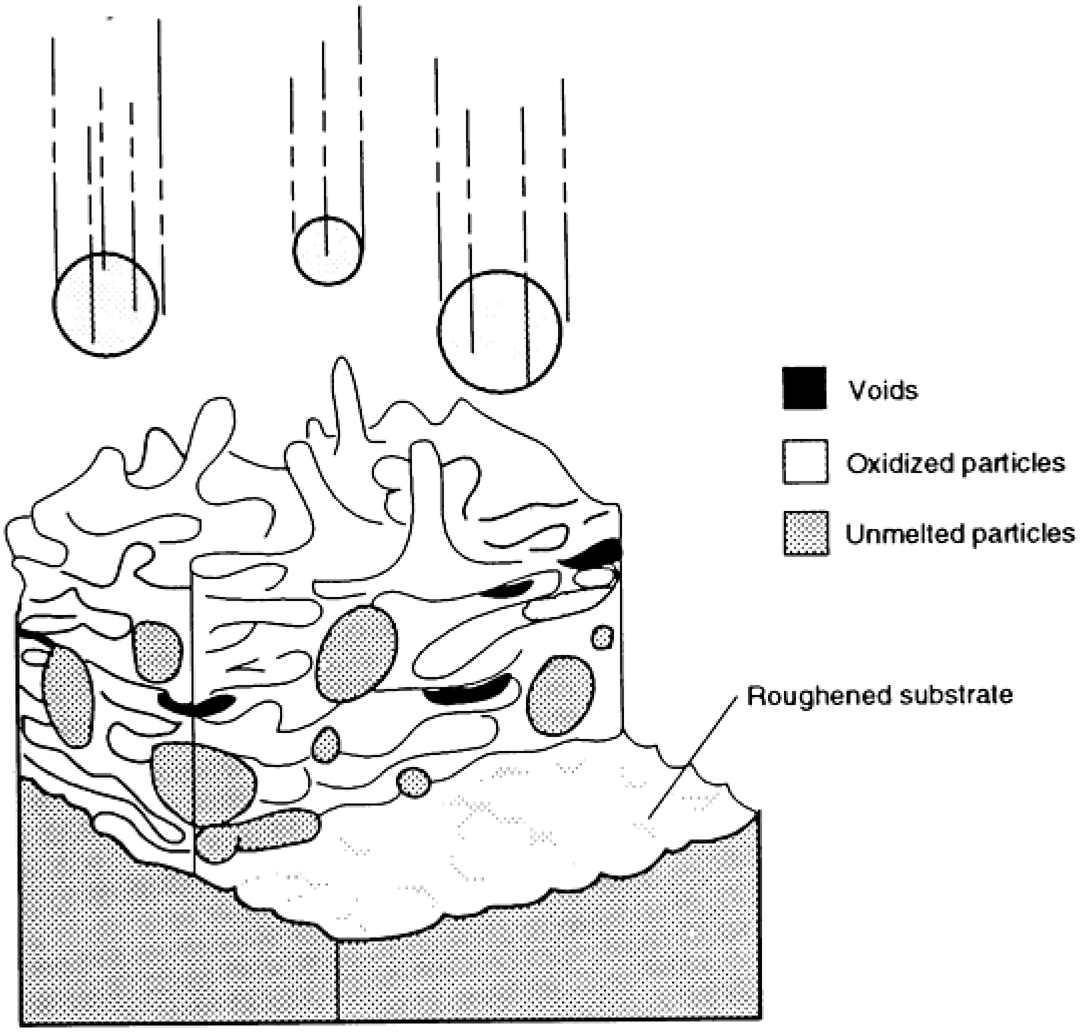


Fig. 7 Schematic showing the buildup of a thermal spray coating. Molten particles spread out and deform (splatter) as they strike the target, at first locking onto irregularities on the substrate, then interlocking with each other. Voids can occur if the growing deposit traps air. Particles overheated in the flame become oxidized. Unmelted particles may simply be embedded in the accumulating deposit. Source: Ref 12

Currently, five different commercially available thermal spray methods are in use:

- Oxyfuel wire (OFW) spray
- Electric arc wire (EAW) spray
- Oxyfuel powder (OFP) spray
- Plasma arc (PA) powder spray
- High-velocity oxyfuel (HVOF) powder spray

Selection of the appropriate thermal spray method is typically determined by the desired coating material, coating performance requirements, economics, and part size and portability. Reference 12 provides detailed information on thermal spray process selection.

Thermal spray coatings are deposited on cast iron substrates for:

- Corrosion resistance
- Wear resistance
- Oxidation resistance
- Dimensional restoration
- Thermal barriers

Corrosion Resistance. Zinc and aluminum and their alloys are the metals most widely used for thermal spray anticorrosion coatings. They are extensively used for the corrosion protection of iron and steel in a wide range of environments and have been shown to provide very long-term protection (over 20 years) in both marine and industrial locations.

Wear coatings are used to resist abrasion, erosion, cavitation, and fretting, and to reduce friction. These coatings consist of a wide range of metals and their alloys, ceramics, cermets, carbides, and even low-friction plastics. Typical coating hardness ranges from 20 to 70 HRC. Metal matrices are hardened by rapid solidification, by dispersions introduced from the spray process, by the addition of separate hard phases (for example, carbides of chromium, tungsten, titanium, and/or tantalum), or by oxide inclusions.

Oxidation protection. Thermal spray coatings are extensively used by industry to protect cast iron components and structures from heat oxidation at surface temperatures to 1095 °C (2000 °F). By ensuring long-term protection, thermal spray coatings show real economic advantages during the service lives of such items. Oxidation-resistant coatings include aluminum, aluminum-iron, nickel-chromium, and MCrAlY materials.

Dimensional Restorative Coatings. Thermal spray is used as a coating to repair or resurface (up to 3 mm, or 0.12 in. thick) worn and/or corroded parts, as well as to repair new part errors (for example, undersize parts), to repair nicks or other blemishes, or to renew surfaces that are corroded or worn in use.

Thermal barrier coatings consist of a low-conductivity (thermal) ceramic deposited over an MCrAlY bond coat. The ceramic of choice is partially-stabilized zirconia (7 to 8 wt% Y_2O_3-ZrO_2) deposited at a thickness of 0.25 mm (0.010 to 0.040 in.) with 10 to 15% porosity. A bond coat of NiCrAlY or CoCrAlY is used at a thickness of 0.125 mm (0.005 in.). Both coatings are used on components used in gas turbine engines and adiabatic engines to improve efficiency and reduce metal temperatures or cooling requirements.

Reference cited in this section

12. J.R. Davis, Hardfacing, Weld Cladding, and Dissimilar Metal Joining, *Welding, Brazing, and Soldering,* Vol 6, *ASM Handbook,* ASM International, 1993, p 789-829

Laser Surface Processing (Ref 13)

High-power lasers have been used to process materials to improve their wear resistance since the late 1960s. Laser surface modification techniques that are used to improve the wear resistance of cast irons include transformation hardening,

melting, and alloying. The processing conditions, examples of microstructures, wear characteristics, and applications associated with each technique are discussed in greater detail in Ref 13.

Laser Transformation Hardening. The wear resistance of highly stressed ferrous alloy components, such as gears and bearings, can be improved by transformation hardening. Because ferrous materials are very good heat conductors, the high heat fluxes generated by lasers are most suitable to heat the surface layer to austenitization levels without affecting the bulk temperature of the sample. The ensuing self-quenching is rapid enough to eliminate the need for external quenching to produce the hard martensite in the heated surface. Because ferrous alloys have high reflectivity, absorptive coatings such as manganese phosphate and graphite are applied to the workpiece for efficient laser heating. Most of these coatings burn off and normally do not affect the microstructure. Processing conditions for laser transformation hardening are typically power densities that range from 5 to 100 MW/m^2 (3.2 to 64.5 $kW/in.^2$) and interaction times ranging from 0.01 to 10 s. Usually, inert gas shielding is used. A rectangular beam is often used for laser transformation hardening. The case depth depends on the hardenability of the material and rarely exceeds 2.5 mm (0.1 in.).

In cast irons, laser heat-treated surfaces appear in light contrast, as shown in Fig. 8(a) for gray iron and in Fig. 8(b) for ductile iron. The microstructure of laser-hardened gray cast iron is generally fine martensite that contains flake graphite, as shown in Fig. 9(a). Acicular bainite can sometimes occur in the martensite matrix. The microstructure of laser-hardened ductile iron is also fine martensite, but contains "bull's eye" graphite nodules, as shown in Fig. 9(b). A closer examination of Fig. 9(b) reveals a narrow region of martensite between the graphite nodule and the ferrite ring, which indicates the extent of carbon diffusion occurring during processing.

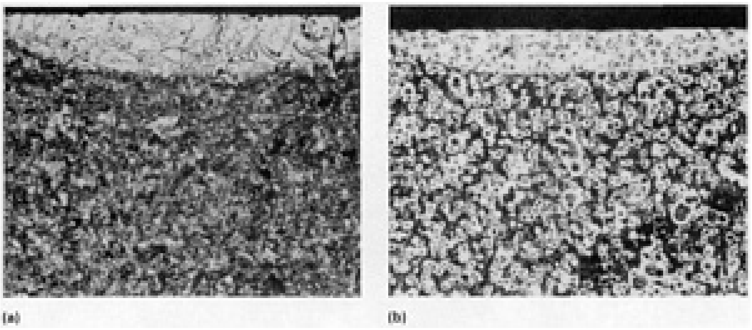


Fig. 8 Cross sections of laser heat-treated surfaces in cast irons. (a) Gray iron. (b) Ductile iron. Source: Ref 13

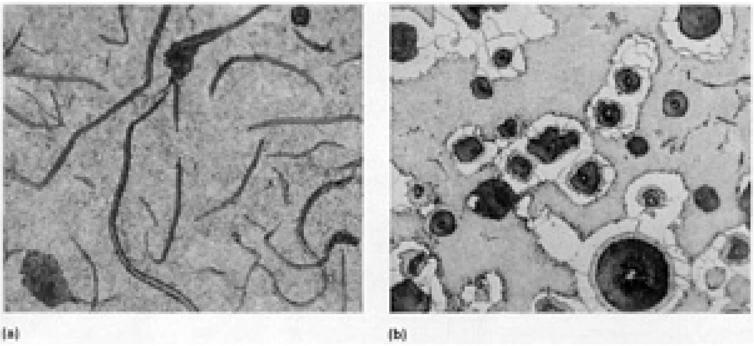


Fig. 9 Microstructures of laser-hardened cast irons. (a) Gray iron. (b) Ductile iron. Source: Ref 13

According to Molian and Baldwin (Ref 14), the extensive case that developed during laser hardening of gray and ductile irons was made up of sequential regions with varying degrees of microstructural modification. The region just below a very thin melt zone contained plate martensite, retained austenite, and graphite, whereas the region just above the base metal contained a mixture of refined martensite and untransformed pearlite.

From their study of pin-on-disk wear behavior of laser-hardened gray and ductile cast irons, Molian and Baldwin (Ref 14) found an improvement in scuffing and sliding wear resistance with an increase in case depth, as shown in Fig. 10. On the same samples, erosive wear test results showed that the erosion rate depended on the surface hardness and the case depth, as shown in Fig. 11, and increased as the matrix microstructure varied from ledeburite to tempered martensite to pearlite (Ref 15).

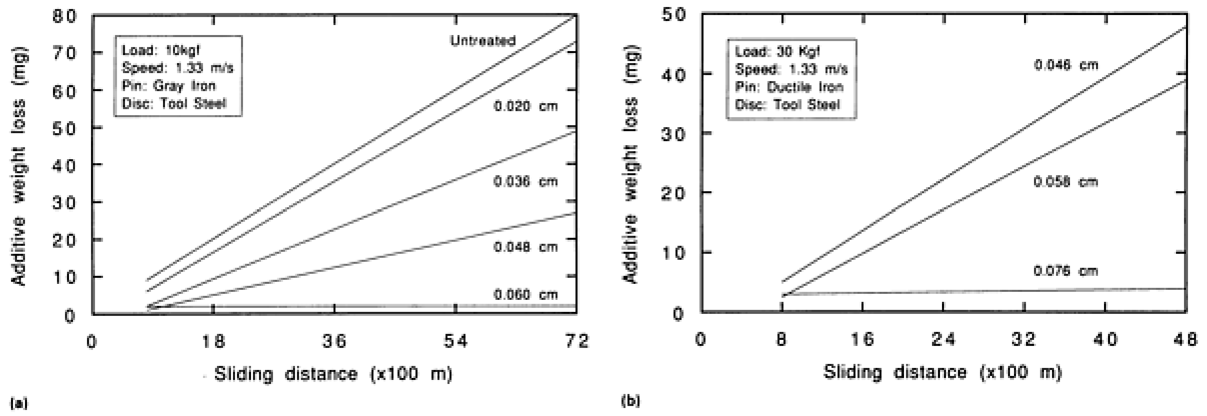


Fig. 10 Sliding wear behavior of laser-hardened cast irons as a function of case depth. (a) Gray iron. (b) Ductile iron. Source: Ref 13

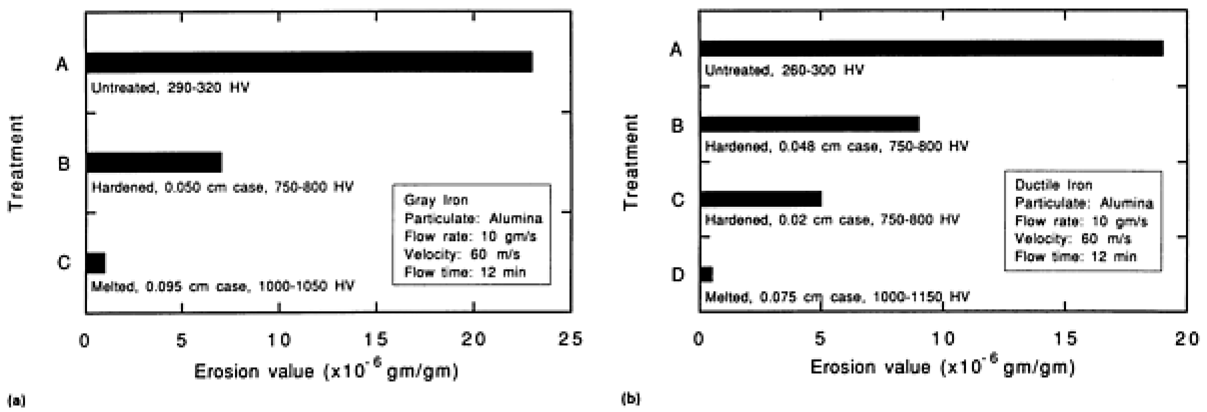


Fig. 11 Erosive wear behavior of laser-hardened cast irons as a function of surface hardness and case depth. (a) Gray iron. (b) Ductile iron. Source: Ref 13

Tomlinson et al. (Ref 16) observed that besides reducing wear, laser hardening of flake graphite iron resulted in very little plastic deformation, no graphite deposition on the opposing metal, and no adhesive damage. Trafford et al. (Ref 17) used a reciprocating pad-on-plate technique to evaluate the wear resistance of laser-processed gray iron and found that fully martensitic and surface-melted ledeburite microstructures had the lowest wear rates (Fig. 12).

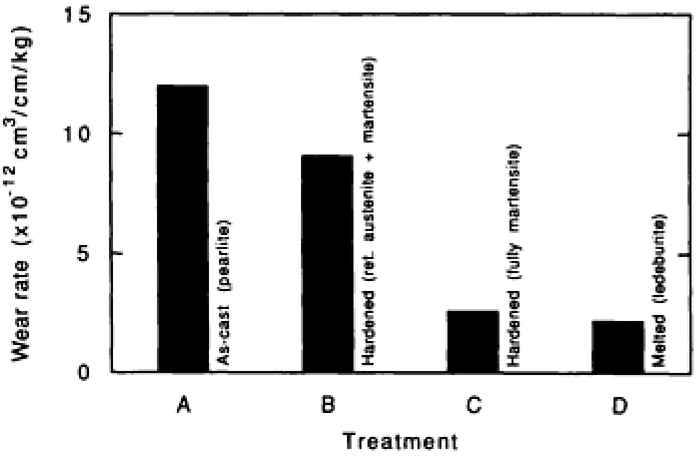


Fig. 12 Abrasive wear rates in gray iron as a function of microstructure arising from various laser-hardening treatments. Source: Ref 13

Example 1: Laser Surface Hardening of Cast Iron Camshaft Lobes

(Ref 18). The surface of the lobes of an automotive camshaft made from ductile cast iron (see Fig. 13) was to be surface hardened to increase wear resistance. The desired case depth, defined as the depth where the hardness was 50 HRC, was 0.5 to 1.0 mm (0.02 to 0.04 in.).

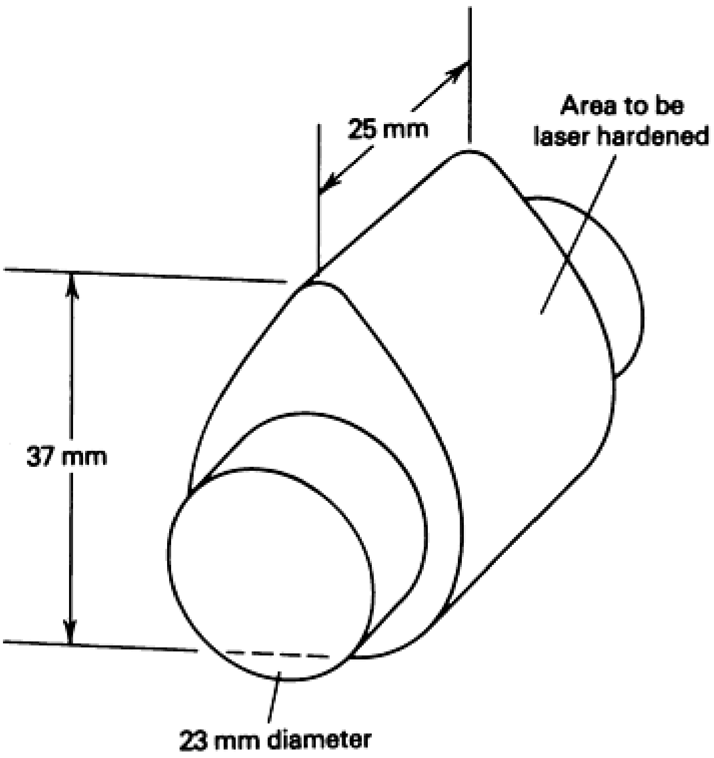


Fig. 13 Ductile cast iron cam from automotive camshaft. Source: Ref 18

A 15 kW CO_2 laser was used for the processing. The optical system delivered a focused spot, with a diameter of 10 mm (0.4 in.) to the workpiece. This spot was scanned over a distance of 22 mm (0.9 in.) normal to the direction of processing. The frequency of scanning was 125 Hz in the normal direction, forming a rectangular spot 22 mm by 25 mm (0.9 by 1.0 in.) on the camlobe surface.

To obtain an even hardened case around the periphery of the camlobe, it was necessary to vary the angular speed of rotation of the lobe under the laser beam. The reason is that the angle of incidence of the laser beam to the workpiece changed during rotation, from nearly normal incidence at the cylindrical portion of the lobe to a grazing incidence of only 20 to 30° at the flat portion. Furthermore, at constant rotational speed, the linear speed of processing would vary as the lobe rotated. This was obtained by mounting the workpiece on a rotary table. The speed of rotation was varied by means of an electromechanical controller in a predetermined manner.

The camlobe was laser hardened using a manganese phosphate coating to increase energy absorption. Because of the design of the workpiece, it was difficult to predict the optimum processing parameters by calculations and the parameters were, therefore, evaluated by trial and error. The results were:

Power input	9 kW
Power density	1600 W/cm^2 (10,300 W/in.^{2})
Linear speed of processing	
at the cylindrical portion	760 mm/min (30 in./min)
at the flat portion	180 mm/min (7 in./min)
Depth of case	0.55 mm (0.022 in.)

The hardness profile of the surface layer of the camlobe is shown in Fig. 14.

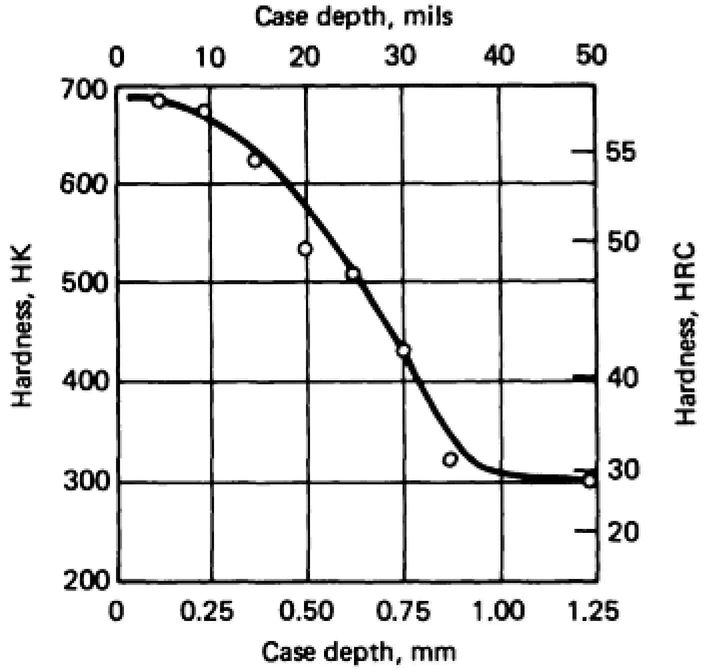


Fig. 14 Hardness profile of laser surface hardened cast iron camlobe. Source: Ref 18

Laser melting requires higher power densities than the levels used for laser transformation hardening. The workpiece is often made absorptive either by using coatings similar to those used for laser heating or by increasing surface roughness, for example, by sand blasting. Laser melting can harden alloys that cannot be hardened by laser transformation hardening. In ferritic malleable gray iron, melting enhances the diffusion of carbon, and the ensuing rapid quench produces a hardened region.

Processing conditions for laser melting are typically a power density from 10 to 3000 MW/m^2 (6.5 to 1935 $kW/in.^2$) and an interaction time from 0.01 to 1 s. Inert gas shielding is used to prevent oxidation of the surface.

Microstructural changes with laser melting are in the forms of grain refinement, solid solutions, and fine dispersions of precipitates. All of these can contribute to the hardening and strengthening of the surface. Laser-melted surfaces of cast irons appear dendritic, as shown in Fig. 15(a) for gray iron and in Fig. 15(b) for ductile iron. Below the melt zone is the heat-affected zone, which appears in lighter contrast in Fig. 15.

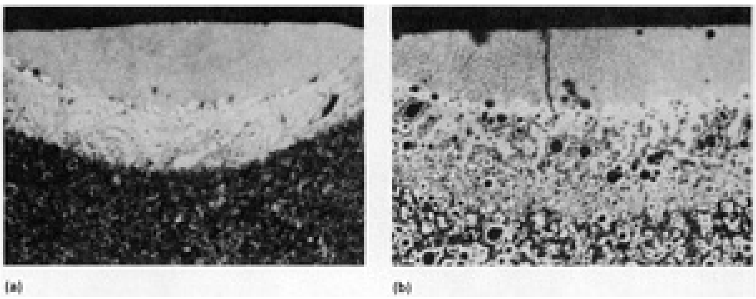


Fig. 15 Cross section of laser-melted cast iron surfaces. (a) Gray iron. (b) Ductile iron. Source: Ref 13

In the solidified melt in cast irons, a ledeburite (mixture of austenite and cementite) structure generally forms. Hardening is caused by graphite dissolution to form cementite and austenite transformation to martensite. Molian and Baldwin (Ref 14) described the formation of predominantly dendritic ledeburite with small amounts of plate-like, high-carbon martensite and retained austenite in the melt zone in gray and ductile irons.

Chen et al. (Ref 19) determined that microstructures in laser-melted ductile iron depended on the solidification rate. Dendritic retained austenite with a continuous interdendritic carbide, with a microhardness from 400 to 650 HV, formed at high solidification rates. A lamellar mixture of ferrite and cementite plates, with a microhardness from 1000 to 1250 HV, formed at low solidification rates.

Bamberger et al. (Ref 20) found that in laser-melted gray cast iron, full dissolution of the graphite occurred, leading to the formation of hot tears on the surface. On the other hand, in laser-melted nodular cast iron, partial dissolution of the graphite occurred, resulting in increased ductility and no hot tearing.

Bergmann (Ref 21) has summarized the wear properties of laser-melted cast irons. For laser-melted gray iron containing flake graphite in a pearlitic matrix, the dry pin-on-disk test demonstrated that the wear behavior improved by an order of magnitude and was better than a fully martensitic structure. In a test involving rolls that ran against one another with a fixed relative slip, it was found that the wear resistance of laser-melted ductile iron was superior to that of 0.6% C steel, case-hardened 16MnCr5 steel, nitrided or carburized 16MnCr5 steel, and a gas-tungsten arc welded melted surface.

Ju et al. (Ref 22) reported significant improvement in erosive wear behavior in laser-melted ductile and gray irons, as shown in Fig. 16. This improvement was due to the presence of mechanically metastable austenite that transforms to martensite when plastic deformation of the near-surface region occurs during wear.

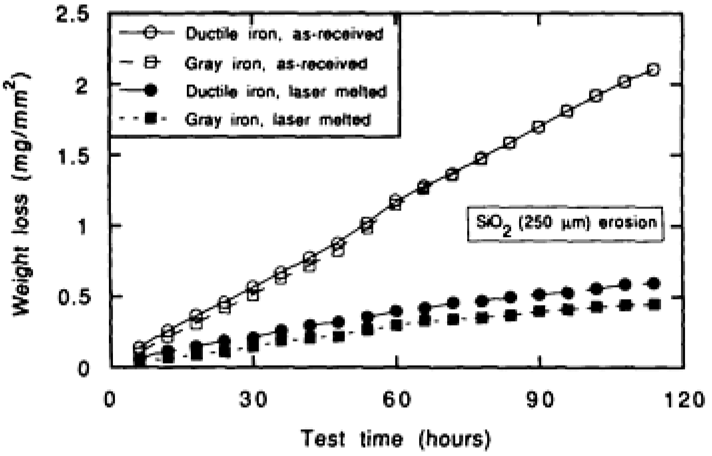


Fig. 16 Erosive wear behavior of as-received and laser-melted gray and ductile irons. Source: Ref 22

Tomlinson et al. (Ref 23) reported that laser melting reduced the amount of cavitation erosion of gray cast iron in distilled water by a factor of 0.3, and, in 3% saltwater, by a factor of 0.57.

Laser Alloying. A technique of localized alloy formation is laser surface melting with the simultaneous, controlled addition of alloying elements. These alloying elements diffuse rapidly into the melt pool, and the desired depth of alloying can be obtained in a short period of time. By this means, a desired alloy chemistry and microstructure can be generated on the sample surface; the degree of microstructural refinement will depend on the solidification rate. The surface of a low-cost alloy, such as cast iron, can be selectively alloyed to enhance properties, such as resistance to wear, in such a way that only the locally modified surface possesses properties typical of tribological alloys. This results in substantial cost savings, and reduces the dependence on strategic materials. Typical processing parameters for laser alloying are a power density from 10 to 3000 MW/m^2 (6.5 to 1935 kW/in.^{2}) and an interaction time from 0.01 to 1 s. An inert shielding gas is normally used.

One method of alloying is to apply appropriate mixtures of powders on the sample surface, either by spraying the powder mixture suspended in alcohol to form a loosely packed coating, or by coating a slurry suspended in organic binders. The use of metal powders in laser alloying is the least expensive, but, with appropriate process modifications, alloys in the form of rods, wires, ribbons, and sheets can also be added.

Cast irons, primarily gray irons, have been laser alloyed with chromium, silicon, carbon, nickel, nickel-aluminum, cobalt, and cobalt-chromium powders. Figure 17 shows the improved cavitation erosion resistance of a gray cast iron containing 2.9 to 3.2% C, 1.7 to 2.1% Si, 0.5 to 0.8% Mn, ≤0.1% P, and 0.06 to 0.11% S that was laser alloyed with chromium. The resulting coating, which was approximately 0.5 mm (0.02 in.) thick, contained 22% Cr and had a hardness value of 700 HV.

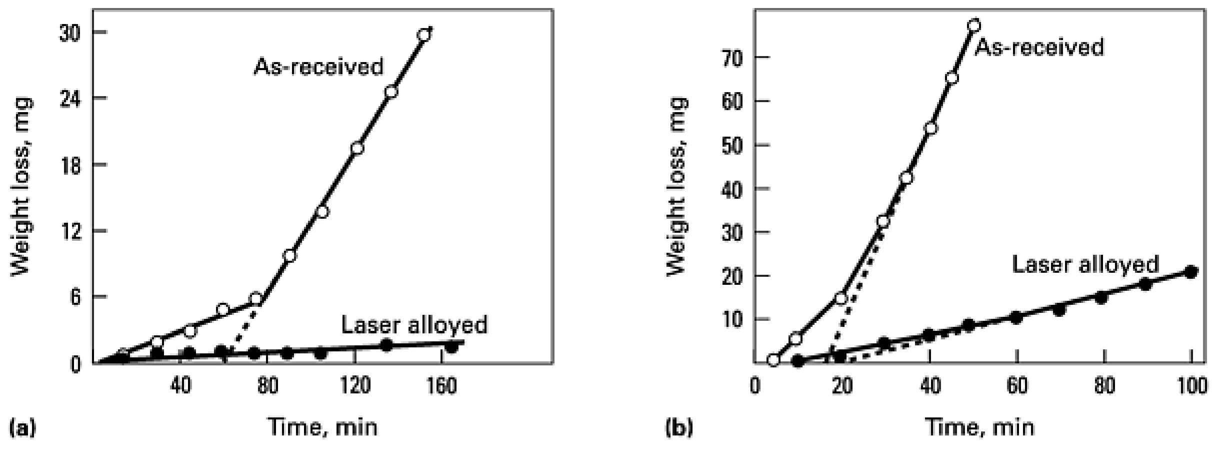


Fig. 17 Effect of laser alloying with chromium on the cavitation erosion resistance of gray cast iron in distilled water (a) and 3% sodium chloride solution (b). Source: Ref 24

References cited in this section

13. K.P. Cooper, Laser Surface Processing, *Friction, Lubrication, and Wear Technology,* Vol 18, *ASM Handbook,* ASM International, 1992, p 861-872
14. P.A. Molian and M. Baldwin, *J. Tribol,.* Vol 108, 1986, p 326
15. P.A. Molian and M. Baldwin, *J. Tribol,.* Vol 110, 1988, p 462
16. W.J. Tomlinson, R.F. O'Connor, and T.A. Spedding, *Tribol. Int,.* Vol 21 (No. 6), 1988, p 302
17. D.N.H. Trafford, T. Bell, J.H.P.C. Megaw, and A.S. Bransden, *Heat Treating, Proceedings of the International Conference,* Metallurgical Society, 1983, p 198
18. O.A. Sandven, Laser Surface Hardening, *Heat Treating,* Vol 4, *ASM Handbook,* ASM International, 1991, p 286-296
19. C.H. Chen, C.P. Ju, and J.M. Rigsbee, *Mater. Sci. Technol.,* Vol 4 (No. 2), 1988, p 161
20. M. Bamberger, M. Boas, and O. Akin, *Z. Metallkde.,* Vol 79, 1988, p 806
21. H.W. Bergmann, *Proceedings of the NATO Advanced Study Institute on Laser Surface Treatment of Metals,* C.W. Draper and P. Mazzoldi, Ed., Martinus Nijhoff, The Netherlands, 1986, p 351
22. C.P. Ju, C.H. Chen, and J.M. Rigsbee, *Mater. Sci. Technol.,* Vol 4 (No. 2), 1988, p 167
23. W.J. Tomlinson, J.H.P.C. Megaw, and A.S. Bransden, *Wear,* Vol 116, 1987, p 249
24. W.J. Tomlinson and A.S. Bransden, Fabrication, Microstructure, and Cavitation Erosion Resistance of a Grey Iron Laser Surface Alloyed With 22% Chromium, *Surface Engineering,* Vol 4 (No. 4), 1988, p 303-308

Surface Hardening

Surface hardening is a generic term covering several processes applicable to a suitable ferrous alloy that produces a surface layer that is harder or more wear resistant than the core. The processes commonly used to surface harden cast irons which will be described in this section include flame hardening, induction hardening, and nitriding. Laser transformation hardening, which is a rapidly emerging technology for improving the performance of iron castings, was described in the previous section on "Laser Surface Processing." Other less commonly used methods for surface hardening of cast irons include boriding, nitrocarburizing, and the thermoreactive deposition/diffusion process (Toyota diffusion coating process). More detailed information on surface hardening can be found in Volume 4, *Heat Treating,* of the *ASM Handbook.*

Flame Hardening of Gray Iron

Flame hardening is the method of surface hardening most commonly applied to gray iron. After flame hardening, a gray iron casting consists of a hard, wear-resistant outer layer of martensite and a core of softer gray iron, which during treatment does not reach the A_1 transformation temperature (in fact, the unhardened metal immediately below the hardened case, which has been heated by the flame to some extent, may even be partially annealed during flame hardening if it is unalloyed).

Recommended Composition. Both unalloyed and alloyed gray irons can be successfully flame hardened. However, some compositions yield much better results than do others. One of the most important aspects of composition is the combined carbon content, which should be in the range of 0.50 to 0.70%, although irons with as little as 0.40% combined carbon can be flame hardened. In general, flame hardening is not recommended for irons that contain more than 0.80% combined carbon because such irons (mottled or white irons) may crack in surface hardening.

The stability of the microconstituents from which the carbon precipitates is a factor in determining the hardness of the flame-hardened iron. One user observed that the stability of microconstituents containing combined carbon is indicated by

the hardness of test specimens annealed at 845 °C (1550 °F). A test of four pearlitic irons from different sources, containing 3.30% C max, 1.40 to 1.60% Si, 0.80 to 1.10% Mn, and 0.15 to 0.20% Cr, gave the results:

Iron	Hardness, HB		Hardness[(a)], HRC
	As-cast	Annealed	
A	220	200	47-50
B	190	180	47-50
C	200	140	35-38

(a) After flame hardening as-cast iron

For maximum hardness, it is advisable to use an iron containing as small an amount of total carbon as is consistent with the production of sound castings free from any danger of cracking. The coarse graphite flakes typical of high-carbon irons should be avoided because they may be burned out during flame heating, thereby producing a porous and unattractive surface.

Because silicon promotes the formation of graphite and of a low combined carbon content, a relatively low silicon content is also advisable. Several users report that silicon content should not exceed 2% in any iron submitted to a flame-hardening operation, although alloy irons containing 2.4% Si can be hardened successfully. They also recommend that manganese content be held in the range of 0.80 to 1.00% to increase carbon solubility in austenite.

Gray iron to be flame hardened should be as free as possible from porosity and from foreign matter such as sand or slag because porosity and even small inclusions of foreign matter can produce a rough surface or result in cracking after hardening. Rough casting surfaces should be sand or shot blasted prior to heat treatment because skin or scale on the surface acts as a heat insulator and reduces the effectiveness of flame hardening.

Effects of Alloying Elements. In general, alloyed gray irons can be flame hardened with greater ease than can unalloyed irons, partly because alloyed gray irons have increased hardenability. Final hardness also may be increased by alloying additions. The maximum hardness obtainable by flame hardening an unalloyed gray iron containing approximately 3% total carbon, 1.7% Si, and 0.60 to 0.80% Mn ranges from 400 to 500 HB. This is because the Brinell hardness value for gray iron is an average of the hardness of the matrix and that of the relatively soft graphite flakes. Actually, the matrix hardness on which wear resistance depends approximates 600 HB. With the addition of 2.5% Ni and 0.5% Cr, an average surface hardness of 550 HB can be obtained. The same result has been achieved using 1.0 to 1.5% Ni and 0.25% Mo. Small additions of chromium are particularly valuable in preventing softening and ensuring the retention of a high content of combined carbon during austenitizing for hardening. Automotive camshafts containing 1% Cr, 0.50% Mo, and 0.8% Mn are easily flame hardened to 52 HRC to a required depth. These parts are not tempered or stress relieved.

Stress Relieving. Whenever practicable or economically feasible, flame-hardened castings should be stress relieved at 150 to 200 °C (300 to 400 °F) in a furnace, in hot oil, or by passing a flame over the hardened surface. Such a treatment will minimize distortion or cracking and will increase the toughness of the hardened layer.

Stress relieving at 150 °C (300 °F) for 7 h was found to remove 25 to 40% of the residual stresses in a flame-hardened casting, while reducing the hardness of the surface by only 2 to 5 points on the HRA scale. Although stress relieving is desirable, it can often be safely omitted.

Hardness. The surface of flame-hardened gray iron typically has a somewhat lower hardness than the metal immediately below the surface (Fig. 18). This decrease in hardness may be caused by the retention of relatively soft austenite at the surface. Surface hardness often can be raised by heating in the range from 195 to 250 °C (380 to 480 °F).

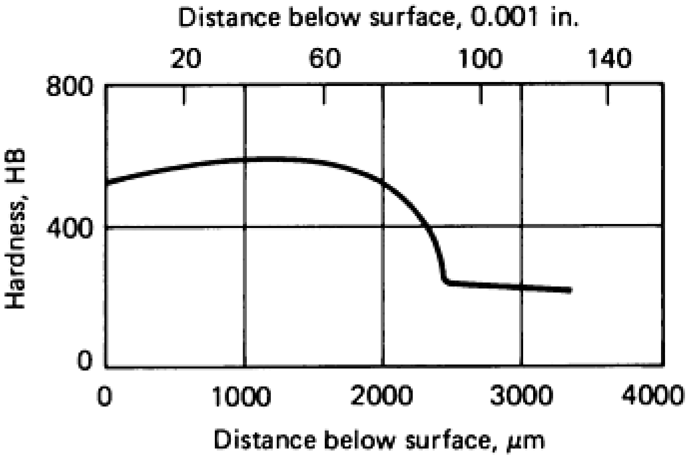


Fig. 18 Typical hardness gradient produced in gray iron by flame hardening

The depth and microstructure of the hardened layer depend on two other factors in addition to temperature: the amount of carbon and alloying elements in solution when the flame-hardened surface is quenched, and the efficiency of quenching. If softness is due to the presence of austenite in the microstructure, subjecting the part to -40 °C (-40 °F) for 1 h will transform the austenite and increase the hardness.

Fatigue strength is usually increased by surface hardening because the treatment induces compressive stresses at the surface. For example, flame or induction heating followed by water quenching induces high compressive stresses (>205 MPa, or 30 ksi) in the fillet areas of crankshafts; however, if self-quenching instead of water quenching is used, undesirable tensile stresses may result at the surface. The degree of improvement in fatigue strength by flame hardening cannot be produced by through hardening.

Quenching. The various methods of flame hardening influence the selection of the quenching medium. In the progressive method, only nonflammable media such as water, soluble-oil mixtures, and solutions of polyvinyl alcohol in water can be employed. Conventional oil cannot be used because of the fire hazard. In spot hardening or spinning methods, in which the flame head is withdrawn from the part before quenching, parts are quenched conventionally by immersion in hot oil.

When quenching is done with water, the water should be at about 30 °C (90 °F) for best results. Lower quenching rates, such as those obtained with 5 to 15% soluble-oil mixtures, compressed air, or compressed air and water at low pressure, are used to prevent cracking. Air quenching is especially suited to highly alloyed cast irons because of their susceptibility to cracking.

Induction Hardening of Gray Iron

Gray iron castings can be surface hardened by the induction method when the number of castings to be processed is large enough to warrant the relatively high equipment cost and the need for special induction coils. Considerable variation in the hardness of the cast irons may be expected because of a variation in the combined carbon content. A minimum combined carbon content of 0.40 to 0.50% C (as pearlite) is recommended for cast iron to be hardened by induction, with the short heating cycles that are characteristic of this process. Heating castings with lower combined carbon content to high hardening temperatures for relatively long periods of time may dissolve some free graphite, but such a procedure is likely to coarsen the grain structure at the surface and will result in undesirably large amounts of retained austenite in the

surface layers. The recommended minimum induction hardening temperature for gray iron is 870 to 925 °C (1600 to 1700 °F).

The surface hardness attained from the induction hardening of gray iron is influenced by the carbon equivalent (%C + 1/3% Si) when this hardness is measured by conventional Rockwell tests. The more graphite that is present in the microstructure, the lower the surface hardness will appear to be after hardening. Table 10 shows the surface hardness of induction-hardened gray iron castings of various carbon equivalents from 3.63 to 4.23. The microstructure of these castings, which were cast in the same manner and cooled at similar rates, contained more and larger graphite flakes as the carbon equivalent increased. This resulted in lower apparent surface hardness after hardening, yet the hardened matrix was consistently 57 to 61 HRC (converted from microhardness).

Table 10 Effect of carbon equivalent on surface hardness of induction-hardened gray irons

Composition, %[(a)]		Carbon equivalent[(b)]	Hardness HRC, converted from		
C	Si		As read	Rockwell 30-N	Microhardness
3.13	1.50	3.63	50	50	61
3.14	1.68	3.70	49	50	57
3.19	1.64	3.74	48	50	61
3.34	1.59	3.87	47	49	58
3.42	1.80	4.02	46	47	61
3.46	2.00	4.13	43	45	59
3.52	2.14	4.23	36	38	61

(a) Each iron also contained 0.50 to 0.90 Mn, 0.35 to 0.55 Ni, 0.08 to 0.15 Cr, and 0.15 to 0.30 Mo.

(b) Carbon equivalent = %C + $\frac{1}{3}$ % Si.

Distortion. Induction hardening causes less distortion than would a similar quenching treatment from a furnace. The maximum warpage in a 560 mm (22 in.) length of bar was found to be 0.03 mm (0.0015 in.) after induction hardening, compared with 0.17 to 0.25 mm (0.007 to 0.010 in.) for the same bars quenched from a furnace. For thin-walled cylinders, distortion is not a problem unless the thickness of the induction-hardened layer exceeds 20% of the wall thickness.

For selective hardening, in place or by scanning, to depths up to 3.8 mm (0.150 in.), water quenching can be used safely. However, the hardening of keyways, cross-drilled holes, or extremely thin walls may require the use of oil to prevent excessive distortion or cracking.

Surface Hardening of Ductile Iron

Ductile iron responds readily to surface hardening by flame, induction, or laser heating, or by nitriding. Because of the short heating cycle in these processes, the pearlitic types of ductile iron ASTM 80-60-03 and 100-70-03 are preferred. Irons without free ferrite in their microstructure respond almost instantly to flame or induction heating and require very little holding time at the austenitizing temperature in order to be fully hardened.

With a moderate amount of free ferrite, the response may be satisfactory, but an entirely ferritic matrix, typical of the grades with high ductility, requires several minutes at 870 °C (1600 °F) to be fully hardened by subsequent cooling. A matrix microstructure of fine pearlite, readily obtained by normalizing, has a rapid response to surface hardening and provides excellent core support for the hardened case.

With proper technique and the control of temperature between 845 and 900 °C (1550 and 1650 °F), the ranges of surface hardness for ductile iron with different matrices expected in commercial production are:

- Ductile iron, fully annealed (ferritic), water quenched behind the flame or induction coil, 35 to 45 HRC
- Ductile iron, predominantly ferritic (partly pearlitic), stress relieved prior to heating, self quenched, 40 to 45 HRC
- Ductile iron, predominantly ferritic (partly pearlitic), stress relieved prior to heating, water quenched, 50 to 55 HRC
- Ductile iron, mostly pearlitic, stress relieved before heating, water quenched, 58 to 62 HRC

Heating time and temperature, amount of dissolved carbon, section size, and rate of quench help to determine final hardness values. Often soluble-oil or polymer quench media are used to minimize quench cracking where the casting section changes.

Flame or induction-hardened ductile iron castings have been used for heavy-duty applications such as foils for cold working titanium, ring gears for paper-mill drives, crankshafts, and large sprockets for chain drives.

The response of ductile iron to induction hardening is dependent on the amount of pearlite in the matrix of as-cast, normalized, and normalized and tempered prior structures. In quenched and tempered iron, the secondary graphite nodules formed during tempering are close enough together to supply sufficient carbon to the matrix by re-solution during induction heating.

In the as-cast condition, a minimum of 50% pearlite is considered necessary for satisfactory hardening with induction heating cycles of 3.5 s and longer and hardening temperatures of 955 to 980 °C (1750 to 1800 °F). Structures containing less pearlite can be hardened by using higher temperatures, but at the risk of retaining austenite, forming ledeburite, and damaging the surface. With more than 50% pearlite, hardening temperatures may be reduced to within the range of 900 to 925 °C (1650 to 1700 °F).

In the Normalized Condition. For heating cycles of 3.5 s and longer, at temperatures of 955 to 980 °C (1750 to 1800 °F), 50% pearlite in a prior structure would be considered a minimum. Normalized and tempered irons exhibit a poor response with lower pearlite content because of the depletion of the matrix carbon. In the tempering operation, the carbon migrates from the pearlite matrix to the graphite nodules. In the heating cycle, carbon is reabsorbed in the matrix from the nodule; however, there is insufficient time for it to migrate throughout the ferritic areas. Another factor in the response of ductile iron is the graphite nodule count; the greater the number of nodules per unit area, the deeper the hardening for any given heat cycle. This effect is more evident as the percentage of ferrite increases (Fig. 19).

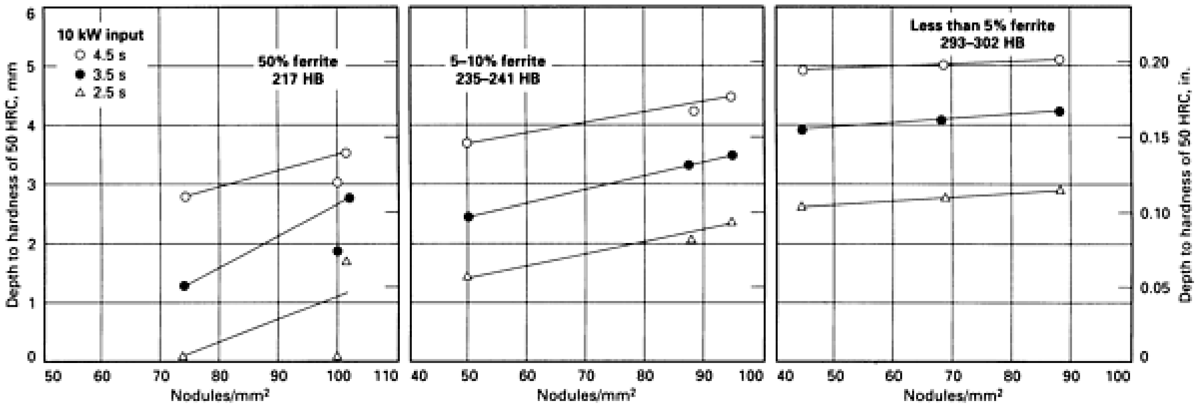


Fig. 19 Relationship between depth of induction hardening to 50 HRC and graphite nodule count in normalized and tempered ductile (nodular) iron

Quenched and Tempered. The response of quenched and tempered nodular iron to induction hardening is excellent over a wide range of microstructures containing up to 95% ferrite. As a prior treatment, quenching and tempering has the advantage of permitting a lower prior hardness; there is a risk of distortion and quench cracking, however.

Nitriding is a case-hardening process that involves the diffusion of nitrogen into the surface at a temperature of about 550 to 600 °C (1020 to 1110 °F). Usually the source of nitrogen is ammonia, and the process produces a surface layer about 0.1 mm (0.004 in.) deep with a surface hardness approaching 1100 HV. The surface layer is typically white and featureless in an etched microstructure, but nitride needles can be found just below it. Alloying elements can be used to increase case hardness, and 0.5 to 1% Al, Ni, and Mo have been reported to achieve useful results. Nitrided cases provide, in addition to very high hardness, increased wear resistance and antiscuffing properties, improved fatigue life, and improved corrosion resistance. Typical applications are for cylinder liners, bearing pins, and small shafts.

Nitriding can also be carried out in liquid salt baths based on cyanide salts. Such processes have lower temperatures of treatment, although case depth may be decreased. More recently, processes for nitriding in a plasma have been developed and applied with success to ductile iron, but the process may be more restricted because of the special equipment and cost likely to be involved.

Surface Hardening of Pearlitic Malleable Iron

Fully pearlitic malleable iron may be surface hardened by either induction heating and quenching or flame heating and quenching. Laser and electron beam techniques also have been used for hardening selected areas on the surface of pearlitic and ferritic malleable iron castings that are free from decarburization. Generally, hardness in the range from 55 to 60 HRC is attainable, with the depth of penetration being controlled by the rate of heating and by the temperature developed at the surface of the part being hardened. In induction hardening, this is accomplished by the close regulation of power output, operating frequency, heating time, and alloy content of the iron.

The maximum hardness obtainable in the matrix of a properly hardened part is 67 HRC; however, conventional hardness measurements show less than the true matrix hardness because of the temper carbon nodules that are averaged into the hardness. Generally, a casting with a matrix microhardness of 67 HRC will have about 62 HRC average hardness, as measured with the standard Rockwell tester.

Rocker arms and clutch hubs are examples of automotive production parts that are surface hardened by induction. Flame hardening requires close control for these applications in order to avoid distortion that would interfere with their operation.

Conversion Coatings

Chemical reactions at casting surfaces can produce iron-containing compounds that provide wear resistance or an attractive appearance or that serve as excellent bonding agents for subsequent organic coatings. Table 11 details common

conversion coatings and their useful properties (chromate and phosphate conversion coatings are discussed in greater detail in the articles "Chromate Conversion Coatings" and "Phosphate Coatings" in this Volume). Most of the successful processes are proprietary, and reproducibility of consistently good finishes is one of the important features.

Table 11 Chemical conversion coatings, structures, and characteristics

Type	Coating structure	Properties	Uses
Chromate	Nonporous film acts as moisture barrier	High corrosion resistance; inhibits corrosion if surface is broken; can be colored	Marine applications; can be decorative; nonporous bond layer for paint
Oxide	Ferric oxide formed from iron	Inhibits formation of ferrous oxide; highly absorbent; some wear resistance	Decorative blue-black coating; readily absorbs overlays of wax or oil
Phosphate	Iron zinc or manganese phosphates are crystalline structures formed on the surface by deposition from chemical solution	Chemically neutral and high adherence to iron surfaces; highly absorbent	Excellent for bonding paint to iron; prevents abnormal wear or seizing during break-in

Source: Ref 7

Phosphate coating is the treatment of cast iron with a dilute solution of phosphoric acid and other chemicals in which the surface of the metal, reacting chemically with the phosphoric acid medium, is converted to an integral, mildly protective layer of insoluble crystalline phosphate. The coating reduces corrosion, prevents surface seizure on initial wear contact, and provides an excellent base for organic paint bonding.

Gray, ductile, and malleable iron castings all lend themselves readily to phosphating. The ability of a cast iron to accept a phosphate coating is not affected by alloy content, but hinges primarily on two requirements: a clean surface, and a metal temperature approximately equal to that of the phosphating bath. Dry machined surfaces need no further cleaning; cast surfaces can be prepared by blasting or other cleaning methods to remove scale and sand.

Oxide Coatings (Ref 7). Conversion of the surface of an iron casting to a magnetic oxide, Fe_3O_4, gives a thin black finish. These films have a certain degree of wear resistance, provide a good bond for paint or lacquer, and have pleasing decorative features. The film layer, if oiled or waxed, provides satisfactory corrosion resistance against handling and storage and is useful with lubrication for sliding and rotating wear applications. The original method of forming a strongly adherent black oxide film is still useful today. The process involves use of steam around an iron part heated above 480 °C (900 °F) and yields a tight oxide coating. Steam generally is introduced to furnace atmospheres to completely replace air while the parts are heated to 590 °C (1100 °F). Twenty minutes at temperature in this atmosphere is sufficient for buildup of a thick, wear-resisting film.

Oxide film finishes can also be produced in a wide variety of proprietary basic-nitrate media. Reproducibility of consistent finishes in large-volume operations is one of their prime features. These provide thinner films that are more suitable for decorative purposes. Sodium carbonate and sodium and potassium nitrates constitute the bulk of the bath solutions. Often these are supplemented with additional agents, such as manganese, to give a mixed oxide film.

Chromate conversion coating is accomplished by immersion of iron in an aqueous solution of chromic acid or chromium salts. This solution can be used as a supplement to cadmium and zinc plating to prevent the formation of powder corrosion products (see Table 9) and it also provides an excellent bond for paints.

Reference cited in this section

7. C.F. Walton and T.J. Ajar, Ed., *Iron Castings Handbook,* Iron Casting Society, 1981, p 755-799

Porcelain Enameling

Porcelain enamels are inorganic vitreous coatings that are matured by heat. The inherently good heat transfer, thermal stability, and rigidity of iron at firing temperatures, coupled with the excellent adherence of vitreous ceramic frits as they fuse onto the cast surface, make the combination of porcelain on iron an excellent product. General corrosion resistance or resistance to specific chemicals can be obtained by selecting the proper porcelain enamel. The scratch resistance and hardness of the enamel coating, which allow the surface to resist abrasion, are almost equal in importance to the corrosion resistance.

Four processes are used to apply enamels: dry, wet, thermal spray (or plasma spray), and electrostatic precipitation. The latter two methods are seldom used on iron castings. Preparations for enameling start by blasting with sand, steel shot, or iron grit.

Dry coating methods use formulations that are mainly silica; these formulations generate a surface with the hardness and abrasion resistance of glass. Fluxes and opacifiers are mixed into the silica, and the mixture is then melted, quenched, and ground to make frit. (Frit is the term applied to the basic coating materials.) After application of a bonding ground coat, relatively heavy, smooth coatings (such as those on sinks and bathtubs) can be obtained by multiple firing. Each firing is followed by hot dusting with additional powdered frit, until the desired finish has been achieved.

Wet methods produce thinner coatings. The powdered frit is suspended in a solution of electrolytes and water or in an organic solvent and is applied by spraying or dipping over the ground coat. The sprayed or dipped coating must be dried prior to firing.

Ground coats that wet iron readily, adhere well, and are compatible with the cover coat are essential to the enameling process. Good ground coats promote adhesion between the enamel layer and the substrate, seal and smooth the irregularities of the surface, and prevent oxidation of the iron casting at firing temperatures. Top coats (cover coats) must provide the desired appearance and must be compatible with the ground coat. Formulation of frits requires the judgment and experience of a frit manufacturer to ensure that the coating provides successful results.

Cast iron for enameling usually has a composition that falls within the following limits:

Constituent	**Amount, %**
Total carbon	3.20-3.60
Silicon	2.30-3.00
Manganese	0.30-0.60
Sulfur	0.50-0.12
Phosphorus	0.40-0.80

Total carbon and silicon should vary in opposite directions within the ranges shown. If both are low, the iron tends to be brittle and to blister during porcelain enameling. If both are high, the iron is soft and warps easily when reheated for porcelain enameling. Manganese and sulfur should range in the same direction, so that all of the sulfur is converted to manganese sulfide. Within the normal range, phosphorus has a negligible effect on the strength of the cast iron at porcelain enameling firing temperatures.

The primary applications for porcelain enameled cast irons are in the manufacture of bathtubs, kitchen sinks, and lavatories. See the article "Porcelain Enameling" in this Volume for more detailed information.

Organic Coatings

Organic coatings have a wide variety of properties, but their primary uses require corrosion resistance combined with a pleasing colored appearance. An organic-base film is often resistant to certain environmental substances but not to others, and so must be chosen for a specific set of well-defined service conditions. For example, a vinyl paint might be used on a pump casing that must operate in contact with acidic industrial waters. However, if the same casing is expected to contact hydrocarbons such as gasoline or solvents, a styrene, epoxy, or phenolic coating would most likely provide superior protection.

Types of Organic Coatings. The term paint was once commonly used to designate all liquid organic coatings, but it is considered inadequate to describe modern liquid organic coatings, which in general are subdivided into enamels, lacquers, aqueous mixtures, suspensions, bituminous substances, and rubber-base products. Resins dispersed in a vehicle--for example, enamels or lacquers--cure to relatively hard gels by polymerization, oxidation, or solvent evaporation. A comparison of the chemical and environmental resistance of common resins is given in Table 12.

Table 12 Properties of organic coatings on iron castings

Resin	Resistance to chemicals and environment[a]										Application method				Curing Method		Typical applications
	Hydro-carbons	Solvents	Acids	Alkalies	Salts	Water	Weathering	Heat	Cold	Abrasion	Need for primer	Spray	Dip	Fluidized bed	Air dry	Bake	
Low cost																	
Phenolic	E	E	E	F	E	E	E	G	E	E	no	yes	yes	no	yes	yes	Appliances
Urea	E	G	E	E	E	G	G	G	G	E	no	yes	yes	no	no	yes	Appliances
Polyester	G	G	G	F	E	G	G	G	G	G	no	yes	yes	no	yes	yes	Thick coatings
Alkyd	G	P	F	F	E	G	E	F	G	G	yes	yes	yes	no	yes	yes	General purpose
Epoxy	E	E	E	E	E	G	G	E	E	E	no	yes	yes	yes	yes	yes	Scratch-resistant finish
Polyethylene	G	E	E	E	E	E	G	F	E	F	no	no	no	yes	no	yes	Coatings
Styrene-butadiene	E	G	E	E	E	E	G	G	E	G	no	yes	yes	no	yes	yes	General purpose
Urethane	G	E	G	G	E	E	E	E	G	G	yes	yes	yes	no	yes	yes	Scuff-resistant coatings: chemical and marine finishes
Moderate cost																	

Vinyl chloride	G	F	E	E	E	E	E	G	G	E	yes	yes	yes	yes	yes	yes	Chemical equipment
Melamine	E	G	E	E	E	G	E	G	G	E	no	yes	yes	no	no	yes	Appliances
Polyamide	F	G	F	E	E	F	P	G	G	E	no	yes	yes	yes	yes	yes	Abrasion-resistant coatings
Vinyl butyral	G	F	F	G	G	G	E	G	E	E	no	yes	yes	no	yes	yes	General purpose, primers
Cellulose nitrate	F	F	G	F	E	E	E	P	G	F	yes	yes	yes	no	yes	yes	High-gloss lacquer
Acrylic	F	P	F	G	E	E	E	P	F	F	yes	yes	yes	no	yes	yes	Water-resistant finishes
Vinyl acetate	F	P	F	F	F	G	E	F	F	E	no	yes	yes	no	yes	yes	Decorative
Cellulose acetate butyrate	F	F	F	F	G	F	E	P	G	F	yes	yes	yes	no	yes	yes	Decorative
High cost																	
Chlorinated polyether	G	E	E	E	E	E	E	G	E	F	no	no	no	yes	no	yes	Chemical equipment
Fluorocarbon	E	E	E	E	E	E	E	E	G	P	yes	yes	no	yes	no	yes	Chemical equipment, nonstick surfaces

Silicone	G	F	G	G	G	E	E	E	E	G	yes	yes	yes	no	yes	yes	Heat-resistant finishes

Source: Ref 7

(a) E, excellent; G, good; F, fair; P, poor.

Enamels consist of milled pigments and other additives dispersed in resins and solvents and are converted from liquids to hard films by oxidation or polymerization. Lacquers are thermoplastic resins dissolved in organic solvents that dry rapidly by evaporation. In aqueous coatings, water is the principal vehicle or reducer. The advantages of water-base paints are nominal cost, nonflammability, true odorlessness, and nontoxicity. The disadvantages are difficulties in wettability, flow, and drying. Rubber-base coatings are noted for their mechanical properties and corrosion resistance rather than their decorative effects. Bituminous paints are black materials in which coal tar is dissolved in a solvent that evaporates. The major uses of bituminous paints are those that require extremely low permeability and high resistance to water. Unusual protection against chemical solutions, or special decorative effects, can be obtained by the use of asphaltic coatings or those produced by japanning, both of which are also considered bituminous coatings.

Fluorocarbon coatings produce an unusual combination of properties. They are tough, stain resistant, and nonsticking, and have a very low coefficient of friction. Fluorocarbon coatings resist all common industrial acids and temperatures to 300 °C (570 °F). Domestic cookware and chemical-processing equipment are two major applications of fluorocarbon coatings on iron castings. Fluorocarbon coatings are sprayed as emulsions of proprietary products onto a primed surface and then fused at temperatures of 385 to 425 °C (725 to 800 °F).

Methods of Application. Organic coatings are applied by spraying, dipping, flow coating, fluidized bed coating, electrostatic deposition, and electrophoresis (electrocoating).

Spraying is adaptable to both low-volume and high-volume workloads. It is done by propelling the coating material toward the workpiece by compressed air, hot spraying, hydraulic-airless, and airless-electrostatic methods. Overspraying is most troublesome with compressed air methods and least troublesome with electrostatic methods.

Dipping has been used for centuries; modern refinements include flow coating and electrophoresis. Not all shapes can be painted by dipping. Pockets can exclude paint from surfaces. The shape of the casting should allow easy draining after dipping. The coating should be selected to inhibit sagging or the formation of droplets on edges. The dipping process is easily automated and can be very efficient in use of materials. A thorough review of organic coatings and their applications, advantages, and limitations is available in Ref 25 and in the articles "Painting" and "Elastomeric Coatings and Linings" in this Volume.

References cited in this section

7. C.F. Walton and T.J. Ajar, Ed., *Iron Castings Handbook,* Iron Casting Society, 1981, p 755-799
25. K.B. Tator, Organic Coatings and Linings, *Corrosion,* 9th ed., Vol 13, *Metals Handbook,* ASM International, 1987, p 399-418

Fused Dry-Resin Coatings

Dry-resin polymers can be applied (by fusion bonding) to iron castings for many of the same applications for which liquid organic coatings are used. Generally, the fused coatings are thick and can be applied very rapidly--often in minutes; in contrast, several hours are required for the drying and curing of a liquid organic coating.

The fusion bonding of polymers on iron castings can be readily accomplished by the application of dry solvent-free powder by fluidized bed coating or electrostatic deposition. The advantages of the process include the use of resins that are insoluble in ordinary solvents, the elimination of carrier solvents, and the ability to combine various plastics in the coating for maximum effectiveness. Sandblasted castings are excellent bases for this process. The plastic films can be easily machined, which contributes to flexibility in manufacturing. Two disadvantages are that thin films are not easily applied and that finding a suitable holding point on a part to be coated in a fluidized bed may be difficult. The six basic types of plastic fusion-bonded finishes, as well as a comparison of their characteristics, are given in Table 13.

Table 13 Relative effectiveness of fusion-bonding resin coatings

	Effectiveness[(a)]					
	Vinyl	Cellulose	Epoxy	Nylon	Chlorinated	Polyethylene

					polyether	
Exterior durablity	E	VG	F	F	F	F
Salt spray resistance	E	G	VG	VG	F	F
Water resistance	E	VG	G	G	E	F
Acid resistance	VG	G	VG	F	E	E
Alkali resistance	VG	G	VG	G	E	E
Solvent resistance	G	F	F	E	VG	G
Abrasion resistance	E	VG	E	E	VG	P
Impact resistance	E	G	(b)	VG	G	P
Heat resistance	VG	G	VG	VG	VG	P
Flexibility	E	G	(b)	G	F	E
Electrical characteristics	VG	VG	E	G	VG	VG
Color range	E	E	P	F	P	F
Gloss	E	E	VG	VG	G	G

Source: Ref 7

(a) E, excellent; VG, very good; G, good; F, fair; P, poor.

(b) Ranges from excellent to poor depending on composition.

In a fluidized bed, castings heated to 175 to 310 °C (350 to 590 °F) are placed in a chamber containing resin powder suspended by upward-moving air. The dry resin floats around the casting, adhering to all the surfaces regardless of the complexity of the shape. Heating fuses the coating into a continuous film. This method produces a uniform coating that covers sharp corners, edges, and projections and that can be applied in a wide range of thicknesses (up to 1.5 mm, or 0.06 in.) in a single application.

In electrostatic deposition, the powdered resin is conveyed to a gun, in which it is given an electrostatic charge. The casting has the opposite charge. The charged powder is attracted to the surface, where it is deposited evenly. The electrostatic process is especially useful for applying thinner coatings because the residual charge on the workpiece is discharged by the powder, or leaks off, thus limiting the amount of powder that can be deposited. Preheating of the casting permits thicker coatings because the initial powder layer fuses as it is applied. Curing is done by reheating the

casting to fuse the resin coating. Primers may be needed for some types of polymers (such as butyrates and vinyls) in order to achieve adequate bonding.

Reference cited in this section

7. C.F. Walton and T.J. Ajar, Ed., *Iron Castings Handbook*, Iron Casting Society, 1981, p 755-799

Surface Engineering of Carbon and Alloy Steels

J.R. Davis, Davis & Associates

Introduction

CARBON AND ALLOY STEELS, the most widely used metallic material, account for more than 80 million tons, or approximately 98% of the annual steel production in the United States (Table 1). Steels are a popular material of choice because they can be manufactured relatively inexpensively in large quantities to very precise specifications. They also provide a wide range of mechanical properties, from moderate yield strength levels (200 to 300 MPa, or 30 to 40 ksi) with excellent ductility to yield strengths exceeding 1400 MPa (200 ksi) with fracture toughness levels as high as 110 MPa $\sqrt{m}$ (100 ksi $\sqrt{in}$).

Table 1 Net shipment of U.S. steel mill products--all grades

Steel products	1992		1991	
	Tons [(a)]	%	Tons [(a)]	%
Ingots and steel for castings	215	0.3	244	0.3
Blooms, slabs, billets	2,255	2.7	2,305	2.9
Wire rods	4,511	5.5	4,366	5.5
Structural shapes (≥ 75 mm, or 3 in.)	5,081	6.2	5,245	6.7
Steel piling	454	0.6	430	0.5
Plates (cut lengths)	4,362	5.3	4,275	5.4
Plates (in coils)	2,740	3.3	2,667	3.4
Rails				
Standard (over 27 kg, or 60 lb)	435	0.5	382	0.5
All other	5	0.0	16	0.0

Railroad accessories	122	0.1	89	0.1
Bars				
Hot rolled	5,806	7.1	5,431	6.9
Bar-size light shapes	1,119	1.4	1,157	1.5
Reinforcing	4,781	5.8	4,859	6.2
Cold finished	1,458	1.8	1,341	1.7
Tool steel	64	0.1	51	0.1
Pipe and tubing				
Standard pipe	1,062	1.3	970	1.2
Oil country goods	979	1.2	1,077	1.4
Line	1,110	1.3	1,439	1.8
Mechanical	790	1.0	744	0.9
Pressure	48	0.1	49	0.1
Structural	142	0.2	151	0.2
Pipe for piling	35	0.0	24	0.0
Stainless	32	0.0	34	0.0
Wire-drawn	900	1.1	865	1.1
Black plate	230	0.3	249	0.3
Tin plate	2,715	3.3	2,754	3.5
Tin-free steel	904	1.1	964	1.2

Tin-coated sheets	78	0.1	74	0.1
Sheets				
Hot rolled	13,361	1.62	13,161	16.7
Cold rolled	12,692	15.4	11,532	14.6
Sheets and strip				
Galvanized-hot dipped	8,199	10.0	6,910	8.8
Electrolytic	2,390	2.9	2,099	2.7
All other metallic coated	1,348	1.6	1,146	1.5
Electrical	436	0.5	458	0.6
Strip				
Hot rolled	550	0.7	533	0.7
Cold rolled	832	1.0	755	1.0
Total Steel Mill Products	**82,241**	**100.0**	**78,846**	**100.0**
Carbon	76,625	93.2	73,480	93.2
Stainless	1,514	1.8	1,449	1.8
Alloy (other than stainless)	4,101	5.0	3,917	5.0

Source: American Iron and Steel Institute

(a) Thousands of net tons.

Following a brief review of the classification of steels, this article will review the following:

- Cleaning methods
- Finishing methods
- Conversion coatings
- Hot dip coating processes

- Electrogalvanizing
- Electroplating
- Metal cladding
- Organic coatings
- Zinc-rich coatings
- Porcelain enameling
- Thermal spraying
- Hardfacing
- Vapor deposited coatings
- Surface modification
- Surface hardening via heat treatment

Emphasis will be placed on the most commonly used methods for surface engineering of steels. No attempt is made at providing detailed information on any given process as this can be found in the cited articles found throughout this Volume. In terms of the coating, surface modification, and surface hardening processes described, the resulting property improvements (corrosion and/or wear resistance) will be stressed rather than the details of the process itself (equipment, plating bath compositions, process controls, etc.). Information on the surface engineering of stainless steels, tool steels, maraging steels, electrical steels, and ferrous powder metallurgy alloys can be found in the articles "Surface Engineering of Stainless Steels" and "Surface Engineering of Specialty Steels" which immediately follow in this Section of the Handbook.

Classification of Steels

Steels can be classified by a variety of different systems depending on:

- *The composition,* such as carbon, low-alloy, or stainless steels
- *The manufacturing methods,* such as open hearth, basic oxygen process, or electric furnace methods
- *The finishing method,* such as hot rolling or cold rolling
- *The product form,* such as bar, plate, sheet, strip, tubing, or structural shape
- *The deoxidation practice,* such as killed, semikilled, capped, or rimmed steel
- *The microstructure,* such as ferritic, pearlitic, and martensitic
- *The required strength level,* as specified in ASTM standards
- *The heat treatment,* such as annealing, quenching and tempering, and thermomechanical processing
- *Quality descriptors,* such as forging quality and commercial quality

Of the aforementioned classification systems, chemical composition is the most widely used and will be discussed below. More detailed information on the classification and designation of carbon and alloy steels can be found in Ref 1.

Carbon Steels

The American Iron and Steel Institute defines carbon steel as follows:

> Steel is considered to be carbon steel when no minimum content is specified or required for chromium, cobalt, columbium [niobium], molybdenum, nickel, titanium, tungsten, vanadium or zirconium, or any other element to be added to obtain a desired alloying effect; when the specified minimum for copper does not exceed 0.40 per cent; or when the maximum content specified for any of the following elements does not exceed the percentages noted; manganese 1.65, silicon 0.60, copper 0.60.

Carbon steel can be classified, according to various deoxidation practices, as rimmed, capped, semikilled, or killed steel. Deoxidation practice and the steelmaking process will have an effect on the characteristics and properties of the steel. However, variations in carbon have the greatest effect on mechanical properties, with increasing carbon content leading to

increased hardness and strength. As such, carbon steels are generally categorized according to their carbon content. Generally speaking, carbon steels contain up to 2% total alloying elements and can be subdivided into low-carbon steels, medium-carbon steels, and high-carbon steels.

As a group, carbon steels are by far the most frequently used steel. Table 1 indicates that more than 93% of the steel produced and shipped in the United States is carbon steel. Chemical compositions for selected carbon steels are provided in Table 2.

Table 2 Carbon steel compositions

Applicable only to structural shapes, plates, strip, sheets, and welded tubing

UNS number	SAE-AISI number	Cast or heat chemical ranges and limits, %[a]			
		C	Mn	P max	S max
G10060	1006	0.08 max	0.45 max	0.040	0.050
G10080	1008	0.10 max	0.50 max	0.040	0.050
G10090	1009	0.15 max	0.60 max	0.040	0.050
G10100	1010	0.08-0.13	0.30-0.60	0.040	0.050
G10120	1012	0.10-0.15	0.30-0.60	0.040	0.050
G10150	1015	0.12-0.18	0.30-0.60	0.040	0.050
G10160	1016	0.12-0.18	0.60-0.90	0.040	0.050
G10170	1017	0.14-0.20	0.30-0.60	0.040	0.050
G10180	1018	0.14-0.20	0.60-0.90	0.040	0.050
G10190	1019	0.14-0.20	0.70-1.00	0.040	0.050
G10200	1020	0.17-0.23	0.30-0.60	0.040	0.050
G10210	1021	0.17-0.23	0.60-0.90	0.040	0.050
G10220	1022	0.17-0.23	0.70-1.00	0.040	0.050
G10230	1023	0.19-0.25	0.30-0.60	0.040	0.050
G10250	1025	0.22-0.28	0.30-0.60	0.040	0.050

G10260	1026	0.22-0.28	0.60-0.90	0.040	0.050
G10300	1030	0.27-0.34	0.60-0.90	0.040	0.050
G10330	1033	0.29-0.36	0.70-1.00	0.040	0.050
G10350	1035	0.31-0.38	0.60-0.90	0.040	0.050
G10370	1037	0.31-0.38	0.70-1.00	0.040	0.050
G10380	1038	0.34-0.42	0.60-0.90	0.040	0.050
G10390	1039	0.36-0.44	0.70-1.00	0.040	0.050
G10400	1040	0.36-0.44	0.60-0.90	0.040	0.050
G10420	1042	0.39-0.47	0.60-0.90 z	0.040	0.050
G10430	0143	0.39-0.47	0.70-1.00	0.040	0.050
G10450	1045	0.42-0.50	0.60-0.90	0.040	0.050
G10460	1046	0.42-0.50	0.70-1.00	0.040	0.050
G10490	1049	0.45-0.53	0.60-0.90	0.040	0.050
G10500	1050	0.47-0.55	0.60-0.90	0.040	0.050
G10550	1055	0.52-0.60	0.60-0.90	0.040	0.050
G10600	1060	0.55-0.66	0.60-0.90	0.040	0.050
G10640	1064	0.59-0.70	0.50-0.80	0.040	0.050
G10650	1065	0.59-0.70	0.60-0.90	0.040	0.050
G10700	1070	0.65-0.76	0.60-0.90	0.040	0.050
G10740	1074	0.69-0.80	0.50-0.80	0.040	0.050
G10750	1075	0.69-0.80	0.40-0.70	0.040	0.050

G10780	1078	0.72-0.86	0.30-0.60	0.040	0.050
G10800	1080	0.74-0.88	0.60-0.90	0.040	0.050
G10840	1084	0.80-0.94	0.60-0.90	0.040	0.050
G10850	1085	0.80-0.94	0.70-1.00	0.040	0.050
G10860	1086	0.80-0.94	0.30-0.50	0.040	0.050
G10900	1090	0.84-0.98	0.60-0.90	0.040	0.050
G10950	1095	0.90-1.04	0.30-0.50	0.040	0.050

(a) When silicon ranges or limits are required, the following ranges and limits are commonly used; up to SAE 1025 inclusive, 0.10% max, 0.10-0.25%, or 0.15-0.35%. Over SAE 1025, 0.10-0.25% or 0.15-0.35%

Low-carbon steels contain up to 0.30% C. The largest category of this class of steel is flat-rolled products (sheet or strip) usually in the cold-rolled and annealed condition. The carbon content for these high-formability steels is very low, less than 0.10% C, with up to 0.4% Mn. Typical uses are in automobile body panels, tin plate, and wire products. For rolled steel structural plates and sections, the carbon content may be increased to approximately 0.30%, with higher manganese up to 1.5%. These latter materials may be used for stampings, forgings, seamless tubes, and boiler plate.

Medium-carbon steels are similar to low-carbon steels except that the carbon ranges from 0.30 to 0.60% and the manganese from 0.60 to 1.65%. Increasing the carbon content to approximately 0.5% with an accompanying increase in manganese allows medium-carbon steels to be used in the quenched and tempered condition. The uses of medium carbon-manganese steels include shafts, couplings, crankshafts, axles, gears, and forgings. Steels in the 0.40 to 0.60% C range are also used for rails, railway wheels, and rail axles.

High-carbon steels contain from 0.60 to 1.00% C with manganese contents ranging from 0.30 to 0.90%. High-carbon steels are used for spring materials and high-strength wires.

High-Strength Low-Alloy Steels

High-strength low-alloy (HSLA) steels are designed to provide better mechanical properties and/or greater resistance to atmospheric corrosion than conventional carbon steels. They are not considered to be alloy steels in the normal sense because they are designed to meet specific mechanical properties rather than a chemical composition (HSLA steels have yield strengths greater than 275 MPa, or 40 ksi). The chemical composition of a specific HSLA steel may vary for different product thicknesses to meet mechanical property requirements. The HSLA steels have low carbon contents (0.05 to ~0.25% C) in order to produce adequate formability and weldability, and they have manganese contents up to 2.0%. Small quantities of chromium, nickel, molybdenum, copper, nitrogen, vanadium, niobium, titanium, and zirconium are used in various combinations. The types of HSLA steels commonly used include:

- *Weathering steels,* designed to exhibit superior atmospheric corrosion resistance
- *Control-rolled steels,* hot rolled according to a predetermined rolling schedule designed to develop a highly deformed austenite structure that will transform to a very fine equiaxed ferrite structure on cooling
- *Pearlite-reduced steels,* strengthened by very fine-grain ferrite and precipitation hardening but with low carbon content and therefore little or no pearlite in the microstructure

- *Microalloyed steels,* with very small additions (generally <0.10% each) of such elements as niobium, vanadium, and/or titanium for refinement of grain size and/or precipitation hardening
- *Acicular ferrite steel,* very low carbon steels with sufficient hardenability to transform on cooling to a very fine high-strength acicular ferrite (low-carbon bainite) structure rather than the usual polygonal ferrite structure
- *Dual-phase steels,* processed to a microstructure of ferrite containing small, uniformly distributed regions of high-carbon martensite, resulting in a product with low yield strength and a high rate of work hardening, thus providing a high-strength steel of superior formability

Table 3 lists chemical compositions for various HSLA steels.

Table 3 Compositional limits for HSLA steel grades described in ASTM specifications

ASTM specification	Type or grade	UNS designation	Heat compositional limits, %(a)									
			C	**Mn**	**P**	**S**	**Si**	**Cr**	**Ni**	**Cu**	**V**	**Other**
A 242	Type 1	K11510	0.15	1.00	0.45	0.05	. . .	. . .	. . .	0.20 min	. . .	. . .
A 572	Grade 42	. . .	0.21	1.35(b)	0.04	0.05	0.30(b)	. . .	. . .	0.20 min(c)	. . .	(d)
	Grade 50	. . .	0.23	1.35(b)	0.04	0.05	0.30(b)	. . .	. . .	0.20 min(c)	. . .	(d)
	Grade 60	. . .	0.26	1.35(b)	0.04	0.05	0.30	. . .	. . .	0.20 min(c)	. . .	(d)
	Grade 65	. . .	0.23(b)	1.65(b)	0.04	0.05	0.30	. . .	. . .	0.20 min(c)	. . .	(d)
A 588	Grade A	K11430	0.10-0.19	0.90-1.25	0.04	0.05	0.15-0.30	0.40-0.65	. . .	0.25-0.40	0.02-0.10	. . .
	Grade B	K12043	0.20	0.75-1.25	0.04	0.05	0.15-0.30	0.40-0.70	0.25-0.50	0.20-0.40	0.01-0.10	. . .
	Grade C	K11538	0.15	0.80-1.35	0.04	0.05	0.15-0.30	0.30-0.50	0.25-0.50	0.20-0.50	0.01-0.10	. . .
	Grade D	K11552	0.10-0.20	0.75-1.25	0.04	0.05	0.50-0.90	0.50-0.90	. . .	0.30	. . .	0.04 Nb, 0.05-0.15 Zr
	Grade K	. . .	0.17	0.5-1.20	0.04	0.05	0.25-0.50	0.40-0.70	0.40	0.30-0.50	. . .	0.10 Mo, 0.005-0.05 Nb

ASTM specification	Type or grade	UNS designation	Heat compositional limits, %[a]									
			C	Mn	P	S	Si	Cr	Ni	Cu	V	Other
A 606	. . .	. . .	0.22	1.25	. . .	0.05	. . .	. . .	. . .	. . .	. . .	. . .
A 607	Grade 45	. . .	0.22	1.35	0.04	0.05	. . .	. . .	. . .	0.20 min[c]	. . .	[d]
	Grade 50	. . .	0.23	1.35	0.04	0.05	. . .	. . .	. . .	0.20 min[c]	. . .	[d]
	Grade 55	. . .	0.25	1.35	0.04	0.05	. . .	. . .	. . .	0.20 min[c]	. . .	[d]
	Grade 60	. . .	0.26	1.50	0.04	0.05	. . .	. . .	. . .	0.20 min[c]	. . .	[d]
	Grade 65	. . .	0.26	1.50	0.04	0.05	. . .	. . .	. . .	0.20 min[c]	. . .	[d]
	Grade 70	. . .	0.26	1.65	0.04	0.05	. . .	. . .	. . .	0.20 min[c]	. . .	[d]
A 618	Grade Ia	. . .	0.15	1.00	0.15	0.05	. . .	. . .	. . .	0.20 min	. . .	. . .
	Grade Ib	. . .	0.20	1.35	0.04	0.05	. . .	. . .	. . .	0.20 min[e]	. . .	. . .
	Grade II	K12609	0.22	0.85-1.25	0.04	0.05	0.30	. . .	. . .	. . .	0.02 min	. . .
	Grade III	K12700	0.23	1.35	0.04	0.05	0.30	. . .	. . .	. . .	0.02 min	0.005 Nb min[f]
A 633	Grade A	K10802	0.18	1.00-1.35	0.04	0.05	0.15-0.30	. . .	. . .	. . .	. . .	0.05 Nb
	Grade C	K12000	0.20	1.15-1.50	0.04	0.05	0.15-0.50	. . .	. . .	. . .	. . .	0.01-0.05 Nb
	Grade D	K02003	0.20	0.70-1.60[b]	0.04	0.05	0.15-0.50	0.25	0.25	0.35	. . .	0.08 Mo
	Grade	K12202	0.22	1.15-	0.04	0.05	0.15-	. . .	. . .	. . .	0.04-	0.01-0.05 Nb[c],

ASTM specification	Type or grade	UNS designation	Heat compositional limits, %[(a)]									
			C	Mn	P	S	Si	Cr	Ni	Cu	V	Other
	E			1.50			0.50				0.11	0.01-0.03 N
A 656	Type 3	. . .	0.18	1.65	0.025	0.035	0.60	. . .	. . .	. . .	0.08	0.020 N, 0.005-0.15 Nb
	Type 7	. . .	0.18	1.65	0.025	0.035	0.60	. . .	. . .	. . .	0.005-0.15	0.020 N, 0.005-0.10 Nb
A 690	. . .	K12249	0.22	0.60-0.90	0.08-0.15	0.05	0.10	. . .	0.40-0.75	0.50 min	. . .	. . .
A 709	Grade 50, type 1	. . .	0.23	1.35	0.04	0.05	0.40	. . .	. . .	. . .	. . .	0.005-0.05 Nb
	Grade 50, type 2	. . .	0.23	1.35	0.04	0.05	0.40	. . .	. . .	. . .	0.01-0.15	. . .
	Grade 50, type 3	. . .	0.23	1.35	0.04	0.05	0.40	. . .	. . .	. . .	[(g)]	0.05 Nb max
	Grade 50, type 4	. . .	0.23	1.35	0.04	0.05	0.40	. . .	. . .	. . .	[(h)]	0.015 N max
A 715	. . .	. . .	0.15	1.65	0.025	0.035	. . .	. . .	. . .	V, Ti, Nb added as necessary		
A 808	. . .	. . .	0.12	1.65	0.04	0.05 max or 0.010 max	0.15-0.50	. . .	. . .	. . .	0.10	0.02-0.10 Nb, V + Nb = 0.15 max
A 812	65	. . .	0.23	1.40	0.035	0.04	0.15-0.50[(i)]	. . .	. . .	. . .	V + Nb = 0.02-0.15	0.05 Nb max
	80	. . .	0.23	1.50	0.035	0.04	0.15-0.50	0.35	. . .	. . .	V + Nb = 0.02-0.15	0.05 Nb max
A 841	. . .	. . .	0.20	[(j)]	0.030	0.030	0.15-	0.25	0.25	0.35	0.06	0.08 Mo, 0.03 Nb,

ASTM specification	Type or grade	UNS designation	Heat compositional limits, %[(a)]									
			C	Mn	P	S	Si	Cr	Ni	Cu	V	Other
							0.50					0.02 Al total
A 871	. . .	. . .	0.20	1.50	0.04	0.05	0.90	0.90	1.25	1.00	0.10	0.25 Mo, 0.15 Zr, 0.05 Nb, 0.05 Ti

(a) If a single value is shown, it is a maximum unless otherwise stated.

(b) Values may vary, or minimum value may exist, depending on product size and mill form.

(c) Optional or when specified.

(d) May be purchased as type 1 (0.005-0.05 Nb), type 2 (0.01-0.15 V), type 3 (0.05 Nb, max, plus 0.02-0.15 V) or type 4 (0.015 N, max, plus V $\geq$4N).

(e) If chromium or silicon are each 0.50% min, the copper minimum does not apply.

(f) May be substituted for all or part of V.

(g) Niobium plus vanadium, 0.02 to 0.15%.

(h) Nitrogen with vanadium content of 0.015% (max) with a minimum vanadium-to-nitrogen ratio of 4:1.

(i) When silicon-killed steel is specified.

(j) For plate under 40 mm (1.5 in.), manganese contents are 0.70 to 1.35% or up to 1.60% if carbon equivalents do not exceed 0.47%. For plate over 40 mm (1 to 5 in.), ASTM A 841 specifies manganese contents of 1.00 to 1.60%.

Alloy Steels

Alloy steels constitute a category of ferrous materials that exhibit mechanical properties superior to plain carbon steels as the result of additions of such alloying elements as nickel, chromium, and molybdenum. Total alloy content can range from 2.07% up to levels just below that of stainless steels, which contain a minimum of approximately 11% Cr. For many alloy steels, the primary function of the alloying elements is to increase hardenability in order to optimize mechanical properties and toughness after heat treatment. In some cases, however, alloy additions are used to reduce environmental degradation under certain specified service conditions. Alloy steels can be classified according to:

- *Chemical composition*, such as nickel steels, nickel-chromium steels, molybdenum steels, chromium-molybdenum steels, and so on, as described in SAE-AISI designations and shown in Table 4

- *Heat treatment,* such as quenched and tempered, normalized and tempered, annealed, and so on

Table 4 SAE-AISI system of designations for carbon and alloy steels

Numerals and digits	Type of steel and nominal alloy content, %
Carbon steels	
10*xx*	Plain carbon (Mn 1.00 max)
11*xx*	Resulfurized
12*xx*	Resulfurized and rephosphorized
15*xx*	Plain carbon (max Mn range: 1.00-1.65)
Manganese steels	
13*xx*	Mn 1.75
Nickel steels	
23*xx*	Ni 3.50
25*xx*	Ni 5.00
Nickel-chromium steels	
31*xx*	Ni 1.25; Cr 0.65 and 0.80
32*xx*	Ni 1.75; Cr 1.07
33*xx*	Ni 3.50; Cr 1.50 and 1.57
34*xx*	Ni 3.00; Cr 0.77
Molybdenum steels	
40*xx*	Mo 0.20 and 0.25
44*xx*	Mo 0.40 and 0.52

Chromium-molybdenum steels	
41*xx*	Cr 0.50, 0.80, and 0.95; Mo 0.12, 0.20, 0.25, and 0.30
Nickel-chromium-molybdenum steels	
43*xx*	Ni 1.82; Cr 0.50 and 0.80; Mo 0.25
43BV*xx*	Ni 1.82; Cr 0.50; Mo 0.12 and 0.25; V 0.03 min
47*xx*	Ni 1.05; Cr 0.45; Mo 0.20 and 0.35
81*xx*	Ni 0.30; Cr 0.40; Mo 0.12
86*xx*	Ni 0.55; Cr 0.50; Mo 0.20
87*xx*	Ni 0.55; Cr 0.50; Mo 0.25
88*xx*	Ni 0.55; Cr 0.50; Mo 0.35
93*xx*	Ni 3.25; Cr 1.20; Mo 0.12
94*xx*	Ni 0.45; Cr 0.40; Mo 0.12
97*xx*	Ni 0.55; Cr 0.20; Mo 0.20
98*xx*	Ni 1.00; Cr 0.80; Mo 0.25
Nickel-molybdenum steels	
46*xx*	Ni 0.85 and 1.82; Mo 0.20 and 0.25
48*xx*	Ni 3.50; Mo 0.25
Chromium steels	
50*xx*	Cr 0.27, 0.40, 0.50, and 0.65
51*xx*	Cr 0.80, 0.87, 0.92, 0.95, 1.00, and 1.05
Chromium (bearing) steels	

50*xxx*	Cr 0.50	C 1.00 min
51*xxx*	Cr 1.02	
52*xxx*	Cr 1.45	
Chromium-vanadium steels		
61*xx*	Cr 0.60, 0.80, and 0.95; V 0.10 and 0.15 min	
Tungsten-chromium steel		
72*xx*	W 1.75; Cr 0.75	
Silicon-manganese steels		
92*xx*	Si 1.40 and 2.00; Mn 0.65, 0.82, and 0.85; Cr 0 and 0.65	
High-strength low-alloy steels		
9*xx*	Various SAE grades	
Boron steels		
*xx*B*xx*	B denotes boron steel	
Leaded steels		
*xx*L*xx*	L denotes leaded steel	

Note: The *xx* in the last two digits of these designations indicates that the carbon content (in hundredths of a percent) is to be inserted.

Because of the wide variety of chemical compositions possible and the fact that some steels are used in more than one heat-treated condition, some overlap exists among the alloy steel classifications, which include (1) low-carbon quenched and tempered (QT) steels, (2) medium-carbon ultrahigh-strength steels, (3) bearing steels, and (4) heat-resistant chromium-molybdenum steels.

Low-carbon quenched and tempered steels combine high yield strength (from 350 to 1035 MPa, or 50 to 150 ksi) and high tensile strength with good notch toughness, ductility, corrosion resistance, or weldability. The various steels have different combinations of these characteristics based on their intended applications. The chemical compositions of typical QT low-carbon steels are given in Table 5. Many of the steels are covered by ASTM specifications. However, a few steels, such as HY-80 and HY-100, are covered by military specifications. The steels listed are used primarily as plate. Some of these steels, as well as other similar steels, are produced as forgings or castings.

Table 5 Chemical compositions for typical alloy steels

Steel	Composition, wt%[a]								
	C	Si	Mn	P	S	Ni	Cr	Mo	Other
Low-carbon quenched and tempered steels									
A 514/A 517 grade A	0.15-0.21	0.40-0.80	0.80-1.10	0.035	0.04	. . .	0.50-0.80	0.18-0.28	0.05-0.15 Zr[b], 0.0025 B
A 514/A 517 grade F	0.10-0.20	0.15-0.35	0.60-1.00	0.035	0.04	0.70-1.00	0.40-0.65	0.40-0.60	0.03-0.08 V, 0.15-0.50 Cu 0.0005-0.005 B
A 514/A 517 grade R	0.15-0.20	0.20-0.35	0.85-1.15	0.035	0.04	0.90-1.10	0.35-0.65	0.15-0.25	0.03-0.08 V
A 533 type A	0.25	0.15-0.40	1.15-1.50	0.035	0.04	. . .	. . .	0.45-0.60	. . .
A 533 type C	0.25	0.15-0.40	1.15-1.50	0.035	0.04	0.70-1.00	. . .	0.45-0.60	. . .
HY-80	0.12-0.18	0.15-0.35	0.10-0.40	0.025	0.025	2.00-3.25	1.00-1.80	0.20-0.60	0.25 Cu, 0.03 V, 0.02 Ti
HY-100	0.12-0.20	0.15-0.35	0.10-0.40	0.025	0.025	2.25-3.50	1.00-1.80	0.20-0.60	0.25 Cu, 0.03 V, 0.02 Ti
Medium-carbon ultrahigh-strength steels									
4130	0.28-0.33	0.20-0.35	0.40-0.60	. . .	. . .	. . .	0.80-1.10	0.15-0.25	. . .
4340	0.38-0.43	0.20-0.35	0.60-0.80	. . .	. . .	1.65-2.00	0.70-0.90	0.20-0.30	. . .
300M	0.40-0.46	1.45-1.80	0.65-0.90	. . .	. . .	1.65-2.00	0.70-0.95	0.30-0.45	0.05 V min
D-6a	0.42-0.48	0.15-0.30	0.60-0.90	. . .	. . .	0.40-0.70	0.90-1.20	0.90-1.10	0.05-0.10 V
Carburizing bearing steels									
4118	0.18-0.23	0.15-0.30	0.70-0.90	0.035	0.040	. . .	0.40-0.60	0.08-0.18	. . .

5120	0.17-0.22	0.15-0.30	0.70-0.90	0.035	0.040	. . .	0.70-0.90	. . .	. . .
3310	0.08-0.13	0.20-0.35	0.45-0.60	0.025	0.025	3.25-3.75	1.40-1.75	. . .	. . .
Through-hardened bearing steels									
52100	0.98-1.10	0.15-0.30	0.25-0.45	0.025	0.025	. . .	1.30-1.60	. . .	. . .
A 485 grade 1	0.90-1.05	0.45-0.75	0.95-1.25	0.025	0.025	0.25	0.90-1.20	0.10	0.35 Cu
A 485 grade 3	0.95-1.10	0.15-0.35	0.65-0.90	0.025	0.025	0.25	1.10-1.50	0.20-0.30	0.35 Cu
Chromium-molybdenum heat-resistant steels									
$2\frac{1}{4}$ Cr-1Mo	0.15	0.50	0.30-0.60	0.040	0.040	. . .	2.00-2.50	0.87-1.13	. . .
5Cr-$\frac{1}{2}$ Mo	0.15	0.50	0.30-0.60	0.030	0.030	. . .	4.00-6.00	0.45-0.65	. . .
9Cr-1Mo	0.15	0.50-1.00	0.30-0.60	0.030	0.030	. . .	8.00-10.00	0.90-1.10	. . .

(a) Single values represent the maximum allowable.

(b) Zirconium may be replaced by cerium. When cerium is added, the cerium/sulfur ratio should be approximately 1.5/1, based on heat analysis.

Medium-carbon ultrahigh-strength steels are structural steels with yield strengths that can exceed 1380 MPa (200 ksi). Table 5 lists typical compositions. Many of these steels are covered by SAE-AISI designations or are proprietary compositions. Product forms include billet, bar, rod, forgings, sheet, tubing, and welding wire.

Bearing steels used for ball and roller bearing applications are comprised of low-carbon (0.10 to 0.20% C) case-hardened steels and high-carbon (~1.0% C) through-hardened steels (Table 5). Many of these steels are covered by SAE-AISI designations.

Chromium-molybdenum heat-resistant steels contain 0.5 to 9% Cr and 0.5 to 1.0% Mo. The carbon content is usually below 0.20%. Table 5 lists typical compositions. The chromium provides improved oxidation and corrosion resistance, and the molybdenum increases strength at elevated temperatures. They are generally supplied in the normalized and tempered, quenched and tempered, or annealed condition. Chromium-molybdenum steels are widely used in the oil and gas industries and in fossil fuel and nuclear power plants. Product forms include forgings, tubing, pipe, castings, and plate.

Reference cited in this section

1. J.R. Davis, Classification and Designation of Carbon and Low-Alloy Steels, *Properties and Selection: Irons, Steels, and High-Performance Alloys,* Vol 1, *ASM Handbook* (formerly 10th ed., *Metals Handbook*), ASM International, 1990, p 140-194

Cleaning of Steels

Cleaning is the process of removing objectionable matter from the surfaces of manufactured products. Drawing and stamping lubricants, cutting fluids, heat treatment scale and oxides, and fingerprints are typical of soils that must be removed.

Important reasons for adequate cleaning of components and products are as follows:

- As an intermediate step to facilitate manufacturing operations, like inspection and assembly
- To prepare surfaces for subsequent operations such as coating
- As a final finish, to improve performance, appearance, and salability

The cleaning and surface preparation of manufactured components and products are accomplished by many different processes. Some of the more common processes include a variety of chemical cleaning methods such as the application of solvents, aqueous cleaners, and acids by soaking or spraying; steam and flame cleaning methods; vapor degreasing; and ultrasonic cleaning. In addition, some of the finishing processes discussed in the following section of this article, for example, dry or wet blasting, are also used for cleaning and surface preparation. Additional information on each of the cleaning procedures described below can be found in the various articles contained in the Section on "Surface Cleaning" in this Volume.

In selecting a cleaning process for steels, many factors must be considered, including: (a) identification and characterization of the soil to be removed; (b) identification of the substrate to be cleaned and the importance of the condition of the surface or structure to the ultimate use of the part; (c) degree of cleanness required, which depends on subsequent operations such as phosphating, plating and painting; (d) capabilities of the available facilities; (e) impact of the process on the environment; and (f) overall cost of the process.

Types of soil may be broadly classified into six groups: (a) pigmented drawing compounds, (b) unpigmented oil and grease, (c) chips and cutting fluids, (d) polishing and buffing compounds, (e) rust and scale, and (f) miscellaneous surface contaminants, such as lapping compounds and residue from magnetic particle inspection.

Dried or oxidized greases, oils, and drawing compounds are very difficult to remove, and thus every effort should be made to clean the parts as soon after processing as possible.

Removal of Pigmented Drawing Compounds. All pigmented drawing lubricants are difficult to remove from metal parts. Consequently, many plants review all aspects of press forming operations to avoid the use of pigmented compounds. Table 6 indicates cleaning processes typically selected for removing pigmented compounds from drawn and stamped parts.

Table 6 Selection guide for cleaning steel surfaces

Processes are listed in order of decreasing preference.

Type of production	In-process cleaning	Preparation for painting	Preparation for phosphating	Preparation for plating
Removal of pigmented drawing compounds[(a)]				
Occasional or	Hot emulsion hand slush,	Boiling alkaline,	Hot emulsion hand slush,	Hot alkaline soak, hot rinse (hand

intermittent	spray emulsion in single stage, vapor slush degrease[b]	blow off, hand wipe Vapor slush degrease, hand wipe Acid clean[c]	spray emulsion in single stage, hot rinse, hand wipe	wipe, if possible), electrolytic alkaline, cold water rinse
Continuous high production	Conveyorized spray emulsion washer	Alkaline soak, hot rinse, alkaline spray, hot rinse	Alkaline or acid(d) soak, hot rinse, alkaline or acid(d) spray, hot rinse	Hot emulsion or alkaline soak, hot rinse, electrolytic alkaline, hot rinse
Removal of unpigmented oils and greases				
Occasional or intermittent	Solvent wipe Emulsion dip or spray Vapor degrease Cold solvent dip Alkaline dip, rinse, dry (or dip in rust preventive)	Solvent wipe Vapor degrease or phosphoric acid clean[d]	Solvent wipe Emulsion dip or spray, rinse Vapor degrease	Solvent wipe Emulsion soak, barrel rinse, electrolytic alkaline rinse, hydrochloric acid dip, rinse
Continuous high production	Automatic vapor degrease Emulsion, tumble, spray, rinse, dry	Automatic vapor degrease	Emulsion power spray, rinse Vapor degrease Acid clean[c]	Automatic vapor degrease, electrolytic alkaline rinse, hydrochloric acid dip, rinse[e]
Removal of chips and cutting fluids				
Occasional or intermittent	Solvent wipe Alkaline dip and emulsion surfactant Stoddard solvent or trichlorethylene Steam	Solvent wipe Alkaline dip and emulsion surfactant Solvent or vapor	Solvent wipe Alkaline dip and emulsion surfactant[f] Solvent or vapor	Solvent wipe Alkaline dip, rinse, electrolytic alkaline[g], rinse, acid dip, rinse[h]
Continuous high production	Alkaline (dip or spray) and emulsion surfactant	Alkaline (dip or spray) and emulsion surfactant	Alkaline (dip or spray) and emulsion surfactant	Alkaline soak, rinse, electrolytic alkaline[g], rinse, acid dip and rinse[h]
Removal of polishing and buffing compounds				
Occasional or intermittent	Seldom required	Solvent wipe Surfactant alkaline (agitated soak), rinse Emulsion soak, rinse	Solvent wipe Surfactant alkaline (agitated soak), rinse Emulsion soak, rinse	Solvent wipe Surfactant alkaline (agitated soak), rinse electroclean[i]
Continuous high production	Seldom required	Surfactant alkaline spray, spray rinse Agitated soak or spray, rinse[j]	Surfactant alkaline spray, spray rinse Emulsion spray, rinse	Surfactant alkaline soak and spray, alkaline soak, spray and rinse, electrolytic alkaline[i], rinse, mild acid pickle, rinse

(a) For complete removal of pigment, parts should be cleaned immediately after the forming operation, and all rinses should be by spraying where practical.

(b) Used only when pigment residue can be tolerated in subsequent operations.

(c) Phosphoric acid cleaner-coaters are often sprayed on the parts to clean the surface and leave a thin phosphate coating.

(d) Phosphoric acid for cleaning and iron phosphating. Proprietary products for high- and low-temperature applications are available.

(e) Some plating processes may require additional cleaning dips.

(f) Neutral emulsion or solvent should be used before manganese phosphating.

(g) Reverse-current cleaning may be necessary to remove chips from parts having deep recesses.

(h) For cyanide plating, acid dip and water rinse are followed by alkaline and water rinses.

(i) Other preferences: stable or diphase emulsion spray or soak, rinse, alkaline spray or soak, rinse, electroclean; or solvent presoak, alkaline soak or spray, electroclean.

(j) Third preference: emulsion spray rinse

Removal of Unpigmented Oil and Grease. Common shop oils and greases, such as unpigmented drawing lubricants, rust-preventive oils, and quenching and lubricating oils, can be effectively removed by several different cleaners. Table 6 lists cleaning methods frequently used for removing oils and greases.

Removal of Chips and Cutting Fluids from Steel Parts. Cutting and grinding fluids used for machining may be classified into three groups, as follows:

- Plain or sulfurized mineral and fatty oils (or combinations of the two), chlorinated mineral oils, and sulfurized chlorinated mineral oils
- Conventional or heavy-duty soluble oils with sulfur or other compounds added and soluble grinding oils with wetting agents
- Chemical cutting fluids, which are water-soluble and generally act as cleaners. They contain soaps, amines, sodium salts of sulfonated fatty alcohols, alkyl aromatic sodium salts of sulfonates, or other types of the soluble addition agents

Usually, all three types of fluids are easily removed, and the chips fall away during cleaning, unless the chips or the part become magnetic. Plain boiling water is often suitable for removing these soils, and in some plants, mild detergents are added to the water to increase its effectiveness. Steam is widely used for in-process cleaning, especially for large components. Table 6 indicates cleaning processes typically used for removing cutting fluids to meet specific production requirements.

Removal of Polishing and Buffing Compounds. Table 6 lists preferred and alternate methods for removing polishing and buffing compounds from sheet metal parts. However, some modification may be required for complete removal of all classes of these soils.

Removal of Rust and Scale. The seven basic methods used for removing rust and scale from ferrous mill products, forgings, castings and fabricated steel parts are:

- Abrasive blasting (dry or wet)
- Tumbling (dry or wet)
- Brushing
- Acid pickling
- Salt bath descaling
- Alkaline descaling
- Acid cleaning

The most important considerations in selecting one of the above methods are:

- Thickness of rust or scale
- Composition of metal
- Condition of metal (product form or heat treatment)
- Allowable metal loss
- Surface finish tolerances
- Shape and size of workpieces
- Production requirements
- Available equipment
- Cost
- Freedom from hydrogen embrittlement

Combinations of two or more of the available processes are frequently used to advantage.

Cleaning Prior to Coating. Chemical cleaning is the most widely used method of providing a suitable surface for subsequent finishing by phosphating, electroplating, organic coating, or other coating processes. Chemical cleaning usually depends upon the use of solvents or a chemical action between the cleaning material and the contaminant. Table 7 compares the most common of the basic chemical cleaning methods. The types of chemical cleaners generally used for removing contaminants from metal surfaces fall into the broad categories of solvent cleaners, solvent emulsion cleaners, alkaline cleaners, and acid cleaners.

Table 7 Comparison of chemical cleaning methods

Factors	Emulsifiable solvent cleaning	Alkali cleaning, immersion or spray	Alkali electrocleaning	Acid pickling	Molten-salt descaling
Equipment	Same as for alkali cleaning without current	Still tanks or conveyorized spray washers of various sizes and capacities	Open steel tanks with dc current source, busbars, and control equipment	Appropriate corrosion-resistant tankage	Low-carbon steel tanks with high-temperature heat source
Cleaning medium	Mineral solvents mixed with suitable emulsifiers; used in water solution	Appropriate proprietary cleaners in water solution properly inhibited for sensitive metals	Same as for alkali cleaning without current	Various acids	Mixture of fused salts
Operating temperature	Depends on flashpoint of solvent. Usually room temperature to 60 °C (140 °F)	Room temperature to 100 °C (212 °F)	50-95 °C (120-200 °F)	Room temperature to 80 °C (180 °F)	205-510 °C (400-950 °F)

Health hazards	Safe when body contact is avoided. Venting may be required.	Safe when body contact is avoided. Venting may be required.	Safe when body contact is avoided. Venting may be required.	Safe with protective clothing, gloves, face shields, goggles, etc. Venting may be required.	Safe with protective clothing, gloves, face shields, goggles, etc.
Fire hazard	Temperature must not exceed flashpoint of solvent.	None	None	None	Slight
Type soil removed	Both organic and inorganic matter	Both organic and inorganic matter	Normally used for final cleaning prior to plating to remove slight contamination and to activate surface	Oxides, scale, rust, etc.	Scale, oxides, etc.
Effect on base metal	None	None when properly inhibited, but caustic alkali will attack aluminum and zinc.	None when properly inhibited	Very slight surface attack when properly controlled	Sometimes slight etch
Time required	1 to 15 min	1 to 30 min	$\frac{1}{2}$ to 3 min	1 to 30 min	Varies from seconds to minutes, depending on the application

Source: Ref 2

Reference cited in this section

2. Chemical Cleaning, in Vol 3, *Materials, Finishing and Coating, Tool and Manufacturing Engineers Handbook,* C. Wick and R.F. Veilleux, Ed., Society of Manufacturing Engineers, 1985, p 18-3

Finishing of Steels

Of the many different processes used for finishing, some simply clean contaminants from surfaces. Others remove or form the surface material to produce the desired results. The finishing processes can be broadly classified into mechanical, thermal, and electrochemical methods, but some combine several methods. Each of these finishing categories will be briefly described below. The reader should also refer to the article "Classification and Selection of Finishing Processes" for additional information. Table 8 compares various finishing methods used for burr removal.

Table 8 Advantages and limitations of various finishing processes

Process	Advantages and typical applications	Possible limitations
Abrasive flow	Removes hard-to-reach burrs. Polishes surfaces	Blind features not deburred
Abrasive blasting	Good for hard metals	Produces matte finish. Dust control required. Burr must be accessible

Barrel tumbling	Low cost. Suitable for all materials	Edges must be exposed. Slow and not effective for interior surfaces and edges
Brushing and buffing	All accessible burrs and edges. Polishes surfaces	
Centrifugal barrel	Fast process. Suitable for all materials. Residual compressive stresses	
Electrochemical	Removes hard-to-reach burrs	Possible stray etching. Limited to conductive metals
Electropolishing	Good for thin burrs. Polishes surfaces	Possible pitting and streaking
Hand deburring	For hard-to-reach areas and small volume requirements.	Usually expensive and inconsistent. Burrs must be accessible
Spindle finishing	Fast process. For uniform shapes	Fixturing needed
Thermal energy	For thin burrs. Deburrs blind features	Covers part with oxide film. Burr area must be free of oil and water
Vibratory	Versatile, economical process. Many deburring and finishing applications	Not usually suitable for removing internal burrs in intersecting holes

Source: Ref 3

Mechanical Finishing

The term "mechanical finishing" encompasses the technology of edge and surface conditioning of metal and nonmetal products for both cosmetic and functional purposes. Generation of smooth and specular surfaces to improve appearance of components is an essential part of the manufacturing cycle of most manufactured products, but functional finishing is still more important. Most mechanisms will run longer and more efficiently if component surfaces and edges are smooth. If an appropriate scratch pattern is generated, edges and surfaces may have much improved retention of lubricants, resulting in still smoother operation. Removal of stress raisers at sharp corners and generation of controlled radii on edges can substantially improve thermal and mechanical fatigue strength of highly stressed components. Removal of tensile stresses by improved surface integrity will reduce or eliminate their contribution to service failures. Moreover, generation of high compressive stresses, which can be achieved by several mechanical finishing processes, can significantly increase resistance to fatigue stresses and thus increase the service life of highly stressed parts. Improved edge and surface condition in passages through which gases or fluids flow reduces "drag" and thus increases flow rates.

Mechanical finishing is an essential part of the manufacturing cycle for most products. A high standard of mechanical finish will normally result in a better product that is also better looking. Proper attention to the technology of mechanical finishing will result in improved productivity as well as an improved product.

Mechanical finishing processes for processing steels may be classified as follows:

- Manual filing, scraping, and deburring
- Polishing, buffing, and brushing
- Abrasive and nonabrasive blasting
- Mass finishing
- Shot peening

- Honing and lapping
- Abrasive flow machining

Polishing, Buffing, and Brushing. Polishing is the mechanical finishing of a product using abrasives which are firmly adhered to a flexible backing, such as with an abrasive belt or with abrasives bonded to a flexible wheel or a flap wheel (while grinding is the use of abrasives firmly bonded to a rigid backing, as is the case with a grinding wheel). Polishing operations usually follow grinding and precede buffing.

Buffing refers to the finishing of a product by means of abrasive loosely adhering to a flexible backing, typically liquid or bar compounds applied to cloth wheels.

Brushing is the use of filament wheels for edge or surface conditioning of a product. Filaments are normally nonabrasive fibers or metal wires, but can be abrasive-laden filaments. Brushing may be done either wet or dry, and may employ compounds loosely applied.

Polishing processes are primarily abrasive processes, whereas in buffing and brushing a substantial part of the action may be plastic deformation of surfaces and edges.

Traditionally, polishing and buffing have been associated with decorative surface finishing operations and surface finishing prior to plating or painting. Modern automated polishing and buffing are more frequently used for improving functional edge and surface condition and are often used to improve product shape and tolerances (replacing some machining operations). Brushing is most often used for cleaning (removing scale, oxide films, rust, and old paint), although it also finds many applications in deburring and in edge and surface conditioning. More detailed information on polishing, buffing, and brushing can be found in the article "Finishing Methods Using Multipoint or Random Cutting Edges" in this Volume.

Blasting processes, both abrasive and nonabrasive, are based on the principle of propelling a series of particles (normally steel shot or grit for blasting steels) against a surface for the purpose of modifying the condition of that surface. In the vast majority of cases, the particles are propelled in a matrix of air or water to the work surface. The basic means of propelling the blasting material is with either air pressure or a centrifugal wheel. Equipment for blast cleaning and finishing is described in the article "Mechanical Cleaning Systems" in this Volume.

Blast finishing processes are used for removal of contaminants, effecting changes in surface condition, deburring, and peening.

Removal of Contaminants. Major applications in this group are removal of sand from castings and removal of scale from forgings. Blasting is also the standard means of removing all scale from steel products and of cleaning paint, rust, oil and other undesirable coatings from part surfaces.

Changes in Surface Condition. Blasting can be used to improve the mechanical bonding of most coatings--paints, galvanized coatings, elastomeric linings, and enamel coatings.

Deburring. Blasting may be used to break off small burrs on some products; if the material is ductile, blasting may blunt burrs and sharp edges. The blasting process is not suitable for generating radii on edges and corners.

Mass finishing normally involves loading of components to be finished into a container together with some abrasive medium, water, and compound. Action is applied to the container to cause the medium to rub against the surfaces, edges, and corners of the components, or to cause the components to rub against each other, or both. This action may deburr, generate edge and corner radii, clean the parts by removing rust and scale, and modify the surface stress. The basic mass finishing processes include:

- Barrel finishing
- Vibratory finishing
- Centrifugal disk finishing
- Centrifugal barrel finishing

- Spindle finishing

Each of these processes is described in the article "Mass Finishing Methods" in this Volume. Table 9 compares the advantages and limitations of mass finishing processes.

Table 9 Advantage and limitations of major mass finishing processes

Mass finishing process	Advantages	Limitations
Rotary barrel	Low initial, operating, and maintenance costs. Batch automation capability	Slow process. High operator skill needed. Large floor space required. No in-process inspection. Wet working area. Little-to-no work in part recesses
Vibratory tub	Faster than barrel. Can handle small to very large and very long parts. Open for in-process inspection. Full automation capability. Batch or continuous operation	Noisy. Slower than high-energy processes (centrifugal barrel and disk). External material handling generally needed
Vibratory bowl	Faster than barrel. Handles very small to large parts. Open for in-process inspection. Integral separation. Less noisy than vibratory tub. Generally lower initial cost and better media-parts mixing than vibratory tub. Economical for general-purpose work, heavy deburring, and continuous processing. Good automation capabilities. Batch or continuous operation	Cannot handle very long parts
Centrifugal barrel	Fast processing. Can handle precision and fragile parts. Produces smooth finishes. Batch automation capability. Versatile-can change from fine finishing to heavy stock removal. Improves fatigue strength. Low floor space needs	No in-process inspection. Complex to automate
Centrifugal disk	Fast processing. Open for in-process inspection. Batch automation capability. Versatile	Limited part sizes. External material handling
Spindle	Fast processing. No impingement of workpieces. Produces smooth finishes. Automation capability with robot reload	Parts must be fixtured. Limited part sizes and geometries (typically used for cylindrical parts). Less versatile than other processes

Source: Ref 4

Shot peening is the cold working of a metal surface with a stream of spherical shot particles applied to the surface at high velocity under carefully controlled conditions. Shot peening is most effective in reducing fatigue failures in parts subject to cyclic loading. Failures originate in surface areas under repeated tensile loading, and cracks will propagate from a surface defect or other stress riser. Shot peening prevents these failures by creating compressive stress layers in the surfaces of parts. As a part is loaded, its critical surface area will not develop tensile stresses until the shot-peen-induced compressive stresses are first overcome, thus permitting an increase in the allowable stress level and hence in the service life of the part. The effect of shot peening in improving the surface integrity of the part is also important. No matter how carefully a part is manufactured, it will exhibit some surface imperfections. These flaws may be localized areas of tensile stresses or phase transformations from machining or grinding, as well as pits, scratches, and other surface defects. As peening cold works the part surface, it blends these surface imperfections and effectively eliminates them as stress concentration points. Table 10 shows the effect of shot peening on the fatigue strength of machined 4340 alloy steel.

Table 10 Effect of shot peening on fatigue strength of 4340 steel

Machining operation	Endurance limit in bending, 10^7 cycles		Gentle grinding, %
	MPa	ksi	
Gentle surface ground	703	102	100
Gentle surface ground and shot peened	772	112	110
Abusive surface ground	430	62	61
Abusive surface ground and shot peened	630	92	90
Electropolished	620	90	88
Electropolished and shot peened	660	96	94

Shot peening has long been used to improve the fatigue characteristics of leaf and coil springs (Fig. 1). Increases in fatigue life up to 800% are often obtained. The process is also used extensively on gears, driveshafts, crankshafts, torsion bars, axles, ball studs, high-strength fasteners, railroad wheels, and oil well drilling equipment. Often it is applied only at a critical area, such as a fillet radius.

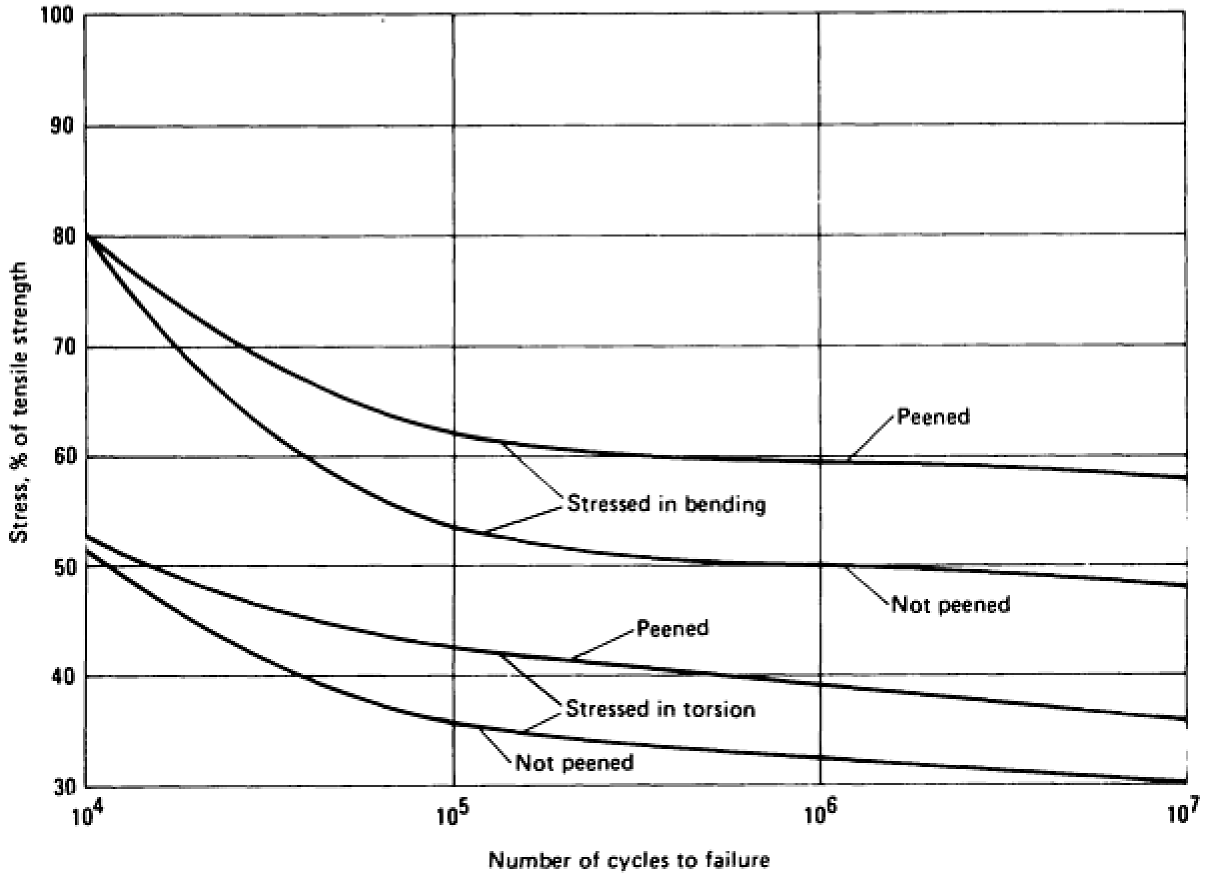


Fig. 1 Fatique curves for peened and unpeened and steel spring wires

Parts requiring shot peening should be clean, dry, and free of any scale. Any material on top of the base material may absorb the energy of the controlled peening process. Degreasing, descaling, or blast cleaning operations are often performed prior to shot peening to ensure proper and beneficial results. Additional information on this process can be found in the article "Shot Peening" in this Volume.

Honing is a controlled, low-speed sizing and surface-finishing process in which stock is removed by the shearing action to the bonded abrasive grains of a honing stone, or stick. Honing machines simultaneously apply several sticks (although one can be used) mounted on the periphery of a cylindrical body to the work surface. The usual purpose of honing is to produce uniform high accuracy and fine finish, and in the most common applications only a few thousandths of an inch of stock is removed although heavy stock removal up to 6.35 mm (0.250 in.) can also be cost effective.

The most frequent application of honing is for finishing inside cylindrical surfaces, but numerous outside surfaces also are honed. Gear teeth, valve components, and races for ball bearings and roller bearings are typical applications of external honing. Microhoning, also known as superfinishing or microfinishing, is closely related to honing. Microhoning uses finer grit (or grain) sizes (320 to 1200) than honing (60 to 600 grit). The primary distinction between honing and microhoning is that the tool rotates in honing, while in microhoning it is always the workpiece that rotates. Microhoning is a special honing operation in which the bonded abrasive stone is subjected to very light pressure and a short, high-frequency stroke.

Honing is generally used to produce surface finishes in the range of 0.80 to 0.20 μm (32 to 8 μin.) R_a (roughness average), while microhoning can be cost effective in producing surface finishes of the order of 0.10 to 0.050 μm (4 to 2 μin.) R_a. Each method can produce even finer finishes, but productivity, as a result, suffers. Figure 2 compares typical ranges of surface finishes obtained by honing and microhoning to other common production finishing processes. More detailed information on honing can be found in the article "Honing" in *Machining,* Volume 16 of the *ASM Handbook.*

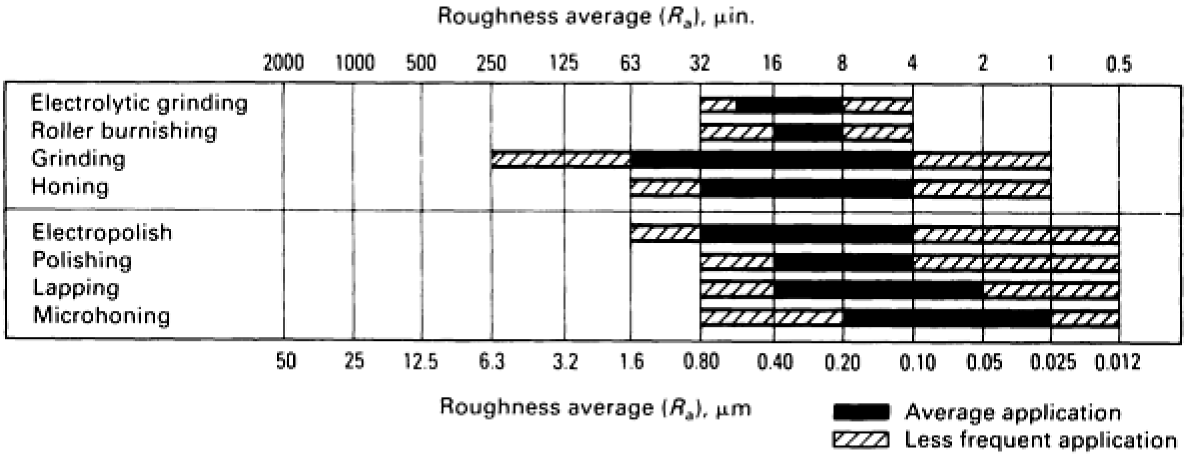


Fig. 2 Typical ranges of surface finish from common production processes. Higher or lower values may be obtained under various conditions.

Lapping is a low-velocity abrading process that removes controlled, very small amounts of material. It is accomplished with loose abrasive grains (usually retained in a viscous or liquid media, called the vehicle) between a tooling plate or wheel, called the lap, and the work surface to be finished. A typical setup for lapping flat steel products is shown in Fig. 3.

Fig. 3 A 1220 mm (48 in.) planetary top plate drive dual-face lapping machine loaded with a variety of components having various configurations and thicknesses to demonstrate the processing capabilities of the equipment. Shown clockwise, starting with the bottom-most carriers, are hardened high-carbon steel shear blades; 102 by 102 mm (4 by 4 in.) photomask blanks used to project microcircuits onto electronic substrates; stainless steel sender bars, which will be etched into optical position indicators; valve plates machined from cutoff hot-rolled bar stock for use in hydraulic motors; and a hardened alloy steel rotary slitter blade.

Lapping is generally a final finishing operation that results in four major refinements in the workpiece: (1) extreme accuracy of dimension, (2) correction of minor imperfections of shape, (3) refinement of surface finish, and (4) close fit between mating surfaces. The life of moving parts that are subject to wear can be greatly increased by eliminating the hills and valleys on workpiece surfaces and creating a maximum percentage of bearing area. Besides developing a workpiece that meets the surface finish requirements and is correct for geometrical and dimensional accuracy, there is no distortion, as lapping procedures do not require the use of magnetic chucks or other holding or clamping devices.

In normal lapping operations, less heat is generated than in most other finishing operations, thus minimizing the possibility of rehardened and decarburized areas on hardened or heat-treated parts. When both sides of a flat piece are lapped in the same operation (Fig. 3), extreme accuracy in flatness and parallelism can be accomplished; and by removing the same amount of stock from both sides of the part simultaneously, any inherent stresses in the piece are equally relieved. Typical applications for lapping include piston rings, crankshafts, ball bearings and bearing assemblies, and gears. More detailed information on lapping can be found in the article "Lapping" in *Machining,* Volume 16 of the *ASM Handbook.*

Abrasive-flow machining (AFM) is a process in which a semisolid abrasive media is forced, or extruded, through a workpiece passage. The media consist of a pliable polymer carrier and a concentration of abrasive grains such as silicon carbide. The viscosity of the carrier and the type, concentration, and size of the abrasive grains can be varied to achieve specific results.

By proper control of parameters and abrasive flow, the AFM process can perform a wide range of precision machining and finishing operations. These operations include deburring, edge radiusing, honing, polishing, and the removal of recast layers from workpiece surfaces. Important features of the process include selectivity, the capability of finishing inaccessible areas, and versatility.

Polishing with AFM can improve surface finishes of 0.75 to 7.5 μm (30 to 300 μin.) to one tenth or less of the original finishes. Material removal by the abrasion results in a dimensional change of about 25 to 35% more than the total roughness of the surface. For example, in reducing a surface finish of 2.5 μm (100 μin.) produced by electrical discharge machining to a finish of 0.25 μm (10 μin.) requires the removal of about 0.03 mm (0.001 in.) of stock. In most cases, stock removal can be held uniform throughout a passage with ±20%.

The finishing of dies (extruding, compacting, cold heading, upsetting, and others) is a major application of the AFM process. Advantages include reduced costs and longer die life. Costs are reduced by eliminating or minimizing the need for time-consuming hand polishing of the dies. Longer die life results from the directional finish produced by AFM and the improved uniformity and quality of the finished surfaces. Other components commonly finished by the AFM process include gears, bearing races and cages, and splined parts. More detailed information on AFM can be found in the article "Abrasive Flow Machining" in *Machining,* Volume 16 of the *ASM Handbook.*

Thermal and Electrochemical Finishing

Thermal Deburring. Burrs and flash, both internal and external, are rapidly burned away using the thermal energy method (TEM). Parts to be processed are loaded in baskets or special fixtures and placed in a water-cooled furnace chamber. A fuel mixture of natural gas and oxygen is then injected into the chamber under pressure. The initial fire or heat is supplied by an ignition system in the form of a spark from an ignitor. The spark causes the combustible gas mixture to ignite, and all the fuel gas is consumed in approximately 2 ms to form a 3300 °C (6000 °F) heat wave.

The heat wave hits everything within the chamber. It hits the water-cooled walls of the chamber, the parent metal of the part or parts, and the burrs within blind holes, external edges, and intersecting holds (small or large) that cannot be reached by hand. The main body of the part becomes warm (usually under 150 °C, or 300 °F), while the flash or burrs (having less mass per surface area) heat up instantly and burst into flames. Heat created by the burning of fuel gas thus triggers the start of a second fire of the burr material itself. Because there is an abundance of oxygen in the initial fuel mixture, burrs will continue to burn until the heat is dispersed throughout the main body of the part.

Applications for the TEM include deburring of various steel castings and machined gears. For the gears, burrs are removed from the teeth and from tapped holes at the rate of 120 gears per hour. More detailed information on thermal deburring can be found in the article "Thermal Energy Method" in *Machining,* Volume 16 of the *ASM Handbook.*

Electropolishing is an electrochemical process for removing metal. Etching, deburring, smoothing, coloring, and machining are typical electropolishing processes. The removal of metal is done anodically in an acid or alkaline solution.

During the process, products of anodic metal dissolution react with the electrolyte to form a film at the metal surface. Two types of films have been observed: (a) a viscous liquid that is nearly saturated, or is supersaturated, with the dissolution products; and (b) anodically discharged gas, usually oxygen. Both types of films exist simultaneously in most commercial electropolishing solutions. The gas appears to be a blanket on the outside of the viscous film. Which type of film predominates depends on (a) the kind of metal, (b) the nature of the electrolyte, and (c) the surface condition prior to electropolishing (i.e., surface contamination, grain size, inclusions).

The most widely used electropolishing solutions for steels contain one or more of the concentrated inorganic acids--sulfuric, phosphoric, and chromic. Table 11 lists conditions for electropolishing alloy steels in acid electrolytes. Some of the steel products that undergo electropolishing are low-alloy (4130, 4140, and similar steels) automotive piston rings, crankpins, cotton-picker spindles, hand tools, gears, television chassis, and paper knives.

Table 11 Conditions for electropolishing steels in acid electrolytes

Type of metal (and product)	Purpose of treatment	Bath volume		Installed power		Current density		Polishing cycle, min	Daily production			Operators
										Area		
		L	gal	A	V	A/dm^2	A/ft^2		No. of parts	m^2	ft^2	
Sulfuric-phosphoric acid electrolytes												
Carbon steels (job-shop work)	Brighten; deburr	1500	400	1500	12	25-40	250-400	Varies	Varies	. . .	. . .	1
4140 steel	Prepare for chromium plate	3200	850	4000	12	15	150	10	7000-10,000	45-75	500-800	3
Sulfuric-phosphoric-chromic acid electrolytes												
Carbon steel	Smooth; deburr	1500	400	. . .	. . .	30	300	2	5000	90	1000	1
4130 steel (tools)	Bright finish	950	250	1500	9	17.5	175	4	2000-5000	. . .	. . .	2

Steels are electropolished for one or more of the following purposes:

- Improve appearance and reflectivity
- Improve resistance to corrosion
- Prepare metals for plating, anodizing, or conversion coating
- Remove edge burrs produced by mechanical cutting tools
- Remove the stressed and disturbed layer of surface metal caused by the cutting, smearing, and tearing action of mechanical stock removal or of abrasive finishing

- Inspect for surface imperfections in cast, forged, or wrought metal
- Remove excess material as desired for milling metal parts

Effect on Fatigue Strength. Removal of not more than 25 μm (1 mil) on the diameter of steel fatigue specimens by electropolishing can lower the endurance limit from 10 million cycles without failure to failure at 100,000 to 120,000 cycles at 520 MPa (75 ksi) (Ref 5). The decrease in diameter is not responsible for the loss. Grinding and hand finishing to the same undersize has no adverse effect.

Static stress-strain values on electropolished specimens showed little or no scatter, and when the electropolished surface was rubbed with used 000 emery paper, the original value for fatigue limit was obtained. The mild treatment indicates that any detrimental effect of an electropolished surface results from removal of a compressively stressed skin. It has been observed that wet blasting raised fatigue strength of electropolished specimens to the level attained by polishing mechanically.

The lower fatigue strength of electropolished specimens appears to be because of removal of, or inability to produce, compressive stress in metal surfaces. Thus, electropolishing is comparable in effect to a stress-relieving anneal. For example, mechanical polishing of a chromium-vanadium steel produced a compressive stress of 350 to 520 MPa (50 to 75 ksi) at a depth of 0.02 to 0.05 mm (0.008 to 0.002 in.) below the surface. The stress was relieved by heating at 500 °C (930 °F) for 2 h, which resulted in lowering the fatigue limit from approximately 580 to 560 MPa (85 to 80 ksi). Similar treatment of a low-carbon steel lowered fatigue limit from approximately 730 to 630 MPa (105 to 90 ksi). Electropolishing lowered fatigue limit comparably.

Fatigue strength is not always lower after electropolishing. In an alternating torsion test, a nickel-chromium-molybdenum steel heat treated to 1450 MPa (210 ksi) had 34% higher fatigue strength after electropolishing a ground surface. The same steel heat treated to a lower tensile strength showed lower fatigue strength after electropolishing.

Because fatigue data for electropolished specimens show considerably less scatter than for mechanically polished specimens, electropolishing tends to show true fatigue value characteristic of a particular metal and metallurgical condition. Thus, any irregularly stressed surface can be removed by electropolishing, and a uniform compressive stress can then be applied by controlled working, such as shot peening (Table 10), wet blasting, or mild abrasive polishing.

Removal by electropolishing of 100 μm (4 mils) of metal from the surface of mechanically polished low-alloy steel containing 0.44% C, 0.61% Mn, 2.48% Ni, 0.82% Cr, and 0.48% Mo that was heat treated to a tensile strength of 1100 MPa (160 ksi) changed the residual surface compressive stress of approximately 170 to 200 MPa (25 to 30 ksi) to a tensile stress of 0 to 34 MPa (0 to 5 ksi). The fatigue limit was lowered about 28 MPa (4 ksi). The stress gradient was approximately 140 to 200 MPa (20 to 30 ksi) in 0.100 mm (0.004 in.) in the mechanically polished surfaces. The residual surface stress in mechanically polished specimens differed by approximately 200 to 240 MPa (30 to 35 ksi) from that of electropolished specimens with comparable surface roughness; fatigue limits differed by approximately 580 to 550 MPa (85 to 80 ksi). Variability of fatigue strength after certain mechanical operations and after electropolishing is shown in Table 12.

Table 12 Typical surface compression stress and fatigue strength of various carbon steels finished mechanically or by electropolishing

Finishing method	Fatigue strength, % of value for mechanical polishing	Depth of cold work		Surface compressive stress	
		mm	in.	MPa	ksi
Mechanical polishing	100	<0.050	<0.002	620	90
Electropolishing	70-90	None	None	None	None

Lathe turning	65-90	0.50	0.02	. . .	. . .
Milling	. . .	0.18	0.007	. . .	. . .
Grinding	80-140	≤.25	≤.01	760	110
Surface rolling	115-190	1.00	0.04	900	130
Shot peening	85-155	0.50	0.02	1030	150

Source: Ref 5

References cited in this section

3. Surface and Edge Finishing Methods, in *Materials, Finishing and Coating, Tool and Manufacturing Engineers Handbook,* C. Wick and R.F. Veilleux, Ed., Society of Manufacturing Engineers, 1985, p 15-24
4. Mass Finishing, in *Materials, Finishing and Coating, Tool and Manufacturing Engineers Handbook,* C. Wick and R.F. Veilleux, Ed., Society of Manufacturing Engineers, 1985, p 16-65
5. L.S. Winter, Electropolishing, Vol 5, 9th ed., *Metals Handbook,* American Society for Metals, 1982, p 303-309

Conversion Coatings

Phosphate or chromate conversion coatings are used to enhance the corrosion resistance of steels. By themselves, they provide slightly better corrosion resistance than bare steel; more often, they are used in conjunction with another coating system. Conversion coatings are applied after hot-dip galvanizing and provide good corrosion protection when topcoated with an organic coating system. More detailed information on conversion coatings can be found in the articles "Phosphate Coatings" and "Chromate Conversion Coatings" in this Volume.

Phosphate Coating

Phosphate coating is the treatment of bare or galvanized steel with a dilute solution of phosphoric acid and other chemicals in which the surface of the metal, reacting chemically with the phosphoric acid medium, is converted to an integral, mildly protective layer of insoluble crystalline phosphate. Phosphate conversion coatings are applied to steel substrates to enhance corrosion resistance, increase paint adhesion, or both.

Phosphate coatings range in thickness from less than 3 to 50 μm (0.1 to 2 mils). Coating weight (grams per square meter of coated area), rather than coating thickness, has been adopted as the basis for expressing the amount of coating deposited.

Types of Phosphate Coatings. The three principal types of phosphate coatings in general use include:

- *Iron phosphate*--lightweight, amorphous phosphate coatings that do not contain significant amounts of divalent metal ions from solution. Coating weights range from 0.16 to 0.80 g/m^2 (15 to 70 mg/ft^2). Although iron phosphate coatings are applied to steel to provide receptive surfaces for bonding of fabrics, woods, and other materials, they are used chiefly as base coatings for subsequent painting.
- *Zinc phosphate*--medium-weight, crystalline phosphate coatings that contain divalent metal ions from the solution and/or the metal surface. Coating weights range from 1.4 to 4.0 g/m^2 (130 to 370 mg/ft^2). Zinc phosphate coatings can be used for any of the following applications of phosphating: (a) as a base for paint or oil; (b) as an aid to cold forming, tube drawing, or wiredrawing; (c) for increasing wear

resistance; or (d) for rustproofing.

- *Heavy phosphate* (manganese phosphates)--heavy coatings that contain divalent metal ions from solution and from the metal surface. Coating weights range from 7.5 to 30 g/m^2 (700 to 2800 mg/ft^2). Manganese phosphate coatings are applied to ferrous parts (bearings, gears, and internal-combustion engine parts, for example) for break-in and for prevention of galling. These coatings are usually dark gray. However, because almost all manganese phosphate coatings are used as an oil base and because the oil intensifies the coloring, manganese phosphate coatings are usually black in appearance.

The characteristics of these three phosphate coating types are summarized in Table 13.

Table 13 Characteristics of phosphate coatings

Characteristics	Type of coating		
	Iron phosphate	**Zinc phosphate**	**Heavy phosphate**
Coating weight	0.16-0.80 g/m^2 (0.0005-0.0026 oz/ft^2)	1.4-4.0 g/m^2 (0.0045-0.013 oz/ft^2)	7.5-30 g/m^2 (0.025-0.1 oz/ft^2)
Types	Cleaner/coater Standard Organic phosphate	Standard Nickel-modified Low-zinc Calcium-modified Manganese-modified	Manganese phosphate Zinc phosphate Ferrous phosphate
Common accelerators	Nitrite/nitrate Chlorate Molybdate	Nitrite/nitrate Chlorate Nitrobenzene sulfonic acid	None Chlorate Nitrate Nitroguanidine
Operating temperatures	Room -70 °C (160 °F)	Room -70 °C (160 °F)	60-100 °C (140-212 °F)
Free acid, points	-2.0 to 2.0	0.5-3.0	3.6-9.0
Total acid, points	5-10	10-25	20-40+
Prephosphate conditioners	None	Titanium phosphate None	Manganese phosphate Titanium phosphate None
Primary use	Paint base for low-corrosion environments	Paint base for high-corrosion environments	Unpainted applications
Limitations	Low painted corrosion resistance; low	Poor unpainted corrosion resistance	Expensive, long

Materials needed for tanks	Low-carbon steel	Low-carbon steel, stainless steel, or plastic-lined steel	Stainless steel or low-carbon steel

Process Details. The application of a phosphate coating as a base for subsequent painting normally comprises five successive operations: (a) cleaning, (b) rinsing, (c) phosphating (by immersion or spraying), (d) rinsing, and (e) chromic acid rinsing. Some of these operations may be omitted or combined, such as cleaning and coating in one operation. Additional operations may be required, depending on the surface condition of the parts to be phosphated or on the function of the phosphate coating. Parts exemplifying these exceptions are:

- Heavily scaled parts, which may require pickling before cleaning
- Parts with extremely heavy coatings of oil or drawing compounds, which may require rough cleaning before the normal cleaning operation
- Parts that are tempered in a controlled atmosphere before being phosphated, which may not require cleaning and rinsing before phosphating
- Parts that are phosphated and later oiled for antifriction purposes, which may have the chromic acid rinse omitted, because corrosion resistance is not required. Some rust-preventive oils negate the need for a chromic rinse while still providing excellent corrosion resistance
- Automotive parts when electrodeposition of a primer is involved. A deionized water rinse is required after the chromic acid rinse

Chromate Conversion Coatings

Chromate conversion coatings are formed by a chemical or an electrochemical treatment of metals or metallic coatings in solutions containing hexavalent chromium (Cr^{6+}) and, usually, other components. The process results in the formation of an amorphous protective coating composed of the substrate, complex chromium compounds, and other components of the processing bath.

Chromate conversion coatings are applied primarily to enhance bare or painted corrosion resistance, to improve the adhesion of paint or other organic finishes, and to provide the metallic surface with a decorative finish. Chromate conversion coatings are most frequently applied by immersion or spraying, but other methods of application, such as brushing, roll coating, dip and squeegee, electrostatic spraying, or anodic deposition, are used in special cases.

Processing Sequence. Chromate coatings are applied by contacting the processed surfaces with a sequence of processing solutions. The processing baths are arranged in a series of tanks, and the surfaces to be processed are transferred through the sequence of stages by using manual, semiautomatic, or automatic control. The chromate coatings are usually applied to metal parts or to a continuous metal strip running at speeds to 5 m/s (1000 ft/min).

The basic processing sequence consists of the following six steps: cleaning, rinsing, conversion coating, rinsing, post-treatment rinsing or decorative color rinsing, and drying. In many applications, this sequence is expanded to accommodate pickling deoxidizing, dyeing, brightening, and other rinsing stages, or the sequence can be shortened when cleaning or post-treatment rinsing is not necessary. Some typical processing sequences are given in Table 14.

Table 14 Typical process sequences for chromating of continuous galvanized strip

Step	Electrogalvanized strip	Step	Hot-dip galvanized strip
1	Electrogalvanizing	1	Hot-dip galvanizing
2	Rinsing: warm water, multiple stages, neutralizing (optional)	2	Surface conditioning: heat treatments

3	Conversion coating: chromate	3	Conversion coating: chromate
4	Rinsing: cold or warm water	4	Drying: warm air
5	Post-treatment: chromate (optional)	5	Oiling (optional)
6	Drying: warm air		
7	Oiling or painting (optional)		

Chromating Galvanized Steels. Although zinc-coated steels provide better atmospheric-corrosion resistance than bare cold-rolled steel, the natural resistance of zinc surfaces to atmospheric corrosion remains low. Most articles coated with zinc by electroplating or hot-dipping are further protected. Chromating is widely used to provide corrosion protection and a decorative finish in bare applications; it can also be used as a pretreatment before painting. The chromate coatings are formed on zinc surfaces from acid solutions containing Cr^{6+}, usually other mineral acids, and accelerators. Chromate coatings on zinc can be categorized as clear, iridescent, and colored.

The largest area for the application of clear coatings is the passivation of hot-dip galvanized steel. Most unpainted zinc and zinc-aluminum coated steel sheet products used for roofs and walls of industrial and farm buildings are chromated on hot-dip galvanizing lines. These chemical treatments are applied in the coating weight range of 0.01 to 0.02 g Cr/m^2 (1 to 2 mg Cr/ft^2), with the upper limit usually defined by the color acceptable to the coated sheet users. On the strip line, coatings are applied by immersing or spraying the freshly prepared galvanized strip in chromating solutions for 1 to 3 s immediately before a set of squeegee rolls, which remove the excess solution from the strip. Broad ranges of chromium concentration and temperatures of 40 to 70 °C (100 to 160 °F) are used to achieve the desired coating weights. The corrosion protection provided by the chromate coatings increases with their color. Typical salt spray corrosion data are given in Table 15.

Table 15 Typical salt spray data for chromate coatings on zinc-coated steel

Substrate	Type of chromate coating	Time to corrosion stain, h
Electroplated zinc	Untreated	<4
	Clear	24-48
	Iridescent	100-200
	Olive drab	100-400
	Electrolytic	1000
Hot-dip zinc	Untreated	<4

Chromate coatings can be deposited electrolytically from baths containing CrO_4^{2-}, PO_4^{3-}, F^-, and other anions. The resulting coatings, which are gray to black in appearance, have superior corrosion resistance and hardness when compared to the conversion coatings (Table 15).

Chromating Bare Steel. Both chemical and electrochemical methods for chromating steel have been used. The chemical method requires high temperatures and prolonged contact times. No-rinse chromate treatments are used on continuous strip lines for paint base applications. They are applied using chemical compositions and wet film thicknesses to give coating weights in the 0.16 to 0.38 g/m^2 (15 to 35 mg/ft^2) range and provide excellent paint base properties. Electrolytically produced chromium/chromium oxide coatings, better known as tin-free steel, are extensively used in the metal-packaging industry.

Hot-Dip Coating Processes

Hot-dip coating processes are used to apply coatings of zinc, aluminum, lead, tin, and some alloys of these metals to carbon steels. The hot-dip process consists of immersing the steel in a molten bath of the coating metal. Zinc coating (galvanizing) protects steel galvanically because the zinc is anodic to the steel base metal and therefore corrodes preferentially in most environments. Hot-dip galvanizing affords adequate atmospheric-corrosion protection to steel. Aluminum hot-dip coatings (aluminizing) provide carbon steels with resistance to both corrosion and heat. In many environments, aluminum protects steel galvanically in much the same way as zinc.

Zinc-aluminum and aluminum-zinc alloys are also applied to steel by hot dipping. Heating aluminized steel results in the formation of an iron-aluminum intermetallic compound that resists oxidation at temperatures up to about 800 °C (1500 °F). Aluminized steel is often used where heat resistance is required--for example, in automotive exhaust systems.

Hot-dip lead coatings are sometimes used on steel that will be exposed to sulfuric acid fumes or other aggressive chemical environments. Terne plate, a lead-tin alloy coating, gives more protection than pure lead coatings and is solderable.

Hot Dip Galvanizing

Hot dip galvanizing is a process in which an adherent, protective coating of zinc and iron-zinc alloys is developed on the surfaces of iron and steel products by immersing them in a bath of molten zinc. Most zinc coated steel is processed by hot dip galvanizing. In general, steels with the following maximum alloying/impurity levels are best suited to galvanizing: 0.05% Si, 0.05% P, 0.25% C, and 1.3% Mn.

Batch Galvanizing. One method of hot dip galvanizing is the batch process, which is used for prefabricated steel items. This method involves cleaning the steel articles, applying a flux to the surfaces, and immersing them in a molten bath of zinc for varying time periods to develop a thick alloyed zinc coating.

The advantage to galvanizing after fabrication is that the zinc completely seals edges, overlaps, rivets, and welds; establishes liquid tightness; and prevents corrosion from starting. Iron and steel in all shapes and sizes can be coated with zinc by batch galvanizing. The process is simple, extremely versatile, and has been used to provide protection to articles ranging from small items, such as bolts, nuts, and miscellaneous hardware, to large items like structural beams for bridges or buildings. The virtually unrestricted size range of parts that can be galvanized and the ability to bolt or weld prefabricated sections after galvanizing enables almost any structure to be built from galvanized steel. Shape is not a restriction to batch galvanizing. Tubes, open vessels, drums, tanks, and complicated shapes such as large heat exchangers are readily galvanized on the inside and outside in one operation.

The thickness of the coating is controlled by the composition of the steel substrate and the immersion time. Part withdrawal rate and any postgalvanizing treatments also influence the coating thickness. Process details (zinc bath temperature, steel surface preparation, degree of wiping, shaking, or centrifuging, and rate of cooling) are described in the article "Batch Hot Dip Galvanized Coatings" in this Volume.

The zinc coating on batch galvanized parts is generally specified in ounces or grams per unit of surface area, measured in either square feet or square meters on a single surface or on one side of the part. With proper coating techniques, the coating weight can usually be controlled between 610 and 1220 g/m^2 (2 and 4 oz/ft^2), equivalent to a coating thickness of approximately 43 to 86 μm (1.7 to 3.4 mils) per side (Ref 6).

Continuous Galvanizing. Steel sheet and wire are coated by a continuous hot dip process; that is, they enter the coating bath in an unending strip. In theory, all continuous hot dip processes are similar in that the steel sheet or wire is subjected to successive cleaning, coating, and postcoating steps.

Typical cleaning steps may include alkaline cleaning or acid pickling (both of which may be electrolytic), oxidation (usually gaseous for sheet, but often in molten lead for wire), and reduction (gaseous). If a gaseous reduction is the final cleaning step, the steel must enter the molten coating bath directly without being exposed to air. When the final cleaning step is an acid pickle (this is usually the case for wire), the steel is then immersed in a liquid flux, which dissolves any remaining oxides, before entering the molten bath. Similarly, gaseous reduction can also be considered a flux treatment. All-gaseous cleaning is used on about 60% of the steel-coating lines. The remaining 40% is approximately half liquid cleaning/flux and half liquid cleaning/gaseous cleaning. Most wire-coating lines use the liquid/flux technique. More detailed information on surface cleaning and fluxing can be found in the article "Surface Preparation for Continuously Applied Coatings" in this Volume.

The clean steel is then immersed in the molten coating bath long enough to allow the coating metal to wet and react with the steel surface. As the coated sheet or wire emerges from the molten bath, it pulls coating metal up from the surface which can then be smoothed or wiped to the desired thickness by a variety of methods. Most sheet-coating lines use a gas-wiping technique in which a jet of steam, air, or gas (such as nitrogen) is directed against the emerging sheet.

The coated steel can be given any number of subsequent mechanical, thermal, or chemical post-treatments designed to impart specific properties. Typically, a coated sheet might be oiled or coated with a chromate solution to inhibit staining or superficial corrosion during storage and transit (see the previous discussion of chromate conversion coating in this article). Waxing would serve the same purpose on wire and would facilitate handling during subsequent processing.

Hot-dipped galvanized coatings are applied by highly mechanized mass production methods at speeds of over 90 m/min (300 ft/min). Several designs of galvanizing lines have been developed for commercial use by the steel suppliers. Most steel suppliers can produce galvanized coils (sheets) in widths of 250 to 1830 mm (10 to 72 in.) and thicknesses of 0.43 to 4.2 mm (17 to 165 mils). Typical applications for mill coated sheets are roofing and siding panels, guardrails, appliance cabinets, automotive body parts, and ductwork.

Coating weights applied by continuous galvanizing vary from 150 to 840 g/m^2 (0.5 to 2.75 oz/ft^2) (Ref 7). The zinc coating may be on one side of the sheet only, of equal weight on both sides of the sheet, or differentially applied (one side has a thicker coating than the other side). Process details are given in the article "Continuous Hot Dip Coatings" in this Volume.

Nature of the Hot Dip Galvanized Coating. Figure 4 shows a photomicrograph of a typical hot dip galvanized coating consisting of a series of layers. These layers are also identified in Table 16. Starting from the base steel at the bottom of the section, each successive layer contains a higher proportion of zinc until the outer layer, which is relatively pure zinc, is reached. Therefore, there is no real line of demarcation between the iron and the zinc; instead, there is a gradual transition through the series of iron-zinc intermetallics, which provide a powerful bond between the base metal and the coating.

Table 16 Properties of alloy layers of hot dip galvanized steels

Layer	Alloy	Iron, %	Melting point		Crystal structure	Diamond pyramid microhardness	Alloy characteristics
			°C	°F			
Eta (η)	Zinc	0.03	419	787	Hexagonal	70-72	Soft, ductile
Zeta (ζ)	$FeZn_{13}$	5.7-6.3	530	986	Monoclinic	175-185	Hard, brittle
Delta (δ)	$FeZn_7$	7.0-11.0	530-670	986-1238	Hexagonal	240-300	Ductile

Gamma (Γ)	Fe_3Zn_{10}	20.0-27.0	670-780	1238-1436	Cubic	. . .	Thin, hard, brittle
Steel base metal	Iron	. . .	1510	2750	Cubic	150-175	. . .

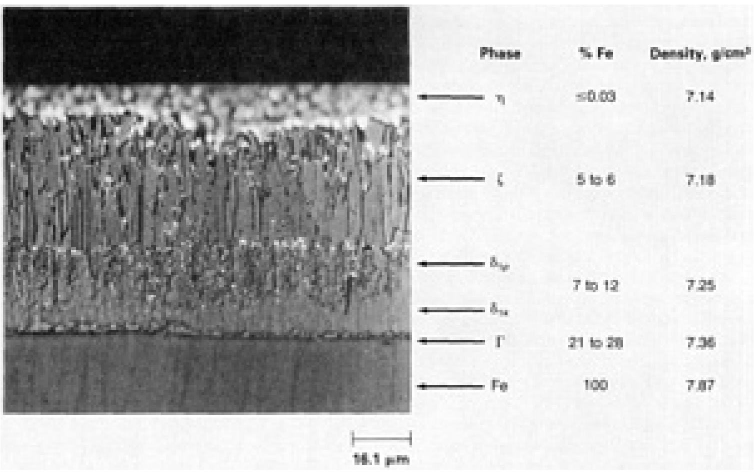


Fig. 4 Typical hot dip galvanized coating. Note the gradual transition from layer to layer, which results in a strong bond between base metal and coating.

Hardness and Abrasion Resistance. The layers that compose the galvanized coating, being discrete zinc-iron alloys, vary in hardness. The free zinc layer (η) is relatively soft, but the alloy layers are very hard, harder even than ordinary structural steels. Typical values for the microhardness and other properties of the various alloy layers are given in Table 16.

The alloy layers are from four to six times more resistant to abrasion than pure zinc. Galvanized coatings exhibit better abrasion resistance compared to paints with the same coating thickness and can be effectively used where excessive abrasive wear is expected, for example, floor gratings, stairs, conveyors, and storage bins.

Adhesion and Impact Resistance. Unlike other coatings, which are mechanically or chemically bonded to the steel, the galvanized coating is metallurgically bonded to and integral with the steel, making conventional measures of bond strength inappropriate for this coating. As a result of the metallurgical bond, the galvanized coating is very adherent.

The structure of the galvanized coating, particularly the relative thicknesses of the δ and ζ layers (Table 16), is primarily influenced by the steel chemistry and, to a lesser extent, by the galvanizing temperature and the duration of immersion. Coating structure has the greatest effect on the impact resistance of the coating. A high relative proportion of ζ phase in the iron-zinc alloy may result in localized flaking if the coating is subjected to heavy impact or excessive twisting or bending. Semikilled steels with silicon contents of 0.05 to 0.12% are the most susceptible to coating brittleness and less adherent coatings.

Corrosion Protection Mechanism. Galvanized coatings protect steel in corrosion service in two ways: barrier protection and cathodic protection. Barrier protection is provided by the galvanized coating and is further enhanced by the formation of a thin, tightly adherent layer of zinc corrosion products on the coating surface. Upon initial weathering of a freshly galvanized surface, ZnO is formed, and it is converted to $ZnOH_2$ in the presence of moisture. Further reaction with CO_2 in the air results in the formation of basic $ZnCO_3$, which is relatively insoluble and impedes further corrosion. The gray patina normally associated with weathered galvanized coatings is the result of this thin layer of basic $ZnCO_3$.

Cathodic protection is provided to the steel by the fact that zinc is anodic to steel in most environments. Minor discontinuities or small areas of exposed steel resulting from drilled holes or cut edges are protected from corrosion by the sacrificial protection afforded by zinc. The corrosion products that result from this action provide further protection.

Atmospheric Exposure. Zinc, steel, and hot dip galvanized coatings have been the subject of long-term atmospheric studies conducted throughout the world (Ref 8, 9). From these studies, the behavior of these materials in a specific atmospheric environment can be reasonably estimated. An exact determination of corrosion behavior is complicated by several factors: the frequency and duration of exposure to moisture (rain, sleet, snow, and dew), the type and concentration of corrosive pollutants, the prevailing wind direction and velocity, and exposure to sea spray or windborne abrasives. All atmospheres contain some type of corrosive agent, and the concentration of these agents, as well as the frequency and duration of moisture contact, determines the corrosion rate of galvanized coatings.

Figure 5 shows the results of outdoor atmospheric-exposure tests designed to measure the protective life of galvanized coatings in various atmospheric environments. The sites were selected as representative of various broad environmental classifications: heavy industrial, moderate industrial (urban), suburban, rural, and marine. Within these broad classifications, the following factors are most significant in influencing the rate of corrosion of the galvanized coating.

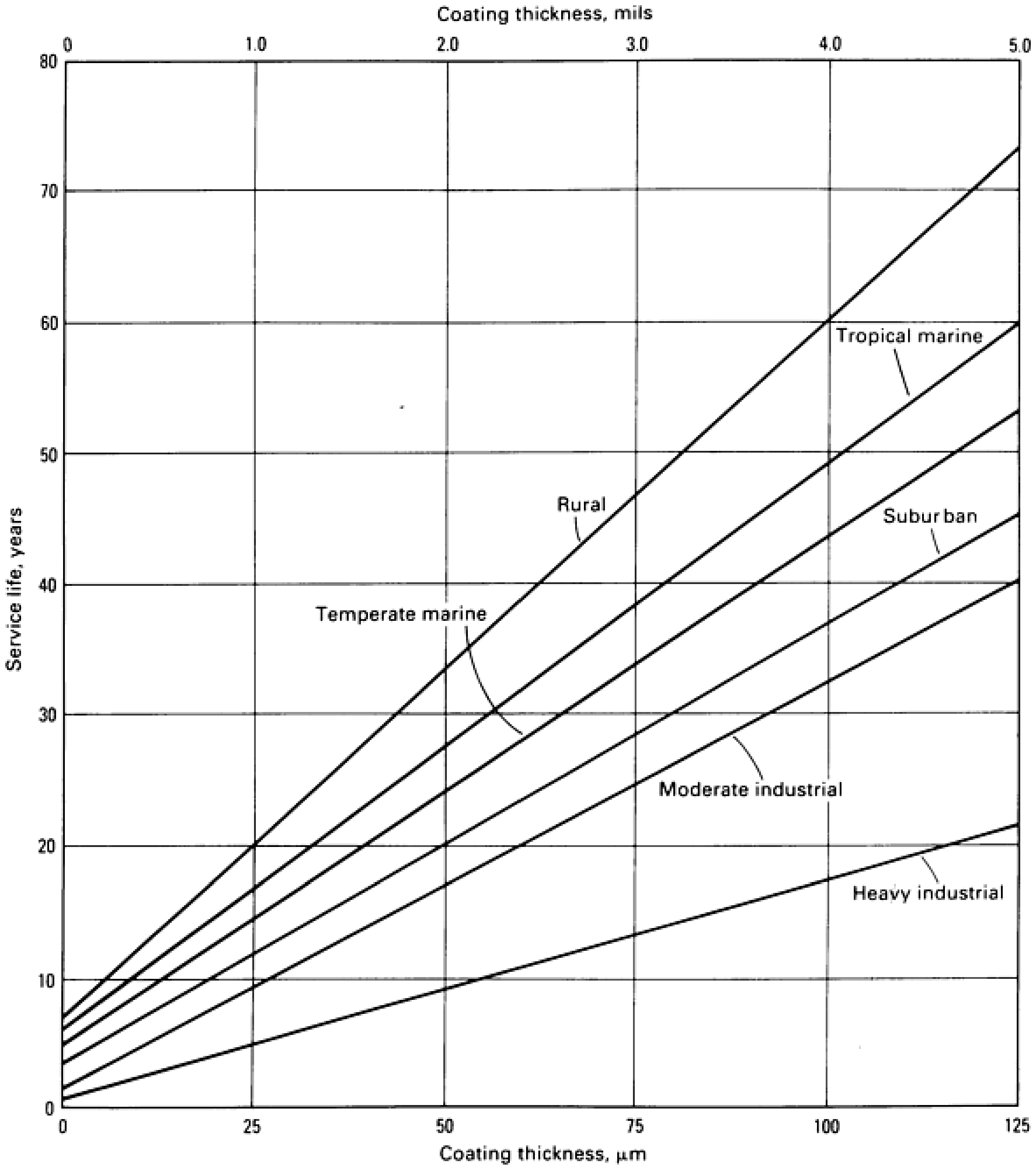


Fig. 5 Service life versus coating thickness for hot dip galvanized steel in various atmospheres. Source: Ref 8

Industrial and Urban Environments. Corrosive conditions are most pronounced in areas with highly developed industrial complexes that release sulfurous gases and corrosive fumes and mists to the atmosphere. These corrodents react with the normally impervious basic $ZnCO_3$ film to produce $ZnSO_4$ and other soluble zinc salts that, in the presence of moisture, are washed from the surface. This exposes fresh zinc to the atmosphere, and another corrosion cycle begins.

Rural and Suburban. The corrosion rate of zinc in these areas is relatively slow compared to that in industrial settings. Once the original weathering occurs, there is little in the atmosphere to convert the basic zinc salts to water-soluble compounds.

Marine Atmospheres. The corrosion rate of zinc and galvanized steel in marine atmospheres is influenced by several factors. Zinc forms a soluble corrosion product, zinc chloride ($ZnCl_2$), in marine atmospheres; therefore, the corrosion rate is influenced by salt spray, sea breezes, topography, and proximity to the coastline. For example, one investigation found that the corrosion rate for zinc exposed 25 m (80 ft) from the ocean was three times that for zinc exposed 250 m (800 ft) from the ocean (Ref 9).

The corrosion product formed in a given type of atmosphere (industrial, marine, and so on) determines the corrosion rate of zinc in that atmosphere. Results from exposures in a variety of atmospheres show that zinc is 20 to 30 times more resistant to corrosion than is steel (Table 17).

Table 17 Weight losses of steel and zinc in various locations

Results are from 2-year atmospheric exposures.

Location	Weight loss, g		
	Zinc	Steel	Steel/zinc loss ratio
Norman Wells, N.W.T., Canada	0.07	0.73	10.4
Phoenix, AZ	0.13	2.23	17.2
Saskatoon, Sask., Canada	0.13	2.77	21.3
Esquimalt, Vancouver Is., Canada	0.21	6.50	31.0
Fort Amidor Pier, Panama C.Z.	0.28	7.10	25.4
Ottawa, Ontario, Canada	0.49	9.60	19.6
Miraflores, Panama C.Z.	0.50	20.90	41.8
Cape Kennedy, 0.8 km (0.5 mile) from ocean	0.50	42.0	84.0
State College, PA	0.51	11.17	21.9
Morenci, MI	0.53	7.03	13.3
Middletown, OH	0.54	14	25.9

Potter County, PA	0.55	10	18.2
Bethlehem, PA	0.57	18.30	32.1
Detroit, MI	0.58	7.03	12.1
Point Reyes, CA	0.67	244.0	364.2
Trail, B.C., Canada	0.70	16.90	24.1
Durham, NH	0.70	13.30	19.0
Halifax, NS (York Redoubt)	0.70	12.97	18.5
South Bend, PA	0.78	16.20	20.8
East Chicago, IN	0.79	41.10	52.0
Brazos River, TX	0.81	45.40	56.0
Monroeville, PA	0.84	23.80	28.3
Daytona Beach, FL	0.88	144.0	163.6
Kure Beach, NC (244 m, or 800 ft), site	0.89	71.0	79.8
Columbus, OH	0.95	16.00	16.8
Montreal, Quebec, Canada	1.05	11.44	10.9
Pittsburgh, PA	1.14	14.90	13.1
Waterbury, CN	1.12	11.00	9.8
Limon Bay, Panama C.Z.	1.17	30.30	25.9
Cleveland, OH	1.21	19.0	15.7
Newark, NJ	1.63	24.7	15.2
Cape Kennedy, 55 m (180 ft) from ocean			

Ground level	1.83	215.0	117.5
9 m (30 ft) elevation	1.77	80.2	45.3
18 m (60 ft) elevation	1.94	64.0	33.0
Bayonne, NJ	2.11	37.70	17.9
Kure Beach, NC (25 m, or 80 ft) site	2.80	260.0	92.9
Halifax, NS (Federal Building) (25m, or 80 ft)	3.27	55.30	16.9
Galeta Point, Panama C.Z.	6.80	336.0	49.4

Seawater and Salt Spray Performance. Table 18 gives the approximate corrosion rates of zinc in various waters, and Fig. 6 illustrates the expected service life of galvanized coatings in areas exposed to salt spray influences. Sea salts are mainly NaCl, with small amounts of calcium, magnesium, and manganese salts. Typical pH is about 8. Compared to other metals and alloys, galvanized coatings provide considerably more protection to steel than many other metals and alloys, even though the anticipated coating life is shorter in seawater and salt spray exposures than a number of other environments.

Table 18 Corrosion of zinc in various waters

Water type	Approximate material loss	
	µm/yr	mils/yr
Seawater		
Global oceans, average	15-25	0.6-1.0
North Sea	12	0.5
Baltic Sea and Gulf of Bothnia	10	0.4
Freshwater		
Hard	2.5-5	0.1-0.2
Soft river water	20	0.8
Soft tap water	5-10	0.2-0.4

Distilled water	50-200	2.0-8.0

Source: Ref 10

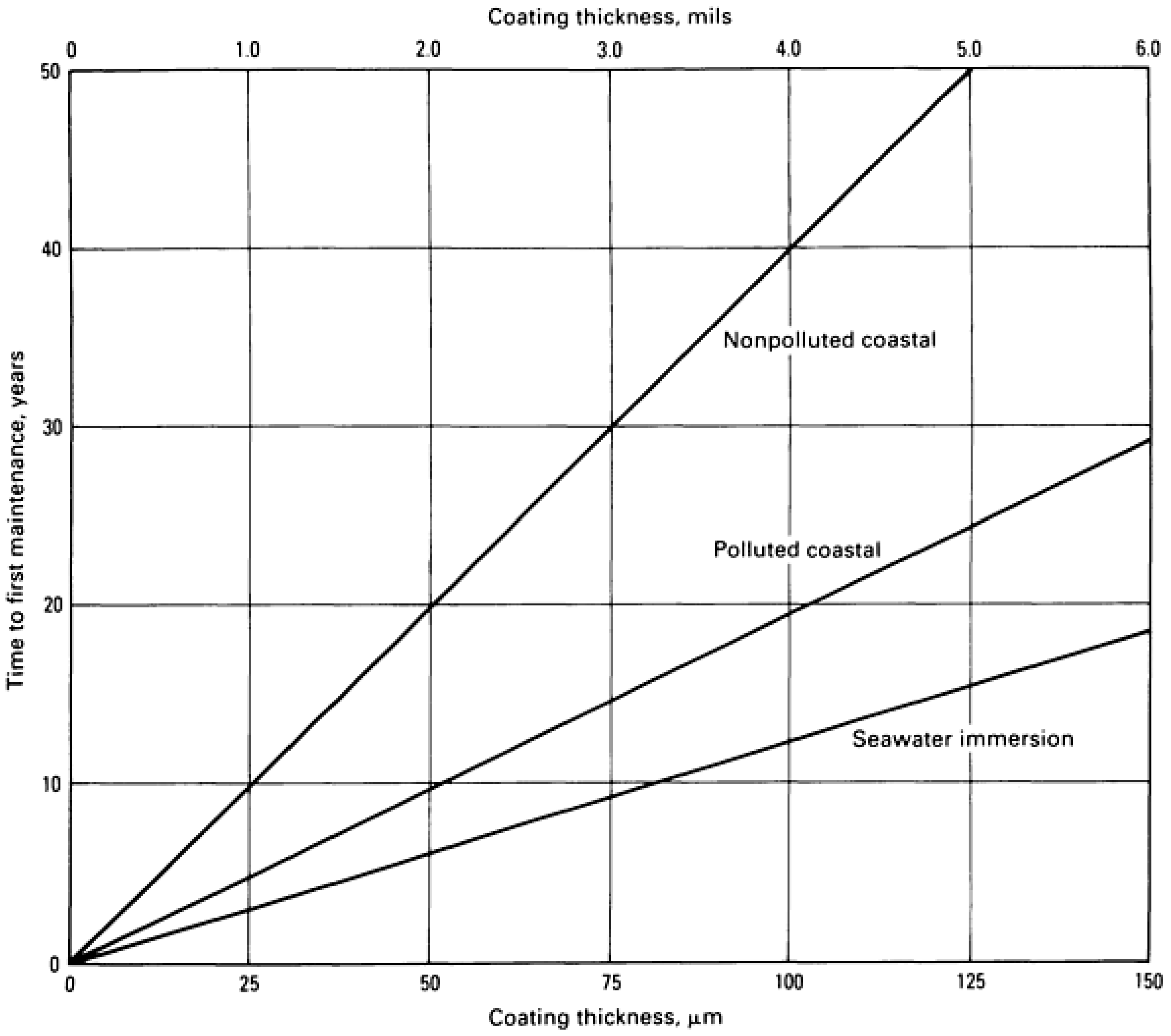


Fig. 6 Time to first maintenance versus coating thickness for hot dip galvanized coatings in seawater immersion and sea spray exposures. Source: Ref 11

Freshwater Performance. The corrosion protection mechanism of zinc in freshwater is similar to that in atmospheric exposures. The corrosion rate depends on the ability of the coating to develop a protective layer of adherent basic zinc salts. This layer denies access to the coating by oxygen and slows the rate of attack. The ability of the water to form scale depends on a number of variables, such as the pH of the water, hardness, total alkalinity, and total dissolved solids. Table 19 demonstrates the effects of various water chemistries on the relative corrosion rates of zinc.

Table 19 Corrosion of zinc in different types of water

Water type	Attacking substances	Passivating substances	Properties of corrosion products		Relative corrosion rate
			Solubility	Adhesion	

Hard water	Oxygen, CO_2	Calcium, magnesium	Very low	Very good	Very low
Seawater	Oxygen, CO_2, Cl^-	Calcium, magnesium	Low	Very good	Moderate
Soft with free air supply	Oxygen, CO_2	. . .	High	Good	High
Soft or distilled with poor air supply	Oxygen	. . .	Very high	Very poor	Very high

Source: Ref 10

Water Temperature. The corrosion rate of zinc in water, and therefore that of the galvanized coating, increases with temperature to between 65 and 70 °C (150 and 160 °F), at which point the rate begins to decrease (Fig. 7). At temperatures near 70 °C (160 °F), a reversal in potential may occur where zinc coatings become cathodic to iron. Low oxygen and high bicarbonate contents favor reversal, but the presence of oxygen, sulfates, and chlorates tends to maintain the natural anodic state of the zinc.

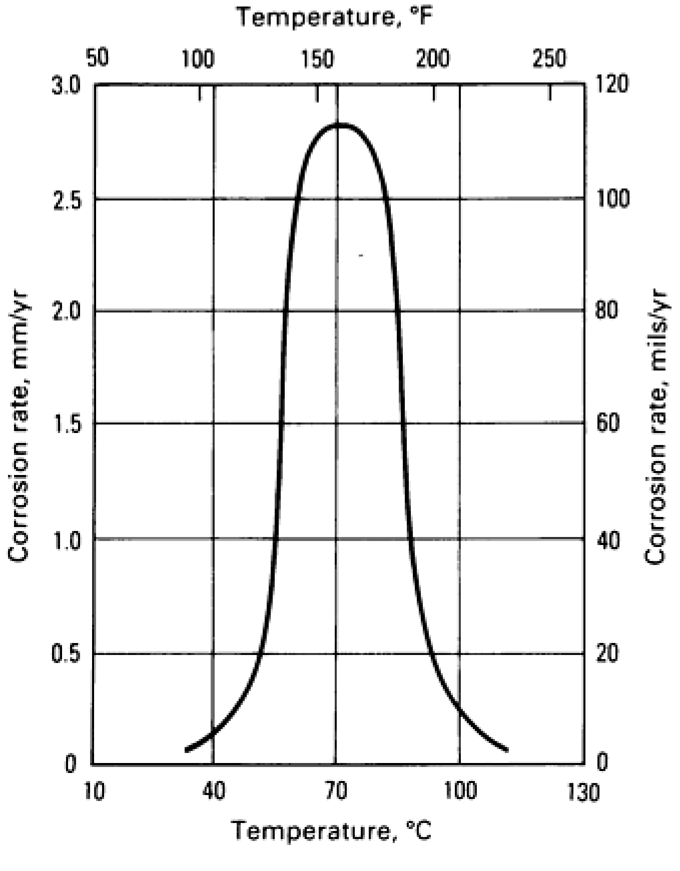


Fig. 7 Influence of water temperature on the corrosion rate of zinc in distilled, aerated water. Source: Ref 12

Water pH. Zinc is an amphoteric metal with the capacity to passivate by means of protective layers. The corrosion rate of zinc decreases with increasing pH and reaches a minimum at 12.0 to 12.5. Most waters are in the pH range of 6 to 8. The scale-forming ability of the water and the concentration of dissolved ions in the water are more important influences on the corrosion rate than pH in this practical exposure range.

Performance in Soils. The corrosion rate and performance of galvanized steels in soils are a function of the type of soil in which the steel is located. Soils can vary considerably in composition and can contain bound and unbound salts, organic compounds, products of weathering, bacteria and other microorganisms, dissolved gases (such as hydrogen, oxygen, and methane), acids, and alkalies. Soils vary in permeability, depending on the soil structure. Although the concentration of oxygen is lower in soils than in air, the CO_2 concentration is higher. Variation among soils is high, and corrosion conditions are complicated.

In general, soils in coarse, open textures are often aerated, and the performance of galvanized steel would be expected to be similar to that in air. In soils with fine textures and high water-holding capacities, such as clay and silt-bearing soils, corrosion rates are likely to be higher. Soil resistivity is recognized as a reliable method of predicting the corrosivity of soils. High-resistivity (poor conducting) soil would be less corrosive than low-resistivity (good conducting) soil. Dry soils are poor conductors and are the least corrosive to zinc.

Painting Galvanized Steel. Galvanized coatings, when used without further treatment, offer the most economical corrosion protection for steel in many environments. The galvanized coating makes an excellent base on which to develop a paint system. Painting of galvanized steel is desirable for aesthetics, as camouflage, as warning or identification markings, to prevent bimetallic corrosion, or when the anticipated environment is particularly severe.

In corrosive atmospheres, a duplex system of galvanized steel top coated with paint has several advantages that make it an excellent system for corrosion prevention:

- The life of the galvanized coating is extended by the paint coating
- The sacrificial and barrier properties of the zinc coating are used if a break occurs in the paint film
- Undercutting of damaged paint coatings, a major cause of failure of paints on steel, does not occur with a zinc substrate
- Surface preparation of a weathered zinc surface for maintenance painting is easier than that for rusted steel

The galvanized coating prevents rusting of steel by acting as a barrier against the environment and by sacrificially corroding to provide cathodic protection. Painting the galvanized coating extends the service life of the underlying zinc because the barrier property of the paint delays the reaction of zinc with the environment. If a crack or other void occurs in the paint and exposes the galvanized coating, the zinc corrosion products formed tend to fill and seal the void; this delays further reaction.

When painted steel is exposed to the environment, rust forms at the steel/paint interface. Because rust occupies a volume several times that of the steel, the expansion resulting from rusting leads to rupture of the steel/paint bond. Further, rust is porous; it accumulates moisture and other reactants, and this increases the rate of attack on the steel. The result is undercutting, flaking, and blistering of the paint film, leading to failure of the paint coating (Fig. 8). Zinc corrosion products occupy a volume only slightly greater (20 to 25%) than zinc; this reduces the expansive forces and conditions that lead to paint failure.

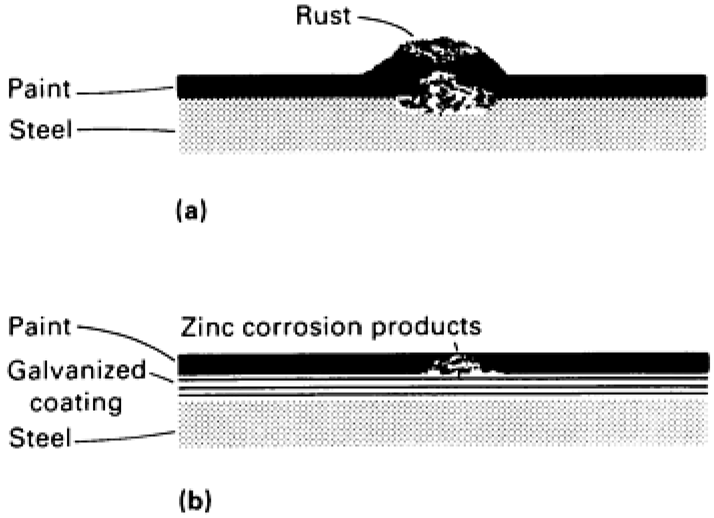


Fig. 8 Illustration of the mechanism of corrosion for painted steel (a) and painted galvanized steel (b). (a) A void in the paint results in rusting of the steel, which undercuts the paint coating and results in further coating degradation. (b) A void in the coating of a painted galvanized steel is sealed with zinc corrosion products; this avoids the undercutting seen in (a) and prevents further deterioration of the painted coating.

A coating system consisting of painted galvanized steel provides a protective service life up to 1.5× that predicted by adding the expected life times of the paint and the galvanized coating in a severe atmosphere (Ref 13). This is demonstrated in Table 20. The synergistic improvement is even greater for mild environments (Ref 14, 15).

Table 20 Synergistic protective effect of galvanized steel/paint systems in atmospheric exposure

Type of Atmosphere	Galvanized steel			Paint			Galvanized plus paint		
	Thickness		Service life[a], years	Thickness		Service life[a], years	Thickness		Service life[a], years
	µm	mils		µm	mils		µm	mils	
Heavy industrial	50	2	10	100	4	3	150	6	19
	75	3	14	150	6	5	225	9	29
	100	4	19	100	4	3	200	8	33
	100	4	19	150	6	5	250	10	36
Metropolitan (urban)	50	2	19	100	4	4	150	6	34
	75	3	29	150	6	6	225	9	52
	100	4	39	100	4	4	200	8	64

	100	4	39	150	6	6	250	10	67
Marine	50	2	20	100	4	4	150	6	36
	100	4	40	100	4	4	200	8	66
	100	4	40	150	6	6	250	10	69

Source: Ref 14

(a) Service life is defined as time to about 5% red rust.

Paint adhesion is the primary concern in painting galvanized steel. The surface of the zinc is nonporous and does not allow mechanical adhesion of the paint. Surface contaminants, such as oils, waxes, or postgalvanizing treatments, also effect adhesion. A fresh zinc surface is reactive to certain paint ingredients, such as fatty acids; this can produce zinc soaps and disrupt the zinc-paint bond.

Galvanized coatings can be successfully painted immediately after galvanizing or after extended weathering. The deliberate use of weathering is not recommended, because weathering may not be uniform, the time required is long (6 to 17 months), hygroscopic impurities can form that may be difficult to remove, and there is exposure to atmospheric pollutants.

Chemical etchants, such as acids or copper sulfate, should not be used for surface preparation. The action of these chemicals is difficult to control, the resulting surface may be nonuniform, and the galvanized coating could be damaged if allowed to remain in extended contact with the chemicals. Long-term adhesion will suffer with this type of treatment, although initial adhesion may be obtained.

Mechanical roughening of the zinc surface through the use of a light blast can provide a good surface for painting. However, careful control of the blast pressure and flow rate must be exercised to avoid excessive removal of the galvanized coating.

Initial adhesion of the paint can be achieved through the use of a pretreatment primer to provide an adequate base for further coating. Long-term adhesion is obtained by the selection of a top coat that is compatible with the primer and galvanized steel. Additional information on various paints can be found in the sections "Organic Coatings" and "Painting With Zinc-Rich Paints" in this article.

Hot Dip Aluminum Coatings

Although zinc is well established as a coating material, aluminum is gaining in popularity. Aluminum-coated steel products are used successfully in corrosive and oxidizing environments in which the temperature ranges from that of outdoor exposure to 1150 °C (2100 °F). Aluminum coatings protect steel from attack by forming a very resistant barrier between the corrosive atmosphere and the steel. The aluminum oxide that forms on the aluminum surface is highly resistant to a wide range of environments.

The process of applying a hot-dipped aluminum coating to steel substrates is also referred to as aluminizing. As in hot dip galvanizing, aluminizing can be carried out by batch or continuous processes. Additional information on batch and continuous hot dip aluminum coating processes can be found in Ref 16 and 17.

The batch aluminizing process consists of cleaning, heating, fluxing, and coating. Organic soils can be removed from the parts to be coated by alkaline cleaning and water rinsing. Steel parts are then descaled by abrasive blasting or acid pickling, followed by rinsing and drying.

Fluxing dissolves any oxide film left on the part surface after cleaning and is carried out in either molten-salt baths or aqueous solutions prior to hot dipping. The salt bath is usually maintained at approximately 600 °C (1100 °F) and the parts are immersed in the bath from 30 s to several minutes. Immediately after fluxing, the parts are immersed in the molten-aluminum bath at 700 °C (1300 °F).

Temperature control of the molten aluminum is important in order to control the coating thickness. Temperatures that are too high increase the thickness of the intermetallic layer and decrease the thickness of the pure aluminum coating. Immersion time must also be closely controlled. Coating thickness is also affected by substrate composition and aluminum coating bath composition.

Parts that can be aluminum hot dipped include fasteners, poppet valves, and blades and nozzle vanes for gas turbines. Parts with small threads are not considered practical, nor are parts that may nest during the coating process.

Continuous Aluminizing. The aluminum dip coating of continuous steel strip, sheet, or tubing is produced on continuous in-line equipment similar to that used for galvanizing. The process consists of surface preparation, heat treatment, and immersion coating with aluminum. Surface preparation may take place in an oxidizing furnace or in a nonoxidizing preheater; if an oxidizing furnace is used, the surface oxides are reduced in a suitable atmosphere. The immersion time, the temperature of the steel before and after immersion, and the temperature of the molten aluminum must be controlled to prevent the formation of an excess of iron-aluminum interfacial alloy. More detailed information on processing of continuous hot-dipped aluminum coatings can be found in the articles "Surface Preparation for Continuously Applied Coatings" and "Continuous Hot Dip Coatings" in this Volume.

Microstructure of Aluminum Coatings. Two types of aluminum coatings are commercially significant. Type 2 uses commercially pure aluminum for the coating, and Type 1 uses an aluminum alloy containing 5 to 11% Si. The microstructure of the Type 2 coating shows a layer of aluminum, often with scattered iron-aluminum intermetallic particles, bonded to the steel substrate by an iron-aluminum intermetallic layer (Fig. 9). This intermetallic layer forms a distinctive serrated boundary with the steel and is generally identified as Fe_2Al_5, although some investigations have found additional iron-aluminum compounds (Ref 18).

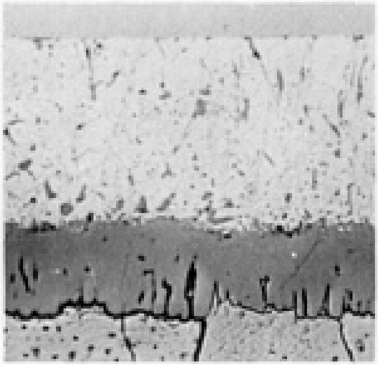


Fig. 9 Microstructure of type 2 aluminum coating on steel. This coating forms a layer of essentially pure aluminum (top) with scattered gray particles of aluminum-iron; the light gray center layer is aluminum-iron, and the bottom layer is the base steel. 1000×

When silicon is added to form a Type 1 coating, a different microstructure results. The intermetallic layer becomes narrower and smoother (Fig. 10), resulting in increased coating ductility relative to the Type 2 coating. With increasing silicon additions, the coating bath temperature can also be lowered, and the growth of the intermetallic layer is further inhibited.

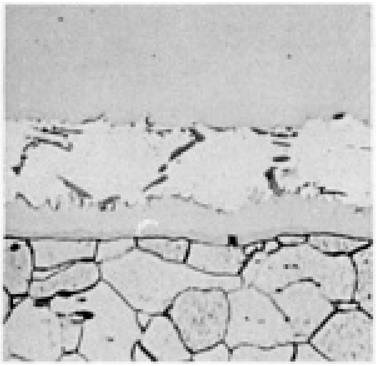


Fig. 10 Microstructure of type 1 aluminum coating on steel. From top: a nickel filler, aluminum-silicon alloy, aluminum-silicon-iron alloy, and steel base metal. 1000×

Beryllium, copper, and some other elements have also been found to retard the growth of the intermetallic layer. Additions of these and other elements to the steel itself can also retard the growth of the alloy layer. The way in which these elements reduce the growth is not understood, although silicon appears to act after being incorporated into the intermetallic layer itself (Ref 19).

Atmospheric Corrosion Resistance. Numerous tests have shown that Type 1 and Type 2 aluminum coatings provide excellent atmospheric corrosion protection for steel. The major difference between the two coatings is the darkening and pinpoint rust formation that occur very early on Type 1 coatings. Weight loss measurements show that overall corrosion losses are nearly identical for both coatings (Ref 20). However, because of this appearance factor, the major use for Type 1 coatings is for high-temperature resistance, especially in automotive exhaust components. Typical atmospheric corrosion data for Type 2 aluminum-coated steel are given in Table 21. Galvanized steel data are included for comparison purposes. On the basis of this and similar investigations, a Type 2 aluminum coating will provide substantially longer life than a galvanized coating of equivalent thickness.

Table 21 Coating thickness losses for galvanized steel and type 2 aluminized steel in atmospheric exposure

Years exposed	Middletown, OH				Kure Beach, NC			
	G90[(a)]		Type 2		G90		Type 2	
	μm	mils	μm	mils	μm	mils	μm	mils
1	2.6	0.1	0.5	0.02	7.0	0.28	1.4	0.04
2	5.2	0.2	0.7	0.028	8.6	0.34	2.4	0.09
4	9.3	0.37	1.2	0.047	12.7	0.5	3.8	0.15
6	14.5	0.57	3.1	0.12	16.2	0.64	4.5	0.18
10	24.4	0.96	2.9	0.11	23.5	0.93	6.0	0.24

Source: Ref 20

(a) G90 galvanized steel has a coating weight of 0.90 oz/ft^2 (270 g/m^2).

In 1961, the American Society for Testing and Materials (ASTM) exposed aluminum-coated wire (all hot dip coated wire is made with a Type 1 coating) and galvanized wire at marine, industrial, and rural atmosphere test sites. Results from unfabricated wire show that (Ref 21):

- Aluminum coatings are rust free 1.3 to 2.2 times longer than zinc coatings of the same thickness (43 μm) in industrial and marine atmospheres
- Zinc coatings are rust free longer at the rural test site, an unexpected result that is possibly explained by the nonuniformity of the aluminum coating. Fabricated wire products made from precoated wire showed virtually no difference between aluminum and zinc coatings

Corrosion Mechanism. Because contact with oxygen results in the formation of a protective aluminum oxide layer, other components of the atmosphere must be responsible for the corrosion of the aluminum coating. Careful analysis of the corrosion products formed on aluminum coatings in industrial and marine atmospheres has shown that the predominant product is an amorphous, hydrated aluminum sulfate. This suggests that SO_2 is an important factor in atmospheric corrosion. This sulfate compound also appears to be more protective than the sulfates found on zinc coatings, which is consistent with observed corrosion behavior.

Aqueous Corrosion Resistance. Aluminum-coated steel has not generally been used in situations requiring aqueous corrosion resistance. There are no counterparts to galvanized water tanks, galvanized pipe, or galvanized pails. However, since 1979 the Type 2 aluminum coating has been used in the manufacture of corrugated steel pipe.

Corrosion in Natural Waters. Numerical data on the corrosion resistance of aluminum coatings are few because of the lack of use. Behavior is usually inferred from aluminum alloy data, but this could be inappropriate because of differences in structure and composition. Nonetheless, studies on aluminum alloys have shown that the air-formed aluminum oxide is destroyed after immersion (Ref 22). Corrosion resistance then depends on the oxide being re-formed from dissolved oxygen quicker than the aluminum is attacked by other ions, such as chlorides (Cl^-), nitrates (NO_3^-), or sulfates (SO_4^{2-}). With the protective aluminum oxide layer in place, the normal mode of failure is pitting, not general dissolution.

In general, soft waters are the least aggressive toward aluminum. The oxide is regarded as stable from pH 5 to 9. However, specific ions can change this range of stability. There is also some evidence that pitting may increase as the pH varies from neutral, but increasing the flow rate, especially at the more extreme pH values, can alleviate pitting. Small concentrations of copper and some other heavy metals can also lead to accelerated pitting. Pitting and corrosion have been observed in less than 3 years on aluminum-coated roofing panels exposed to stagnant water (Ref 23). On the other hand, when under a constant flow of relatively soft neutral pH water, corrugated steel pipe made from Type 2 aluminum-coated steel gives excellent service (Ref 24).

Corrosion in Seawater. Unlike aluminum alloys, aluminum-coated steel is not used in seawater. Corrosion rates are too high to provide economical use except as part of a more complex protection system. Typical thickness loss after 1 year of immersion in seawater has been reported to be 198 μm (7.8 mils) for Type 1 and 38 μm (1.5 mils) for Type 2 aluminum-coated sheets (Ref 20).

Corrosion in Soils. As with aqueous environments, aluminum-coated steel does not have a history of use in soils. Behavior would be expected to depend on pH, resistivity, and especially the chemistry of the soil. The mode of failure should be pitting.

Elevated-Temperature Exposure. Successful application of aluminum-coated steel for resistance to oxidation and corrosion at elevated temperatures depends on the physical and mechanical properties of the alloy chemical bond between the aluminum and the steel. It is important that the hot strength of the steel be suitable for the stress and temperatures

encountered. Low-carbon HSLA steels alloyed with titanium or niobium offer improved high-temperature creep resistance when used as substrates for aluminum coatings.

Aluminum coatings that contain from 5 to 11% Si minimize the thickness of the iron-aluminum alloy bond and improve formability. Undiffused, such coatings retain excellent heat reflectivity at temperatures to 480 °C (900 °F).

Above 480 °C (900 °F), further alloying occurs between the aluminum coating and steel base. Because the rate of alloying is dependent on time and temperature, all coating converts to aluminum-iron-silicon alloy with sufficient time at temperature. The refractory alloy formed is extremely heat-resistant and resistant to spalling up to 680 °C (1250 °F). Spalling at service temperatures above 680 °C (1250 °F) can be overcome by the use of heat-resistant aluminized steel that contains sufficient titanium to stabilize carbon and nitrogen as well as maintain excess titanium in solution (Ref 25).

Table 22 lists applications for steels that have been prepared by batch hot dipping in aluminum and then heat-treated to diffuse the aluminum into the steel. This treatment eliminates spalling and provides an impervious protective coating during high-temperature service.

Table 22 Applications of diffused aluminum hot dip coatings for resistance to oxidation and corrosion at 455 to 980 °C (850 to 1800 °F)

Product and base metal	Type of service
Heat treating equipment	
Burner pipes, 5Cr-0.5Mo	Oxidation, 870 °C (1600 °F)
Fixtures, low-carbon and medium-alloy steels	Carburizing, carbonitriding
Flue stacks, low-carbon steel	Oxidation, sulfur corrosion
Furnace insulation supports, low-carbon and medium-alloy steels	Oxidation, 540-650 °C (1000-1200 °F)
Pyrometer protection tubes, 310 and 316 stainless steel, low-carbon steel	Oxidation, 980 °C (1800 °F)
Heat exchanger components	
Boiler soot blowers, 1Cr-0.5Mo	Oxidation, sulfur attack
Boiler tubing, 2Cr-05.Mo	Oxidation, 540-595 °C (1000-1100 °F)
Cylinder barrel, air-cooled engine, Nitralloy	Oxidation to 480 °C (900 °F)
Preheater tubing, 1Cr-0.5Mo	Oxidation, 650 °C (1200 °F)
Tubing, low-carbon steel, 1.5Cr-0.5Mo	Hydrogen sulfide gases
Fasteners	

Steel fasteners for chemical piping and boilers	Oxidation to 480 °C (900 °F)
High-temperature fasteners	Oxidation to 760 °C (1400 °F)
Studs, 4140, for chemical and oil refineries	Oxidation and ease of removal after service at 480 °C (900 °F)
Miscellaneous equipment	
Chemical reactor tubing, low-carbon steel	Carbonization, iron contamination
Chimney caps, low-carbon steel	Oxidation and corrosion
Recuperator tubing, 2.5Cr-0.5Mo	Oxidation and sulfidation
Refinery tubing, 304 stainless steel, 2.25Cr-1Mo	Oxidation and sulfidation
Sulfuric acid converters, 5Cr-0.5Mo	Sulfur dioxide corrosion, 705 °C (1300 °F)

The use of aluminum-coated plain carbon steel for complicated heat-treating fixtures subjected to temperatures lower than 870 °C (1600 °F) may decrease overall fixture cost in comparison to fixtures made of the highly alloyed austenitic steels normally used for this application. Figure 11 shows the effects of coating thickness and operating temperature on oxidation resistance for coated and uncoated heat-treating fixtures made of 1020 steel.

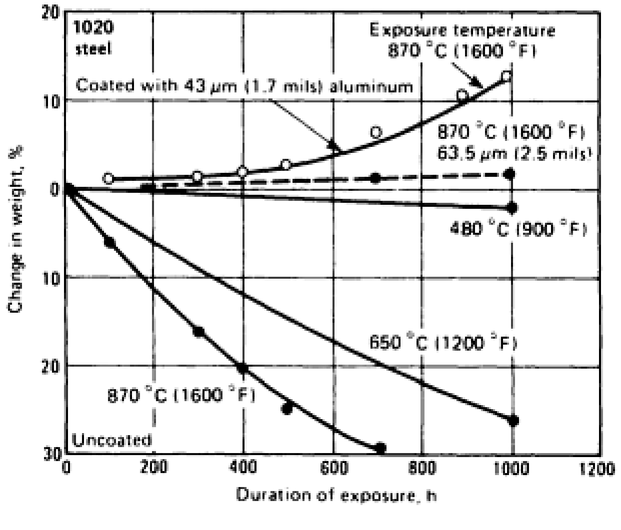


Fig. 11 Effects of coating thickness and exposure temperature on oxidation of coated and uncoated steel. Oxidation at 480 to 870 °C (900 to 1600 °F). Steel 6.4 mm ($\frac{1}{4}$ in.) thick was completely oxidized after 700 h at 870 °C (1600 °F).

Compared to solid stainless steel, aluminum-coated carbon steel offers greater resistance to attack by hydrogen sulfide. One set of test data indicated that, at 595 °C (1110 °F), aluminized carbon steels offer more than 100 times the resistance

of 18-8 stainless steel to pure hydrogen sulfide. Other data have shown them to be 25 times more resistant than straight chromium steel.

References cited in this section

6. Hot Dipping, *Materials, Finishing and Coating, Tool and Manufacturing Engineers Handbook,* C. Wick and R.F. Veilleux, Ed., Society of Manufacturing Engineers, 1985, p 23-11
7. Hot Dipping, *Materials, Finishing and Coating, Tool and Manufacturing Engineers Handbook,* C. Wick and R.F. Veilleux, Ed., Society of Manufacturing Engineers, 1985, p 23-12
8. R.M Burns and W.W. Bradley, *Protective Coatings for Metals,* 2nd ed., Reinhold, 1955, p 128
9. S.K. Coburn, C.P. Larrabee, H.H. Lawson, and G.B. Ellis, Corrosiveness at Various Atmospheric Test Sites as Measured by Specimens of Steel and Zinc, in *Metal Corrosion in the Atmosphere,* STP 435, American Society for Testing and Materials, 1968, p 371-372
10. C.J. Sunder and W.K. Boyd, *Zinc: Its Corrosion Resistance,* 2nd ed., International Lead Zinc Research Organization, 1983, p 113-150
11. "Code of Practice for Protective Coating Iron and Steel Structures Against Corrosion," BS 493, British Standards Institution, 1977, p 23
12. P.C. Birkemoe, W.D. Crouch, and W.H. Munse, "Design Criteria for Joining Galvanized Structurals," Annual Report, ZM-96, International Lead Zinc Research Organization, April 1969
13. J.F.H. van Eijnsbergen, Twenty Years of Duplex Systems, *Metallwissenschaft Technik,* Vol 29 (No. 6), June 1975
14. J.F.H. van Eijnsbergen, Supplement (to Twenty Years of Duplex Systems), *Thermisch Verzinken,* Vol 8, 1979
15. D.S. Carr, "Performance of Painted Galvanized Steel," Paper presented at the Semi-Annual Meeting, Houston, TX, American Hot Dip Galvanizers Association, Sept 1982
16. Aluminum Coatings, in *ASM Specialty Handbook: Aluminum and Aluminum Alloys,* J.R. Davis, Ed., ASM International, 1993, p 180-195
17. Hot Dipping, *Materials, Finishing and Coating, Tool and Manufacturing Engineers Handbook,* C. Wick and R.F. Veilleux, Ed., Society of Manufacturing Engineers, 1985, p 23-13
18. S.G. Denner, et al., Hot Dip Aluminizing of Steel Strip, *Iron Steel Int.,* June 1975, p 241-252
19. G. Eggler, et al., On the Influence of Silicon on the Growth of the Alloy Layer During Hot Dip Aluminizing, *J. Mater. Sci.,* Vol 21, 1986, p 3348-3350
20. H.F. Graff, Aluminized Steel, in *Encyclopedia of Materials Science and Engineering,* Pergamon Press, 1986, p 138-141
21. V.I. Kelly, in *Atmospheric Corrosion Investigation of Aluminum-Coated, Zinc-Coated, and Copper Bearing Steel Wire and Wire Products (A 12 Year Report),* STP 585, American Society for Testing and Materials, 1975
22. H.P. Godard, et al.,*The Corrosion of Light Metals,* John Wiley & Sons, 1967, p 11
23. L. Allegra, et al., Resistance of Galvanized, Aluminum-Coated, and 55% Al-Zn Coated Sheet Steel to Atmospheric Corrosion Involving Standing Water, in *Atmospheric Corrosion,* W.H. Ailor, Ed., John Wiley & Sons, 1982, p 595-606
24. G.E. Morris and L. Bednar, Comprehensive Evaluation of Aluminized Steel Type 2 Pipe Field Performance, in *Transportation Research Record 1001,* National Research Council, Transportation Research Board, 1984, p 49-60
25. Y.-W. Kim and R.A. Nickola, "A Heat Resistant Aluminized Steel for High Temperature Applications," SAE Technical Paper, Series 300316, SAE Congress, 1980

Hot Dip Aluminum-Zinc Coatings

Many attempts have been made to improve the corrosion resistance of both galvanized and aluminum coatings through alloying. Although combinations of these two elements with each other were known to provide an attractive degree of corrosion resistance, hot dip coatings did not become feasible until the discovery that silicon inhibits the rapid alloying reaction with steel (Ref 26). The 55Al-Zn coating was first available commercially in 1972. This composition was selected from a systematic investigation of aluminum-zinc alloys, with up to 70% Al providing the best combination of galvanic protection and low corrosion rate. Current use varies from metal roofing, for which it is the major coated steel used, to automotive components, appliances, and, most recently, corrugated steel pipe.

Aluminum-zinc alloy coatings of steel sheet and wire are applied on continuous hot dip coating lines with in-line gas cleaning and heat treating of the steel substrate. With a nominal composition of 55% Al, 43.4% Zn, and 1.6% Si, the coating provides the durability and high temperature resistance of aluminum coatings with the sacrificial protection characteristics of zinc coatings. Silicon is added to the coating bath to control growth of an intermetallic layer. Steel sheet and wire products coated with 55% aluminum-zinc alloy are especially useful in applications requiring superior atmospheric corrosion resistance, cut edge protection, and/or high-temperature oxidation resistance. Processing details for aluminum-zinc coatings are given in Ref 16.

Microstructure of 55Al-Zn Coating. The 55Al-Zn coating has a two-phase structure of cored aluminum-rich dendrites and a zinc-rich interdendritic constituent (Fig. 12). This overlay is bonded to the steel substrate by a thin intermetallic layer whose composition is 48% Al, 24% Fe, 14% Zn, and 11% Si. X-ray diffraction suggests a structure similar to $Al_{13}Fe_4$. In addition, silicon particles are often found in the interdendritic region. By volume, the coating is approximately 80% Al + Si and 20% Zn. The effect of cooling rate during solidification is manifested in the spacing between the dendritic arms. Faster cooling (used commercially) results in finer spacing, which improves corrosion resistance.

Fig. 12 Microstructure of an aluminum-zinc coated sheet

Protection by Aluminum-Zinc Alloy Coatings. The 55Al-Zn coating provides both barrier and galvanic protection. Because the zinc-rich constituent is intimately distributed throughout the coating, it will be in contact with exposed steel at any break in the coating and at cut edges. Although less galvanic protection is available than with pure galvanized coatings, the alloy coating lasts longer because the overall corrosion rate is controlled by the aluminum-rich phase, which corrodes much more slowly than zinc.

Atmospheric Corrosion Resistance. Samples of 55Al-Zn-coated steel have been tested in atmospheric exposure for over 20 years. Figure 13 shows thickness loss with time for the first 13 years of exposure in four different atmospheres. Compared to galvanized panels exposed at the same time, the 55Al-Zn coating provides two to six times the corrosion resistance (based on equal coating thicknesses). Although these results were based on pilot line samples, subsequent testing of commercial 55Al-Zn sheet steel for 10 years shows a slightly greater advantage over galvanized steel (Ref 28).

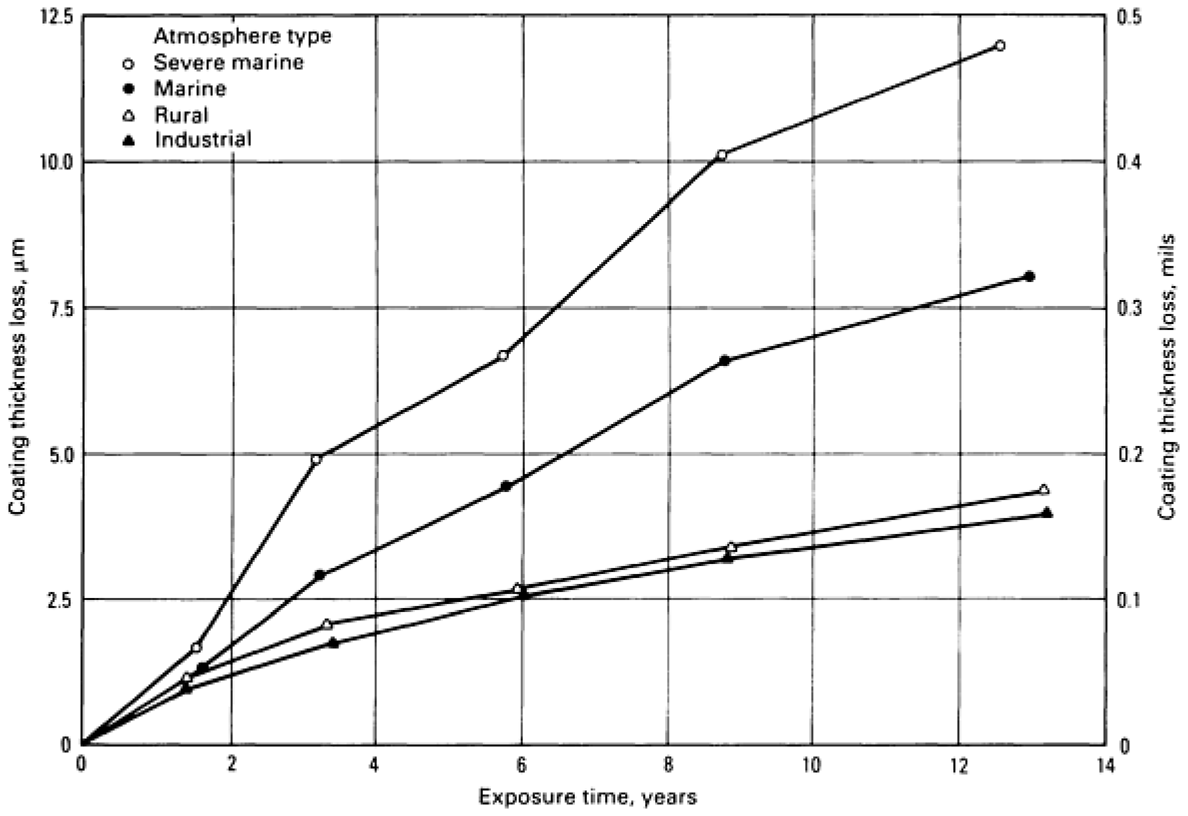


Fig. 13 Coating thickness loss of 55Al-Zn-coated steel in four atmospheres. Source: Ref 27

Corrosion Mechanism. The zinc-rich constituent of the coating has been observed to corrode preferentially. As these regions are removed, their space is taken by corrosion products that become mechanically locked into the interdendritic spaces. These corrosion products are mostly amorphous aluminum or hydrated aluminum-zinc sulfates--similar to the corrosion products found on the coating surface of aluminum and 55Al-Zn coatings. These sulfates are adherent and may help explain the improved durability of the aluminum-zinc coating. Support for this mechanism is also obtained from aqueous corrosion studies in which the corrosion potential is observed to change that of a galvanized coating upon immersion to a value approaching that of aluminum after subsequent corrosion (Ref 29).

Aqueous Corrosion Resistance. The 55Al-Zn coating is finding increased use in applications demanding resistance to aqueous corrosion, especially where wet/dry cycles are obtained.

Corrosion in Natural Waters. As with other coatings, the corrosion of 55Al-Zn coating would be expected to vary with the specific properties of the water. It is not known how water hardness will affect corrosion, but in distilled water (very soft) and distilled water containing 85 mg/L of Cl^- ion, the 55Al-Zn coating is much more resistant than a galvanized coating (Table 23). In similar tests, 55Al-Zn and galvanized panels were immersed for 90 days in distilled water containing 45 ppm of SO_4^{2-} and 10 ppm of Cl^- at pH values from 3 to 11 (Ref 31). The pH was maintained through sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH) additions. As Table 24 demonstrates, the 55Al-Zn retains more coating than the galvanized at all pH values, especially within the 5 to 9 range most characteristic of natural waters.

Table 23 Average coating thickness loss of galvanized and 55Al-Zn-coated steel after 56 days of immersion

Material	Thickness loss	
	Distilled water	85 mg/L NaCl

	µm	mils	µm	mils
Galvanized	1.06	0.042	1.26	0.049
55Al-Zn	0.015	0.0005	0.133	0.005

Source: Ref 30

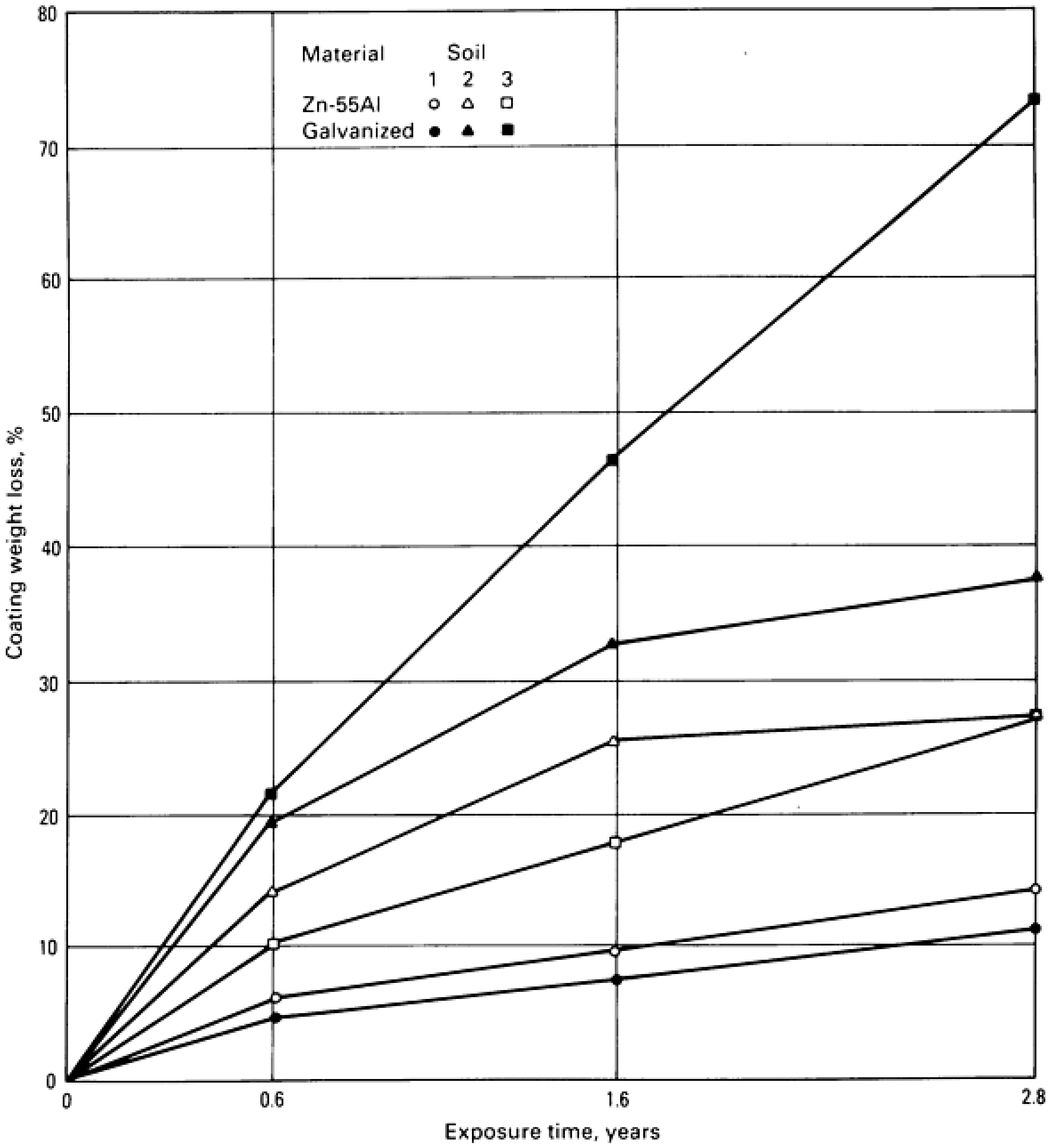
Table 24 Coating weight losses of galvanized and 55Al-Zn-coated steels after a 90-day immersion in water of various pHs

pH	Coating weight loss, %	
	Galvanized	55Al-Zn
3	32	31
5	45	2
7	41	4
9	40	8
11	33	26

The longest service history of exposure to natural water for the 55Al-Zn coating is obtained from corrugated steel pipe installed between October, 1973, and October, 1974 (Ref 32). Water chemistry, pH, and resistivity varied widely from site to site and sometimes changed considerably with time. Erosion and abrasion caused additional wear factors.

Overall, 55Al-Zn applied at a coating weight of 180 g/m^2 (0.6 oz/ft^2) provides greater durability than a 600 g/m^2 (2 oz/ft^2) galvanized coating. Continued monitoring of these sites suggests an average of 10 years of additional life for the 55Al-Zn coating in the pipe inverts, the point of severest corrosion and wear.

Corrosion in Soils. There are few performance data for the 55Al-Zn coating in soil. The corrugated steel pipe exposures described previously provide the longest history of soil exposure, but because most culverts fail from the inside, exterior soil corrosion was not monitored closely in these tests. Some data are available from laboratory tests in which 16-gage coated steel panels were buried in test soils and monitored for coating loss (Ref 32). Figure 14 shows coating loss and the soil characteristics. These data suggest that the 55Al-Zn coating should provide corrosion resistance in soil similar to that of a galvanized coating.



Soil number	Description	pH	Resistivity, Ω· cm
1	Native shale, clay: wet to dry	4	76,000
2	Native shale with chloride and sulfate salts: wet and dry	5	35,000
3	Native shale, clay, and bentonite with chloride and sulfate salts: wet	6	1,700

Fig. 14 Corrosion of galvanized steel and 55Al-Zn-coated steel in three soils. Soil characteristics are also given.

Source: Ref 32

Hot Dip Lead Alloy (Terne) Coatings

Long terne steel sheet is carbon steel sheet that has been coated by bath or continuous hot dip processes with terne metal (lead with 3 to 15% Sn). This coated sheet is duller in appearance than conventional tin-coated sheet; this accounts for the name terne, which means dull or tarnished in French. The smooth, dull coating gives the sheet corrosion resistance, formability, excellent solderability, and paintability. The term long terne is used to describe terne-coated sheet, whereas short terne is used for terne-coated plate.

Applications. Because of its unusual properties, long terne sheet has been adapted to a wide variety of applications. Its principal use is in automotive gasoline tanks. Its excellent solderability and special corrosion resistance make the product well-suited for this application. Other typical applications include:

- Automotive parts such as air conditioners, air filters, cylinder head covers, distributor tubes, oil filters, oil pans, radiator parts, and valve rocker arm covers
- Caskets
- Electronic chassis and parts for radios, tape recorders, and television sets
- File drawer tracks
- Fire doors and frames
- Furnace and heating equipment parts
- Railroad switch lamps
- Small fuel tanks for lawn mowers, power saws, tractors, and outboard motors

Forming. Long terne sheet is often produced in accordance with ASTM A 308. For applications requiring good formability, the coating is applied over commercial quality, drawing quality, or drawing quality special killed low-carbon steel sheet. The terne coating acts as a lubricant and facilitates forming, and the strong bond of the terne metal allows it to be formed along with the base metal. When higher strength is required, the coating can be applied over low-carbon steel sheet of structural (physical) quality, although this will result in some loss in ductility. The mechanical properties of long terne sheet are essentially the same as those of hot dip galvanized or aluminized steel sheet.

Corrosion Characteristics. Lead has excellent corrosion resistance, and terne metal is principally lead, with 3 to 15% tin added to react with the steel to form a tight intermetallic bond. However, because lead does not offer galvanic protection to the steel basis metal, care must be exercised to avoid scratches and pores in the coating. Small openings can be sealed by corrosion products of iron, lead, and oxygen, but larger ones can corrode in an environment unfavorable to the steel base metal.

Joining. Long terne sheet can be readily soldered with noncorrosive fluxes using normal procedures because the sheet is already presoldered. This makes it a good choice for applications in which ease of solderability is important, such as television and radio chassis and gasoline tanks. It also can be readily welded by either resistance seam welding or spot welding; however, when the coating is subjected to high temperatures, significant concentrations of lead fumes can be released. Therefore, the U.S. Occupational Safety and Health Administration and similar state agencies have issued standards that must be followed when welding, cutting, or brazing metals containing lead or metals coated with lead or lead alloys.

Painting and Handling Considerations. Long terne sheet has excellent paint adherence, which allows it to be painted using conventional systems; however, it is not usually painted. When painting is done, no prior special surface treatment or primer is necessary, except for the removal of ordinary dirt, oil, and grease. Oiled sheet, however, should be thoroughly cleaned to remove the oil. Alternatively, a wash primer treatment or a paint that will tolerate a slight residue of manufacturing oil can be used.

Long terne sheet normally is furnished dry and requires no special handling. It should be stored indoors in a warm, dry place. Unprotected outdoor storage of coils or bundles can result in white or gray staining of the terne coating. Also, if pores are present in the terne coating, rust staining can occur.

Nickel terne coated steel includes an electrolytic flash coating of nickel (1 to 1.5 g/m^2) underneath a conventional lead-tin coating for enhanced corrosion resistance. Applications are similar to the conventional long terne coatings described above.

Composite Coatings. A variation of long terne coated steel employs a subsequent prepainted organic coating on each surface for some fuel tanks. The outer surface has a zinc-rich organic coating to provide added exterior corrosion protection, while the inner surface has an aluminum-rich organic coating to augment the lead-tin coatings resistance to gasoline, and low concentrations of methanol- and ethanol-containing fuels.

References cited in this section

16. Aluminum Coatings, in *ASM Specialty Handbook: Aluminum and Aluminum Alloys,* J.R. Davis, Ed., ASM International, 1993, p 180-195
26. J.C. Zoccola, et al., Atmospheric Corrosion Behavior of Aluminum-Zinc Alloy Coated Steel, in *Atmospheric Factors Affecting the Corrosion of Engineering Metals,* STP 646, American Society for Testing and Materials, 1978, p 165-184
27. H.E. Townsend and J.C. Zoccola, Atmospheric Corrosion Resistance of 55% Al-Zn Coated Sheet Steel: 13-Year Test Results, *Mater. Perform.,* Vol 18, 1979, p 13-20
28. H.E. Townsend and A.R. Borzillo, Twenty-Year Atmospheric Corrosion Tests of Hot Dip Coated Sheet Steel, *Mater. Perform.,* to be published
29. J.H. Payer, Electrochemical Methods for Coatings Study and Evaluation, in *Electrochemical Techniques for Corrosion,* R. Baboian, Ed., National Association of Corrosion Engineers, 1977
30. J.B. Horton, et al., Corrosion Characteristics of Zinc, Aluminum, and Al-Zn Alloy Coatings on Steel, in *Proceedings of the Sixth International Congress on Metallic Corrosion* (Sydney, Australia), 1975
31. S.A. Kriner, unpublished research, 1985
32. A.J. Stavros, Galvalume Corrugated Steel Pipe: A Performance Summary, in *Transportation Research Record 1001,* National Research Council, Transportation Research Board, 1984, p 69-76

Electrogalvanizing

The development of continuous electrogalvanizing lines added another dimension to zinc-coated steel, that is, very thin, formable coatings ideally suited to deep drawing or painting. Zinc is electrodeposited on a variety of mill products by the steel industry: sheet, wire, and, in some cases, pipe. Electrogalvanizing at the mill produces a thin, uniform coat of pure zinc with excellent adherence. The coating is smooth, readily prepared for painting by phosphatizing, and free of the spangle that is characteristic of some other zinc coatings.

Electrogalvanized steel is produced by electrodepositing an adhering zinc film on the surface of sheet steel or wire. These coatings are not as thick as those produced by hot dip galvanizing and are mainly used as a base for paint. Processing details applicable to electrogalvanizing can be found in the article "Continuous Electrodeposited Coatings" in this Volume.

The coating produced on strip coils or sheets has a coating weight in the range of less than about 18 to 60 g/m^2 (0.06 to 0.2 oz/ft^2), or 1.3 to 4.3 μm (0.05 to 0.17 mil) thick on each side. A small amount carries considerably less--approximately 7.6 g/m^2 (0.025 oz/ft^2), or 0.5 μm (0.21 mil) on each side.

Zinc is usually electrodeposited on steel wire in the range of 90 to 915 g/m^2 (0.3 to 3 oz/ft^2). The diameter of plated wire (including wire that is cold drawn after plating) usually ranges from 0.23 to 4.9 mm (0.009 to 0.192 in.). Steel carbon contents range from 0.08 to 0.85%. Tensile strengths range from 345 to 2070 MPa (50 to 300 ksi). Heat-treated and coated wire can be cold drawn to approximately 95% reduction in area, depending on chemical composition, heat treatment, and diameter.

Nature of the Electrogalvanized Coating. The pure zinc coating deposited is highly ductile. Because of its excellent adhesion, electrogalvanized steel strip and wire have good working properties, and the coating remains intact after severe deformation.

Electrodeposited zinc coatings are simpler in structure than hot dip galvanized coatings. They are composed of pure zinc and have a homogeneous structure. Surfaces have a smooth texture whose appearance can be varied by additives and special treatments in the plating bath. They can be used where a fine finish is needed.

Electrogalvanizing provides adequate protection for many types of mild exposures. These coatings are frequently treated with chromate conversion solutions to improve appearance, reduce staining, and retard the formation of white corrosion products under high-humidity conditions.

Advantages and Limitations. In electrogalvanizing, steel strip or wire is continuously fed through suitable entry equipment, a series of washes and rinses, and a plating bath. Either an acid sulfate zinc or cyanide zinc bath is used as the plating bath. Both produce even, adhering zinc deposits. Although brighteners are not used for electrogalvanizing, grain refiners are usually added to help produce a fine, tightknit zinc surface on the steel.

Zinc electrodeposits are considered to have the best adhesion of any metallic coating. Good adhesion depends on very close physical conformity of the coating with the base metal. Therefore, particular care must be taken during initial cleaning. Electrodeposition affords a continuous process for applying zinc coatings to parts that cannot be hot dipped. They are especially useful where a high processing temperature could damage a part.

Applications. Electrogalvanized sheets are produced in various tempers suitable for simple bending or forming, for curving, and for rolling into cylinders without fluting. Spot welding is easily accomplished if care is taken.

Electrogalvanized steel is easily prepared to receive decorative finishes. Much of it is produced with a phosphate treatment or an organic coating. The phosphate treatment provides an adequate surface for a good bond with organic finishing materials. Organic coating applied over electrozinc thus treated maintains good adhesion in adverse conditions, such as sudden changes in temperature and high humidity. Phosphated electrogalvanized steel is used for parts subject to atmospheric corrosion or salt spray and for parts that will be lacquered or painted. Phosphate treatment increases corrosion resistance markedly, particularly in atmospheres with a high sulfur content.

Electrogalvanized sheet is used for manufacturing water cooler housings, exterior panels of ranges, freezers, dryers, washers, air conditioners, and other major appliances. It is used for deep-drawn parts for kitchen cabinets, refrigerators, and allied products instead of plain cold rolled sheet because zinc holds better in the dies and reduces breakage significantly. Bakery goods and other merchandizing display cases, stud systems for steel building construction, acoustical ceiling members, and television antennas are also made of electrogalvanized steel.

Sheets for automotive applications can be electrogalvanized on one side only. The galvanized side protects against corrosion, and the bare side can take the baked enamel finish required by the outer automobile surface.

Electrogalvanized wire is especially useful in applications in which the wire must be bent, twisted, or wrapped around its own diameter. When formed, the coating does not crack, peel, or flake. Many chain link fences are made from zinc-electrocoated wire because it is not rough and therefore is safe to handle. The wire is used for conveyor belts, twisted wire brushes, chains, baskets, kitchen utensils, staples, cages, bobby pins, clotheslines, and telephone and transmission wire.

Electroplating

Electroplated coatings are applied to steel for corrosion resistance, appearance, solderability, or other special requirements. A wide variety of materials are electroplated on steel, including nickel, chromium, zinc, cadmium, and tin. Multilayer coatings can also be applied by electroplating; an example is the copper-nickel-chromium plating system used for bright automotive trim. This section will review some of the more widely used electroplating processes for steels. More detailed information on each of the processes described below can be found in the articles contained in the Section entitled "Plating and Electroplating" in this Volume.

Surface Preparation for Electroplating

Preparation for plating is one of the most critical of all cleaning operations, because maximum adhesion of the plated coating to the substrate is the major requirement for quality work. Maximum adhesion depends on both the elimination of surface contaminants in order to induce a metallurgical bond whenever possible and the generation of a completely active surface to initiate plating on all areas. In addition to pickling or other descaling operations, adequate cleaning requires multistage cycles, usually comprised of the following steps: (a) precleaning with a solvent to remove most of the soil; (b) intermediate cleaning with alkaline cleaners; (c) electrocleaning to remove the last traces of solids and other contaminants that are especially adherent; (d) acid treatment and surface conditioning to remove light oxide films formed during previous cleaning processes and to microetch the surface; and (e) electrolytic (anodic) desmutting to remove any smut formed during acid pickling of heat treated high-carbon steel parts. Low-carbon steels do not require this desmutting step. Anodic electrocleaning also offers oxidation or conditioning of scale. The oxidized or softened scale is easily removed in subsequent acid pickling. The types of cleaning usually employed in the above steps are:

- *Precleaning:* cold solvent, vapor degreasing, emulsifiable solvent, solvent emulsion spray, or alkaline spray with or without solvent emulsion
- *Intermediate alkaline cleaning:* soak cleaning with 30 to 90 g/L (4 to 12 oz/gal) of cleaner at 80 °C (180 °F) to boiling, spray cleaning with 4 to 15 g/L (0.5 to 2 oz/gal) at 65 to 80 °C (150 to 180 °F), and barrel cleaning with 7.5 to 45 g/L (1 to 6 oz/gal) at temperatures below 80 °C (180 °F)
- *Electrocleaning:* cathodic, anodic, or periodic-reverse
- *Acid treatment:* practice is highly specific for the metal being processed
- *Anodic desmutting:* necessary to remove carbon smut

The ASTM recommended practice for cleaning steels with carbon contents less than 0.35% C is ASTM B 183 (Ref 33); ASTM B 242 covers surface preparation of steels with carbon contents of $\geq$0.35% C (Ref 34). Additional information on cleaning carbon and alloy steels prior to electroplating can also be found in the article "Classification and Selection of Cleaning Processes" in this Volume.

Nickel Plating

Electrodeposits of nickel exhibit a wide variety of properties, depending on composition of the plating bath and operating conditions. They may be classified according to application or appearance as general-purpose, black, and bright. More detailed information on plating bath chemistries and processing parameters can be found in the article "Nickel Plating"in this Volume.

Plating Baths. General-purpose nickel deposits, produced by Watts, sulfamate and fluoborate baths, are essentially sulfur-free. They are used primarily to protect steels against corrosive attack in rural, marine, and industrial atmospheres.

Black nickel deposits are used primarily for decorative effect and to provide nonreflecting surfaces. Black nickel deposits are produced by sulfate or chloride baths containing zinc (Zn^{2+}) and thiocyanate (CNS^{-}) ions.

Bright nickel plating baths are modifications of the Watts nickel solution and contain organic or combined organic and inorganic brightening agents; these additions serve to produce a high degree of brightness, leveling reflectivity, and hardness. A wide variety of additives are used, usually in highly specific combinations. Their function is to produce as brilliant and ductile a deposit as possible over a wide range of current densities and operating conditions. Some of these additives are consumed very slowly during electrolysis; others are consumed more rapidly.

Applications and Properties. Nickel plating is widely used for decorative purposes. Bright nickel plate--especially in combination with a lower layer of sulfur-free, semibright nickel and a much thinner upper layer of chromium--is very widely used over steel to provide a bright and corrosion-resistant finish with a nontarnishing and wear-resistant surface. Typical applications are decorative trim for automotive and consumer products. For best corrosion resistance, the chromium deposit should be microdiscontinuous (microcracked or microporous).

Nickel deposits are also used for nondecorative purposes to improve or modify surface properties such as corrosion resistance, hardness, wear, and magnetic characteristics. For example, in the automotive industry, nickel coatings, generally greater than 125 μm (5 mils) thick, are deposited on pistons, cylinder walls, ball studs, transmission thrust washers, and different pinion cross-shafts to improve wear resistance. The most widely used solution for plating nickel for wear applications is the Watts solution. Its main components are nickel sulfate, nickel chloride, and boric acid. Organic addition agents in the plating solution can increase the hardness and wear resistance mainly by decreasing the grain size. Nickel usually is deposited with a tensile internal stress. Some sulfur compounds can cause the stress to become compressive, but also make the deposit more brittle, especially under elevated-temperature conditions. The nickel sulfamate plating solution produces low-stress deposits. It is possible to codeposit such metals as tungsten and molybdenum with nickel, even though they cannot be plated alone in aqueous solutions. Inclusion of hard particles or those of solid lubricants can also improve the wear or friction properties of electroplated nickel.

Improved wear resistance resulting from the incorporation of SiC particles is shown in Fig. 15. In the test on which the data of Fig. 15 are based, a plated block was pressed against a lubricated steel ring. Further improvement that was due to phosphide precipitates in heat-treated Ni-P-SiC coatings is also seen in this figure.

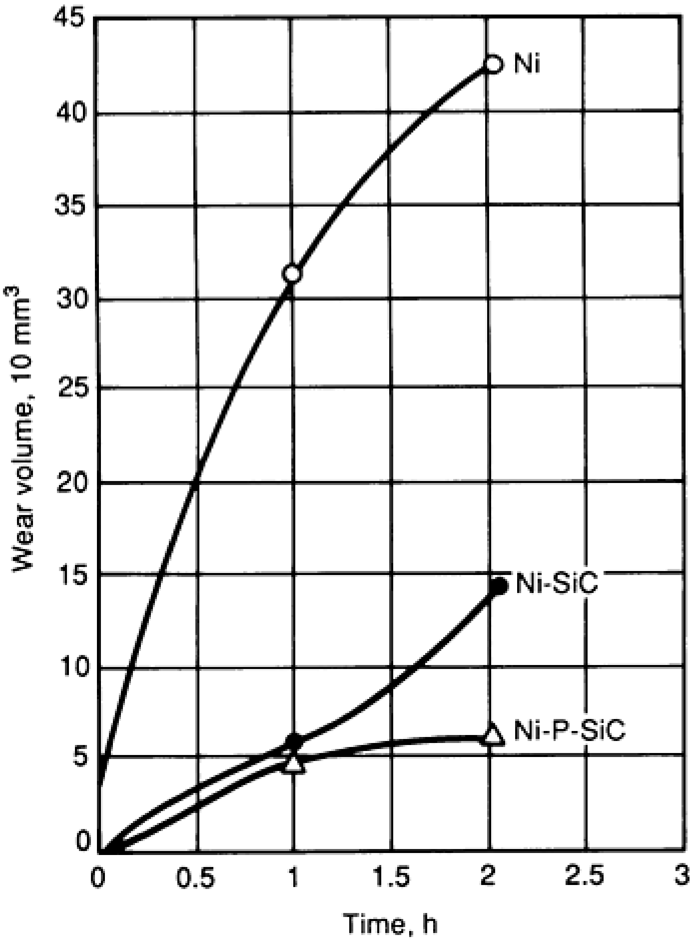


Fig. 15 Effects of codeposited SiC particles and phosphide precipitates on wear of electrodeposited nickel heat treated for 1 h at 400 °C (750 °F). Source: Ref 35

The hardness of nickel deposits can vary from about 150 to 500 on the Vickers scale. The hardness depends on the plating conditions, that is, current density, solution pH and temperature, and composition. Pulse plating can increase the hardness.

The coefficient of friction and wear rates of electroplated nickel are generally greater than those of chromium or electroless nickel deposits (Fig. 16).

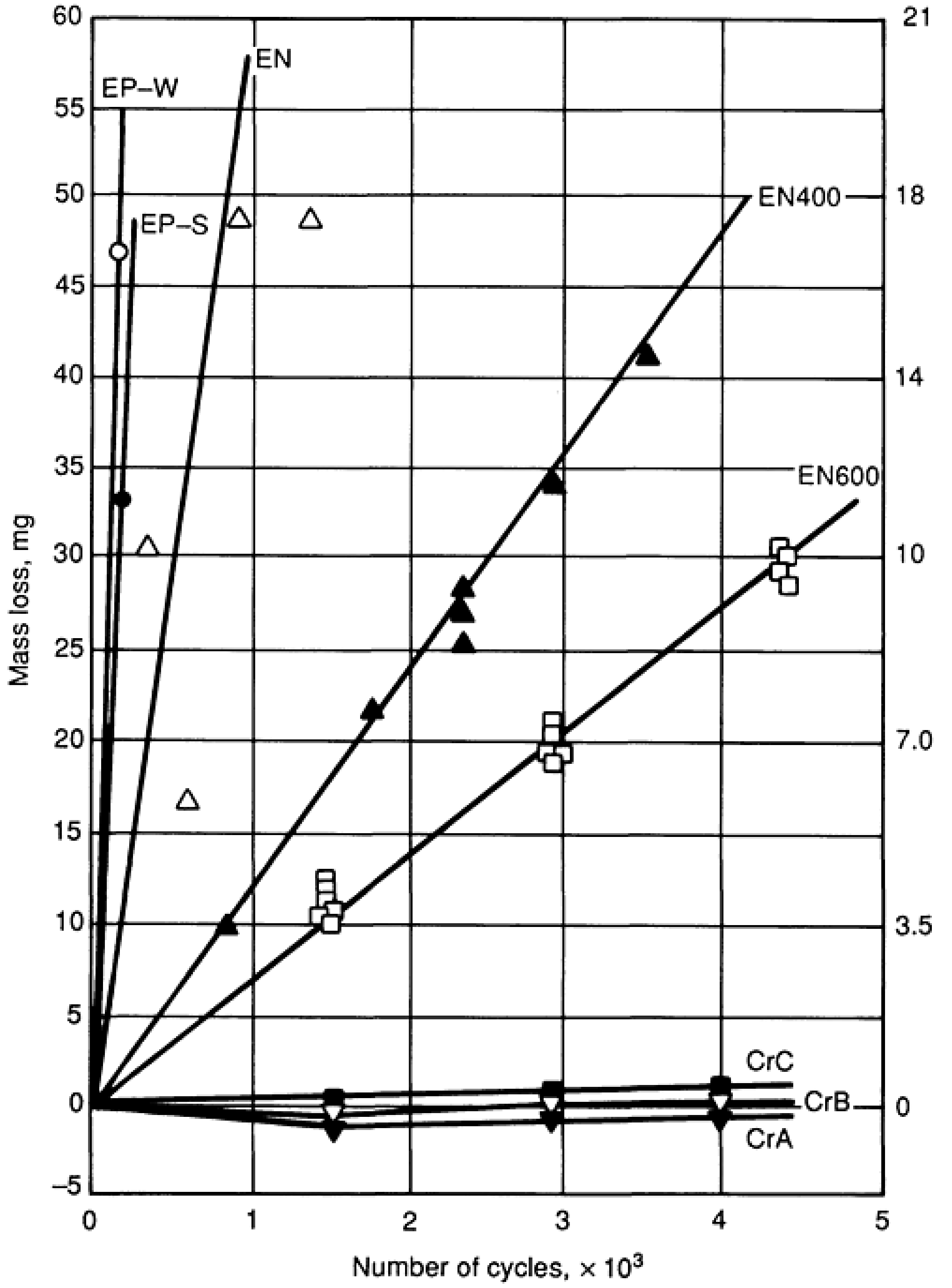


Fig. 16 Effect of number of cycles on wear loss of plated pin versus steel blocks in a Falex test for three chromium deposits (CrA, CrB, and CrC), heat treated electroless nickel deposits (EN400 and EN600), a non-heat-treated electroless nickel deposit (EN), and two electroplated nickel deposits from a sulfamate solution (EP-S) and a Watts solution (EP-W). Source: Ref 36

Depending on the substrate and the end use of the plated product, nickel may be applied directly to the substrate or over another metal coating such as copper and/or chromium. Because of their importance in the automotive industry, nickel-chromium (with or without a copper underlayer) coatings have been subjected to many changes and exhaustive testing over a long span of years. Figure 17 shows a history of the development and use of nickel-chromium coatings. Significant developments in this history were the determination that the basic corrosion resistance of these systems is controlled by the thickness and composition of the nickel layer, the invention of the leveling copper and nickel plating processes, the

development of semibright and bright nickel plating, the emergence of crack-free and microcracked chromium, and the evolution of duplex and triplex (multilayer) nickel-chromium systems.

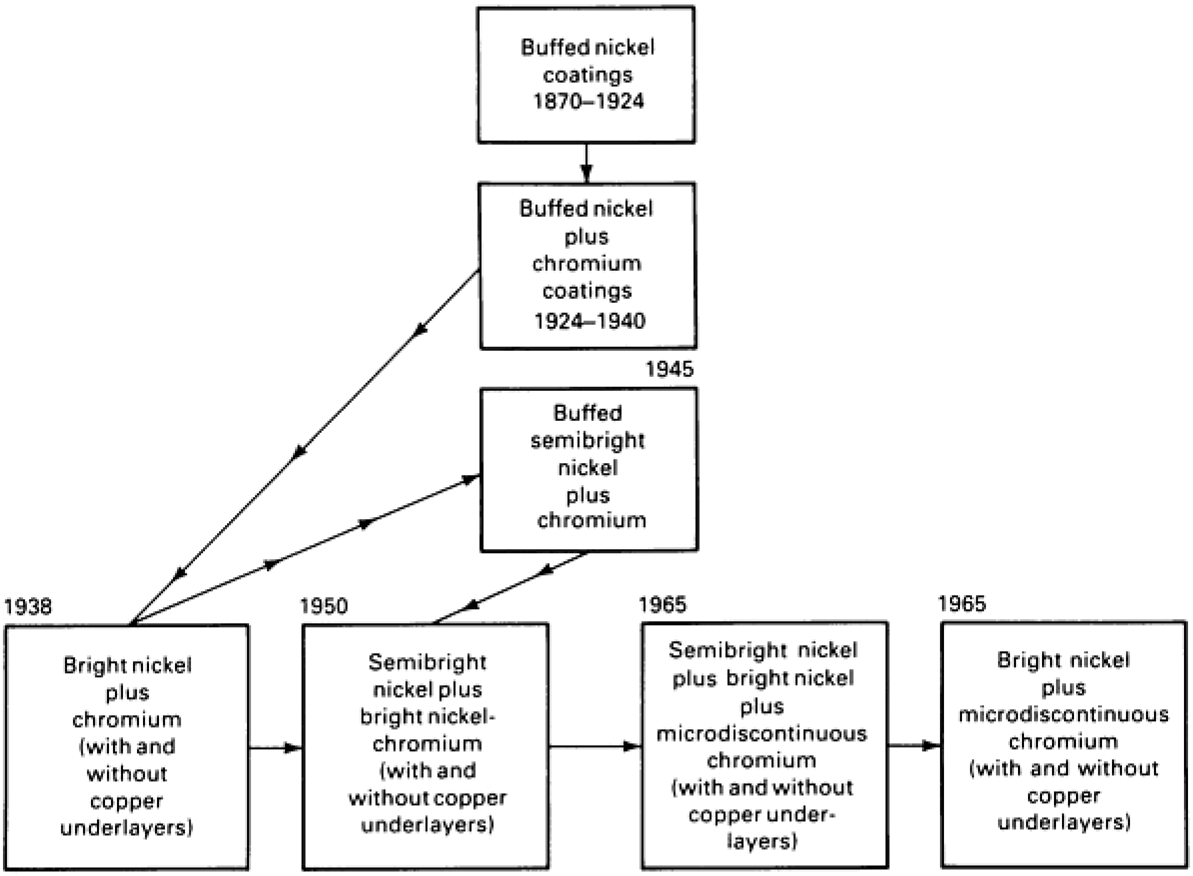


Fig. 17 History of the development of nickel and nickel-chromium coatings showing time of introduction and periods of use. Source: Ref 37

In nickel-chromium systems, the chromium layer is very thin--of the order of only 0.25 μm (0.01 mil). However, the corrosion resistance of chromium plate depends not so much on its thickness as on its physical state. Crack-free, or nonporous, chromium is excellent, but does not remain crack-free in service. A small number of cracks are detrimental, but the presence of many fine microcracks may be beneficial (Ref 38). Microcracked chromium deposits cause the galvanic-corrosion action to be spread over a very wide area and therefore do not suffer from localized corrosion. Microcracked chromium, in combination with duplex or triplex nickel, is the most durable of these coatings. The results of marine exposure for 36 months on variations of these coatings on steel are shown in Fig. 18. Recommended minimum thicknesses and typical applications of bright nickel-chromium coatings are listed in Table 25.

Table 25 Recommended minimum thicknesses and typical applications for electrodeposited bright nickel-chromium coatings on steel, iron, or zinc die-cast substrates

Service conditions	Classification[(a)]		Minimum thickness				Typical applications
			Nickel		Chromium		
	Nickel	Chromium	μm	mils	μm	mils	
Mild (normally warm, dry, indoor atmospheres; minimum	b	r	10	0.4	0.1	0.004	Household appliances, interior auto hardware, hair dryers, fans, inexpensive cooking utensils,

wear or abrasion)	p	r	10	0.4	0.1	0.004	coat and luggage racks, standing ashtrays, interior trash receptacles, inexpensive light fixtures
	d	r	10	0.4	0.1	0.004	
	b	mc	10	0.4	0.8	0.03	
	p	mc	10	0.4	0.8	0.03	
	d	mc	10	0.4	0.8	0.03	
	b	mp	10	0.4	0.3	0.012	
	p	mp	10	0.4	0.3	0.012	
	d	mp	10	0.4	0.3	0.012	
Moderate (indoor exposure where condensation may occur, as in kitchens or bathrooms)	b	r	20	0.8	0.3	0.012	Steel and iron: stove tops, oven liners, home, office, and school furniture; bar stools, golf club shafts. Zinc alloys: bathroom accessories, cabinet hardware
	p	r	20	0.8	0.3	0.012	
	d	r	20	0.8	0.3	0.012	
	b	mc	15	0.6	0.8	0.03	
	p	mc	15	0.6	0.8	0.03	
	d	mc	15	0.6	0.8	0.03	
	b	mp	15	0.6	0.3	0.012	
	p	mp	15	0.6	0.3	0.012	
	d	mp	15	0.6	0.3	0.012	
Severe (occasional or frequent wetting by rain or dew; possible exposure to cleaners and saline solutions)	d	r	30	1.2	0.3	0.012	Patio, porch, and lawn furniture; bicycles; scooters; wagons; hospital furniture; fixtures; cabinets
	d	mc	20	0.8	0.8	0.03	
	d	mp	25	1.0	0.3	0.012	
	p	r	40	1.6	0.3	0.012	

	p	mc	30	1.2	0.8	0.03	
	p	mp	30	1.2	0.3	0.012	
Very severe (damage from wear or abrasion likely in addition to corrosive media)	d	r	40	1.6	0.3	0.012	Auto bumpers, grilles, hubcaps, and lower body trim; light housings
	d	mc	30	1.2	0.8	0.03	
	d	mp	30	1.2	0.3	0.012	

Source: Ref 39

(a) Nickel classifications: b, fully bright; p, dull or semibright; d, double layer or triple layer nickel coating, with the bottom layer containing less than 0.005% S and the top layer more than 0.04% S. If there are three layers, the middle layer should contain more sulfur than the top layer. Chromium classifications: r, regular (conventional) chromium; mc, microcracked chromium having more than 750 cracks/in.: mp, microporous chromium containing a minimum of 64,500 pores/in.^{2} that are visible to the unaided eye.

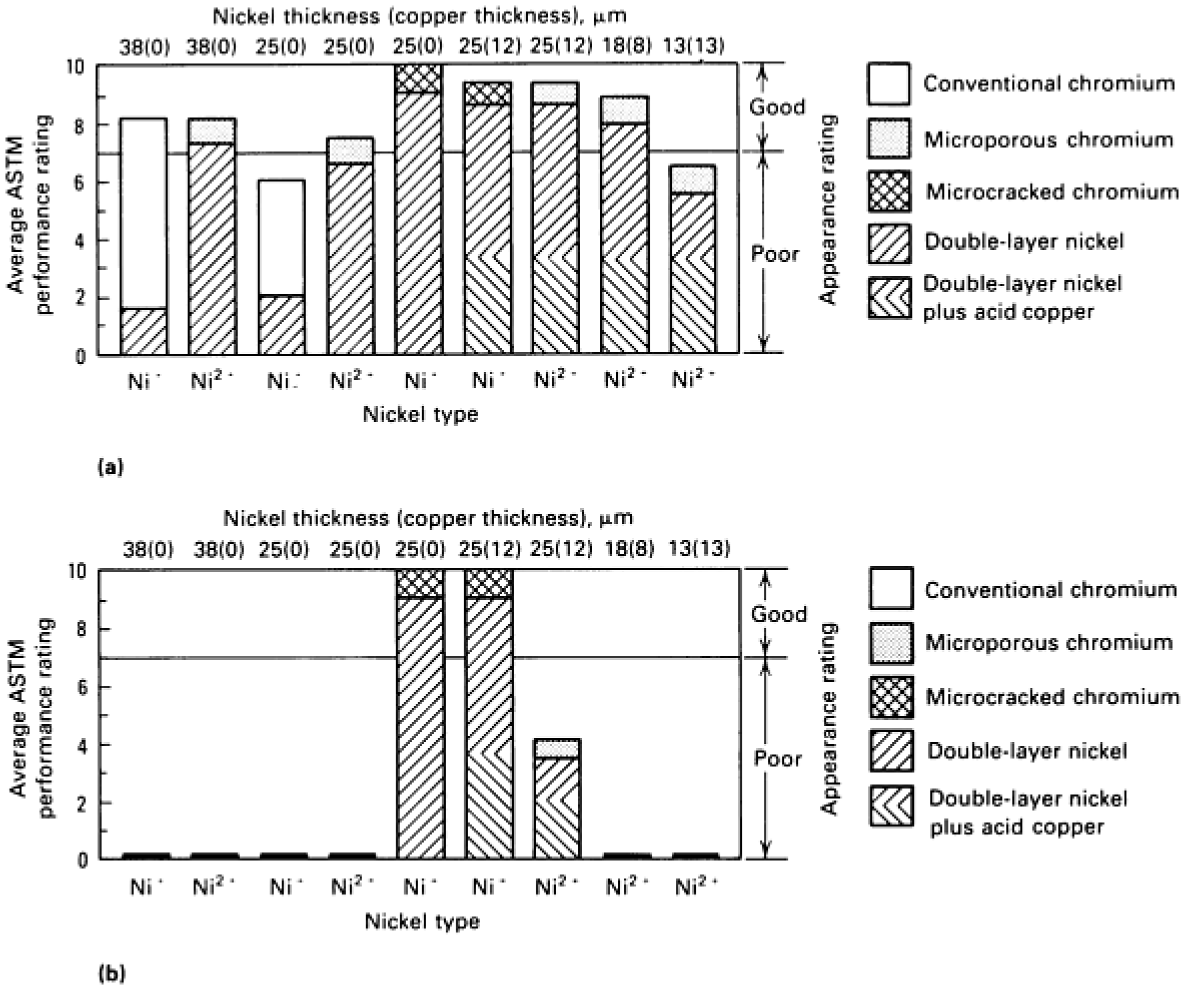


Fig. 18 Performance in a marine atmosphere of various types of nickel-chromium and copper-nickel-chromium coatings on flat (a) and contoured (b) steel panels. ASTM performance rating: 10, best; 0, worst. Test duration: 36 months. Source: Ref 37

Electroless Nickel Plating

Electroless nickel plating is used to deposit nickel without the use of an electric current. The coating is deposited by an autocatalytic chemical reduction of nickel ions by hydrophosphite, aminoborane, or borohydride compounds. Details of the process can be found in the article "Electroless Nickel Plating" in this Volume. When sodium hypophosphite is the reducing agent, the deposit generally contains between 3 and 11% P. The boron contents of electroless nickel range from 0.2 to 4 wt% and from 4 to 7 wt% when the reducing agents are an aminoborane and sodium borohydride, respectively.

Electroless nickel is an engineering coating, normally used because of excellent corrosion and wear resistance. Because of these properties, electroless nickel coatings have found many applications, including those in petroleum, chemicals, printing, mining, aerospace, nuclear, and automotive industries.

Electroless nickel can be heat treated to hardnesses comparable to those of electrodeposited chromium. The maximum hardness can be attained in 1 h at about 400 °C (750 °F) or 10 h at 260 °C (500 °F). The hardness of as-plated nickel-phosphorus alloys varies from 500 to 650 on the Vickers scale. As-plated nickel-boron deposits are generally harder than the nickel-phosphorus ones. The ability of electroless nickel deposits to maintain their hardness under elevated-temperature service conditions increases with increasing phosphorus or boron content, but decreases rapidly above 385 °C (725 °F). Nickel-boron coatings tend to better withstand wear at elevated temperatures and are therefore more widely used under these conditions.

Wear rates of electroless nickel are summarized in Fig. 16. As this figure indicates, the wear loss of heat treated electroless deposits is lower than either electroplated nickel or non-heat-treated electroless deposits.

Coefficients of friction of electroless nickel in the as-deposited condition (EN) and heat treated at 400 °C (750 °F) (EN400) and at 600 °C (1110 °F) (EN600) are compared in Table 26 to the three chromium alloys depicted in Fig. 16. Additional information on the friction and wear characteristics of electroless nickel deposits can be found in Ref 36.

Table 26 Coefficients of friction of chromium versus electroless nickel

Coating	Coefficients of friction	
	Counterface diamond	Counterface plain carbon steel
CrA	0.040	0.88
CrB	0.035	0.82
CrC	0.030	0.81
EN	0.180	0.96
EN400	0.300	0.95
EN600	0.060	0.90

Source: Ref 36

Chromium Plating

Plating Baths. Most chromium plating is done from hexavalent chromic acid (CrO_3) baths, but trivalent systems are gaining in popularity. Hexavalent chromium plating baths consist of chromic acid and small amounts of a sulfate catalyst (SO_4^{2-}). Recently, mixed catalyst baths containing fluoride compounds in addition to chromic acid and sulfate have been employed. Proprietary self-regulating baths control the concentration of the catalyst automatically. Bath formulations and process controls are discussed in the articles "Industrial (Hard) Chromium Plating" and "Decorative Chromium Plating" in this Volume.

Applications and Properties. As implied above, chromium plating is divided into decorative and hard coatings. Decorative coatings are applied over a base deposit of nickel or copper plus nickel to provide color and tarnish resistance. Coating thicknesses are usually less than 1 μm (0.04 mil). Decorative chromium coatings are most often found on automobiles, furniture, and kitchen appliances.

Hard chromium coatings are generally deposited directly on the base material without a nickel undercoat in thicknesses ranging from 1 to 500 μm (0.04 to 20 mils). Hard coatings provide resistance to wear, heat, abrasion, and/or corrosion. Typical applications for hard coatings include hydraulic pistons and cylinders, piston rings, wearing parts in business machines, aircraft engine parts, yarn and thread guides for textiles, plastics molds, and various parts of nuclear reactors where galling is a particular concern.

Microcracks are present in most electroplated hard chromium deposits. Figure 19 shows a typical microcrack structure. The density of the microcracks in chromium deposits varies from 0 to more than 1200 cracks/cm (3000 cracks/in.), depending on bath chemistry, current density, and temperature. The number of microcracks increases with the concentration of the catalyst in the plating bath. The depth of a microcrack is less than about 8 μm (0.3 mil) on a deposit that is 130 μm (5 mils) thick with crack counts of about 800 cracks/cm (2000 cracks/in.).

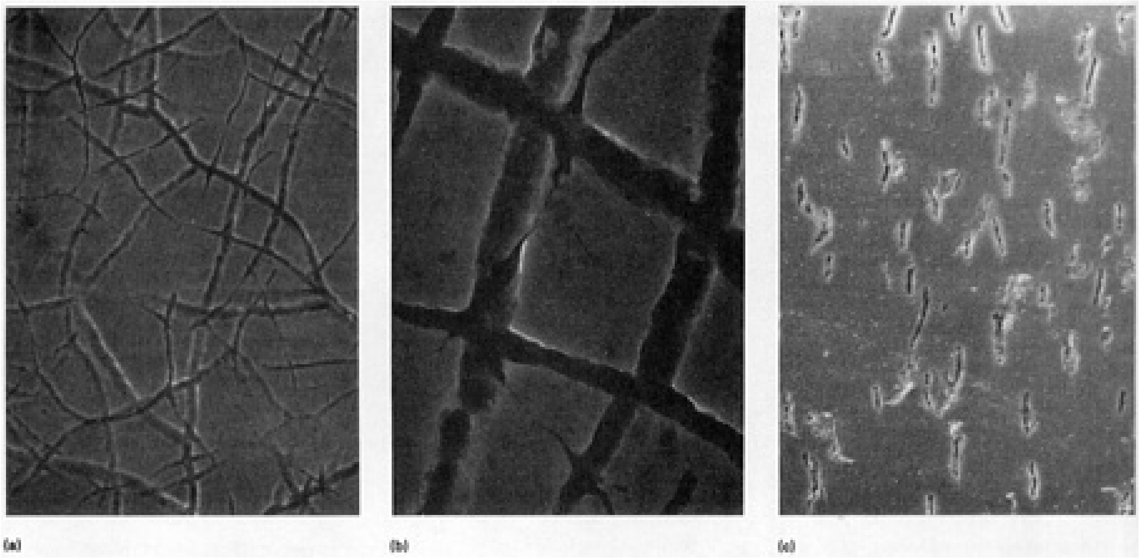


Fig. 19 Photomicrographs of chromium deposits (plated in a high-efficiency etch-free bath) after etching. (a) and (b) Deposit plated at 78 A/dm^2 (5 A/in.^{2}) and at 55 °C (130 °F). (a) 540×. (b) 2300×. (c) Cross section of a chromium deposit plated at 93 A/dm^2 (6 A/in.^{2}) and at 58 °C (135 °F). The specimen was polished before etching. 880×. Both deposits contain 800 microcracks/cm (2000 microcracks/in.).

Electroplated hard chromium is chemically resistant to most compounds and offers excellent corrosion protection in various environments. Electroplated chromium for atmospheric corrosion applications should be between 20 and 25 μm (0.8 and 1 mil) thick. For corrosion resistance in chemical exposures, electroplated chromium should be 50 to 75 μm (2 to 3 mils) thick. A detailed review on the corrosion resistance of electroplated chromium can be found in Ref 40.

The hardness of hard chromium varies from about 900 to 1100 on the Knoop and Vickers hardness scales. These values are considerably higher than the hardness of bulk chromium. Deposits from trivalent solutions are softer than those that are plated from hexavalent chromium solutions. However, after heat treating at about 700 °C (1290 °F), a hardness comparable to that of hard chromium can be achieved (Ref 41).

Chromium deposits are characterized by high internal tensile stresses that can reach 1000 MPa (145 ksi). These stresses can reduce the fatigue properties of coated components. Hydrogen is also codeposited with chromium and can diffuse into components, causing hydrogen embrittlement. Heat treatments are typically required to relieve the stresses and hydrogen effects, but can reduce the hardness.

The coefficients of friction of hard chromium against hard materials are generally the lowest of any electrochemically deposited coatings. The actual values vary considerably, depending on the test method, the mating surfaces of the materials, and the degree of lubrication. Some values of static and sliding coefficients of friction are listed in Table 27. In general, hard chromium has a lower wear rate than either electroplated or electroless nickel, which are the two competing materials. Wear rates are compared in Fig. 16.

Table 27 Coefficients of friction for hard chromium electrodeposits

Couple	Static coefficient	Sliding coefficient
Chromium-plated steel versus itself	0.14	0.12
Chromium-plated steel versus steel	0.15	0.13

Steel versus steel	0.30	0.20

Source: Ref 42

Zinc Plating (Ref 43)

Plating Baths. Zinc is deposited from three different baths: the conventional cyanide bath, the acid chloride bath, and the alkaline noncyanide (or zincate) bath. Compositions and processing conditions for these plating baths are described in the article "Zinc Plating" in this Volume. Cyanide baths offer the ease of control and normally trouble-free plating. However, the cost and toxicity associated with cyanide baths have prompted platers to install low-cyanide solutions or cyanide-free baths.

Chloride zinc baths have been available since the late 1960s. The original baths were chelated or based on complexing agents such as ammonium chloride. Today, state-of-the-art chloride baths use potassium or ammonium chloride. The advantages of the chloride systems include brilliant deposits, high cathode efficiency, low electric power consumption, and a nontoxic, easily treated electrolyte. The disadvantages are poor throwing power, a higher initial equipment investment, and higher brightener costs compared to the alkaline processes.

Alkaline noncyanide electrolytes consist of zinc and sodium hydroxide. In the absence of cyanide, proprietary sequestering agents are sometimes used to yield grain refinement. Alkaline noncyanide electrolytes are simple and low cost. The solutions and rinse waters are easily treated, and metal hydroxide sludges are reduced owing to low zinc content in the bath. These baths, however, offer the lowest cathode efficiency, and the deposits may be yellowish in color. Blistering is common at higher thicknesses and may be related to the greater hydrogen occlusion.

Applications and Properties. Zinc is plated over steel on a wide variety of parts where sacrificial corrosion resistance is required. The conventional zinc coating is dull gray in color with a matte finish, but whiter and more lustrous deposits can be produced by the use of proprietary addition agents. Zinc plate is almost always passivated with a chromate coating for added corrosion protection. The effects of chromate conversion coatings on the corrosion resistance of electrodeposited zinc are listed in Table 28. Coating thickness ranges from 5 to 25 μm (0.2 to 1 mil), depending on the particular application.

Table 28 Recommended minimum thicknesses and typical applications for zinc and cadmium coatings electrodeposited on iron and steel

Service conditions	Coating thickness		Chromate finish	Time to white corrosion in salt spray, h	Typical applications
	μm	mils			
Electrodeposited zinc					
Mild (indoor atmosphere: minimum wear and abrasion)	5	0.2	None	. . .	Screws, nuts and bolts, buttons, wire goods, fasteners
			Clear	12-24	
			Iridescent	24-72	
			Olive drab	72-100	
Moderate (mostly dry, indoor atmosphere; occasional condensation, wear, and abrasion)	8	0.3	None	. . .	Tools, zipper pulls, shelves, machine parts

occasional condensation, wear, and abrasion)			Clear	12-24	
			Iridescent	24-72	
			Olive drab	72-100	
Severe (exposure to condensation; infrequent wetting by rain; and cleaners)	13	0.5	None	. . .	Tubular furniture, window screens, window fittings, builders' hardware, military hardware, appliance parts, bicycle parts
			Clear	12-24	
			Iridescent	24-72	
			Olive drab	72-100	
Very severe (exposure to bold atmospheric conditions; frequent exposure to moisture, cleaners, and saline solutions; likely damage by abrasion or wear)	25	1	None	. . .	Plumbing fixtures, pole line hardware
Electrodeposited cadmium					
Mild (see above)	5	0.2	None	. . .	Springs, lock washers, fasteners, tools, electronic and electrical components
			Clear	12-24	
			Iridescent	24-72	
			Olive drab	72-100	
Moderate (see above)	8	0.3	None	. . .	Television and radio chassis, threaded parts, screws, bolts, radio parts, instruments
			Clear	12-24	
			Iridescent	24-72	
			Olive drab	72-100	
Severe (see above)	13	0.5	None	. . .	Appliance parts, military hardware, electronic parts for tropical service
			Clear	12-24	
			Iridescent	24-72	

			Olive drab	72-100	
Very severe (see above)(b)	25	1	None	. . .	. . .
			Clear	24	
			Iridescent	24-72	
			Olive drab	72-100	

Source: Ref 39

(a) Thickness specified is after chromate conversion coating, if used.

(b) There are some applications for cadmium coatings in this environment; however, these are normally satisfied by hot-dipped or sprayed coatings.

The formation of white corrosion products in marine environments makes zinc less desirable than cadmium; but because it is less toxic and less expensive and its electrolytes are more easily waste treated, zinc has replaced cadmium in many applications. Zinc coatings are also superior to cadmium coatings in industrial environments. Common applications for zinc plating include fasteners, wire goods, tools, and sheet metal parts.

Cadmium Plating (Ref 43)

Plating Baths. Cadmium is primarily plated from a cyanide electrolyte. Acid cadmium baths are also used to a limited extent, and are fluoborate, sulfate, or chloride in nature. The acid-type baths are more desirable if hydrogen embrittlement is a problem, and their waste treatment is simplified. However, the cyanide baths are easier to control than the acid baths. Typical cadmium plating compositions are described in the article "Cadmium Plating" in this Volume.

Applications and Properties. Cadmium provides galvanic protection when deposited on steel. The government is by far the largest specifier of cadmium, for military applications. As shown in Table 28, deposit thicknesses range from 5 to 25 μm (0.2 to 1 mil), depending on the degree of exposure to corrosion, and wear. As with zinc electroplates, chromate conversion coatings improve the corrosion resistance of cadmium electrodeposits. Cadmium is generally preferred for the protection of steel in marine environments whereas zinc is preferred in industrial environments. The coefficient of friction of cadmium is less than that of zinc; therefore, cadmium is preferred for fastening hardware and connectors that have to be taken on and off repeatedly. Typical applications include springs, lock washers, fasteners, electronic and electrical parts, washing machine parts, and military hardware. Because it is toxic, cadmium plating should never be used on parts that will come in contact with food or beverages.

Avoiding Hydrogen Embrittlement. Cadmium deposited from a cyanide solution is more likely to produce hydrogen embrittlement than any other commonly plated metal. Heat treated high-strength steels, particularly those plated and used at 35 HRC and above, are susceptible to hydrogen embrittlement.

Although the thickness of the plated deposit appears to have no direct bearing on hydrogen embrittlement, it is always more difficult to release the hydrogen (by baking) from heavy deposits. By adhering to the following procedures, hydrogen embrittlement can be minimized:

- Use mechanical cleaning methods, such as brushing, blasting, and tumbling
- Wherever possible, avoid the use of strong acid pickling solutions and extended exposure to acid pickling

- If pickling is essential to the preparation of medium-strength and high-strength steel parts, bake the parts at 175 to 205 °C (350 to 400 °F) for 3 h after pickling and before plating
- In plating, use the higher current densities to produce a more porous deposit; 7 A/dm^2 (70 A/ft^2) in a cyanide bath without brighteners has been satisfactory for steel at 46 HRC
- After plating, bake parts at 175 to 205 °C (350 to 400 °F) for 3 to 24 h. The shorter baking periods are generally adequate for parts with a tensile strength below about 1520 MPa (220 ksi); longer baking periods are recommended for steel of tensile strength above about 1520 MPa (220 ksi) or lower strength parts if sharp notches or threads exist. Parts greater than 25 mm (1 in.) thickness should also be baked for 24 h. The elapsed time between plating and baking must never exceed 8 h, and baking should be carried out as soon as possible, preferably within 4 h
- Plate parts to a thickness of about 5 μm (0.2 mil), bake for 3 h at 195 °C (385 °F), activate in cyanide, and then complete the plating to required final thickness

Tinplate

The term *tinplate* refers to a low-carbon steel strip product coated on both sides with a thin layer of tin. Electrolytic tinplate can be produced with either equal or unequal amounts of tin on the two surfaces of the steel base metal. Nominal coating thicknesses for equally coated tinplate range from 0.38 to 1.5 μm (15 to 60 μin.) on each surface. The thicker coating on tinplate with unequal coatings (differential tinplate) rarely exceed 2.0 μm (80 μin.). Tinplate is produced in thicknesses from 0.15 to 0.60 mm (0.006 to 0.024 in.). For almost 200 years, tinplate has been the primary material used to make containers (tin cans) for the long-term storage of food. More than 90% of the tinplate manufactured worldwide is used to make food cans, and nearly all food cans are made of tinplate.

Modern tinplate is much more sophisticated than a simple coating of tin on steel. To achieve the demanding deep-drawing properties necessary for the production of can bodies for two-piece can manufacture, the steel base for tinplate is often continuously cast using the most current technology. Inclusions or other defects in the steel may otherwise cause breakage in the can-body drawing operation. Because the economics of canmaking depend on high-speed operation using a continuous coiled strip, such breakage cannot be tolerated due to the lost production time; therefore, the steel must be as clean as possible.

In preparing the base steel, the metal is processed to strip form, the final step being a cold reduction that brings the strip to a thickness that is typically from 0.15 to 0.50 mm (6 to 20 mils). Next, the strip is annealed and then temper rolled to obtain the desired mechanical properties. At the final stage of temper rolling, textured rolls can be used to produce a special surface finish for particular applications. A cold reduction in place of temper rolling yields a product that is termed double reduced.

The coiled steel is now ready for the tinplate line. It is first welded to the end of the previous coil to form a continuous strip for processing. The strip passes through cleaning and pickling sections to prepare it for plating, then immediately through the plating cells, where up to 11.2 g/m^2 (1 g/ft^2) of tin is deposited. Tin may be plated from either alkaline electrolytes (stannate) or acid electrolytes (sulfate, fluoborate). Plating bath compositions and operating conditions are described in the article "Tin Plating" in this Volume.

The production steps that typically follow plating create additional layers in the tinplate structure that significantly affect corrosion properties. Upon exiting the plating cells, the tinplate has a matte surface that is usually reflowed by momentarily melting the tin coating in a resistance or induction heating unit. In doing so, a thin layer of tin-iron intermetallic compound is formed at the tin/steel interface. Next, an extremely thin passivation film based on chromium oxide is created by immersion or spraying of chromic acid (H_2CrO_4) on the tinplate surface or by passing the tinplate through a solution of $Na_2Cr_2O_7$, with or without the simultaneous application of electrical current. Finally, a very thin, uniform layer of lubricant, usually either dioctyl sebecate or acetyl tributyl citrate, is electrostatically applied.

Therefore, as supplied to the canmaker, the typical tinplate product consists of five layers, the innermost being a steel sheet about 200 to 300 μm (7.8 to 11.7 mils) thick. This steel is covered on each side with perhaps 0.08 μm (0.004 mil) of tin-iron intermetallic compound. The next layer is free tin that is perhaps 0.3 μm (0.012 mil) thick, with a passivation film of about 0.002 μm (0.00008 mil) and an oil film also about 0.002 μm (0.00008 mil) thick. All five layers affect corrosion behavior. Reference 44 is an excellent source of information on the corrosion characteristics of tinplate.

References cited in this section

33. "Standard Practice for Preparation of Low-Carbon Steel for Electroplating," ASTM B 183, *Annual Book of ASTM Standards,* Vol 02.05, ASTM, Philadelphia, PA
34. "Standard Practice for Preparation of High-Carbon Steel for Electroplating," ASTM B 242, *Annual Book of ASTM Standards,* Vol 02.05, ASTM, Philadelphia, PA
35. X. Changgeng, D. Zonggeng, and Z. Lijun, The Properties of Electrodeposited Ni-P-SiC Composite Coatings, *Plat. Surf. Finish,* Vol 75 (No. 10), 1988, p 54
36. D.T. Gawne and U. Ma, Friction and Wear of Chromium and Nickel Coatings, *Wear,* Vol 129, 1989, p 123
37. G.A. DiBari, Decorative Electrodeposited Nickel-Chromium Coatings, *Met. Finish.,* Vol 75 (No. 6 and 7), June-July, 1977
38. C.L. Faust, "Electroplating," Course 22, Metals Engineering Institute, American Society for Metals, 1983
39. Quality Metal Finishing Guide, Metal Finishing Suppliers' Association
40. A.R. Jones, Corrosion of Electroplated Hard Chromium, *Corrosion,* Vol 13, *ASM Handbook* (formerly 9th ed., *Metals Handbook*), ASM International, 1987, p 871-875
41. M. Takaya, M. Matsunaga, and T. Otaka, Hardness of Deposits from Trivalent Chromium Sulfate/Potassium Formate Baths, *Plat. Surf. Finish.,* Vol 74 (No. 6), 1987, p 90
42. G. Dubpernell, Chromium, Chapter 5, *Modern Electroplating,* 3rd ed., John Wiley and Sons, 1974, p 87-151
43. Electroplating, in *Vol 3, Materials, Finishing, and Coating, Tool and Manufacturing Handbook,* Society of Manufacturing Engineers, 1985, p 20-8 to 20-10
44. D.J. Maykuth and W.B. Hampshire, Corrosion of Tin and Tin Alloys, *Corrosion,* Vol 13, *ASM Handbook* (formerly 9th ed., *Metals Handbook*), ASM International, 1987, p 770-783

Metal Cladding

Carbon steels can be bonded to more corrosion-resistant materials, such as copper and stainless steels, by a variety of techniques. The resulting lamellar composite material has specific properties not obtainable in a single material.

The principal cladding techniques include hot roll bonding, cold roll bonding, explosive bonding, centrifugal casting, brazing, and weld cladding, although adhesive bonding, extrusion, and hot isostatic pressing have also been used to produce clad metals. With casting, brazing, and welding methods, one of the metals to be joined is molten when a metal-to-metal bond is achieved. With hot/cold roll bonding and explosive bonding processes, the bond is achieved by forcing clean oxide-free metal surfaces into intimate contact; this causes a sharing of electrons between the metals. Gaseous impurities diffuse into the metals, and nondiffusible impurities consolidate by spheroidization. These non-melting techniques involve some form of deformation to break up surface oxides, to create metal-to-metal contact, and to heat in order to accelerate diffusion. The techniques differ in the amount of deformation and heat used to form the bond and in the method of bringing the metals into intimate contact. More detailed information on metal cladding techniques can be found in Ref 45, 46, and 47.

Noble metal clad systems are materials having a relatively inexpensive carbon steel base metal covered with a corrosion-resistant metal. Clad metals of this type are typically used in the form of strip, plate, and tubing. The noble metal cladding ranges from commonly used stainless steels, such as type 304, to high-nickel alloys, such as Inconel 625. These clad metals find various applications in the marine, chemical-processing, power, and pollution control industries. Specific uses include heat exchangers, reaction and pressure vessels, furnace tubes, tubes and tube elements for boilers, scrubbers, and other systems involved in the production of chemicals.

Transition Metal Systems. A clad transition metal system provides an interface between two incompatible metals. It not only reduces galvanic corrosion where dissimilar metals are joined but also allows welding techniques to be used when direct joining is not possible.

The principle of a clad transition metal is illustrated in Fig. 20. In this example, aluminum is joined to low-carbon steel through a steel-clad aluminum transition metal. Steel and aluminum form brittle intermetallic compounds and are difficult to weld directly. The transition metal insert allows steel to be welded to steel and aluminum to aluminum; the actual bond

between the steel and the aluminum occurs in the clad transition. In addition, the dissimilar-metal crevice is eliminated, which reduces susceptibility to galvanic corrosion.

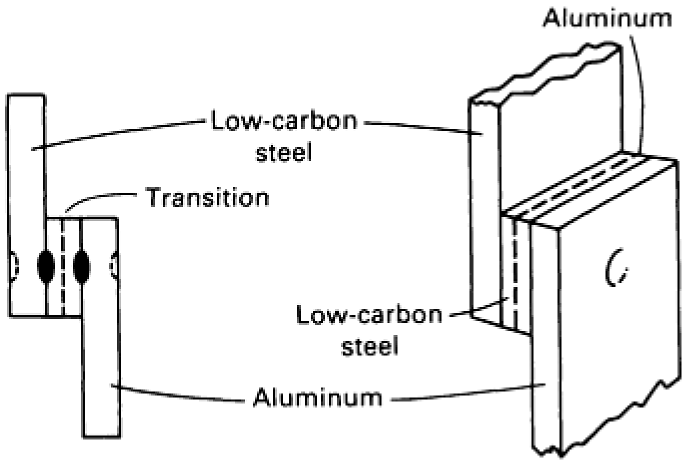


Fig. 20 Illustration of a steel-clad aluminum transition insert used for joining aluminum to carbon steel

Complex Multilayer Systems. In many cases, materials are exposed to dual environments; that is, one side is exposed to one corrosive medium, and the other side is exposed to a different one. A single material may not be able to meet this requirement, or a critical material may be required in large quantity.

Clad metals provide an ideal solution to the materials problem of dual environments. For example, in automobile windshield wiper sockets (Fig. 21), wear resistance is required on the mating surface, atmospheric-corrosion resistance is required on the external surface, and high strength is incorporated into the design. Multilayer phosphor-bronze-clad, steel-clad copper is used in this application. The phosphor bronze provides the required bearing surface, copper provides atmospheric-corrosion resistance, and steel provides the required strength.

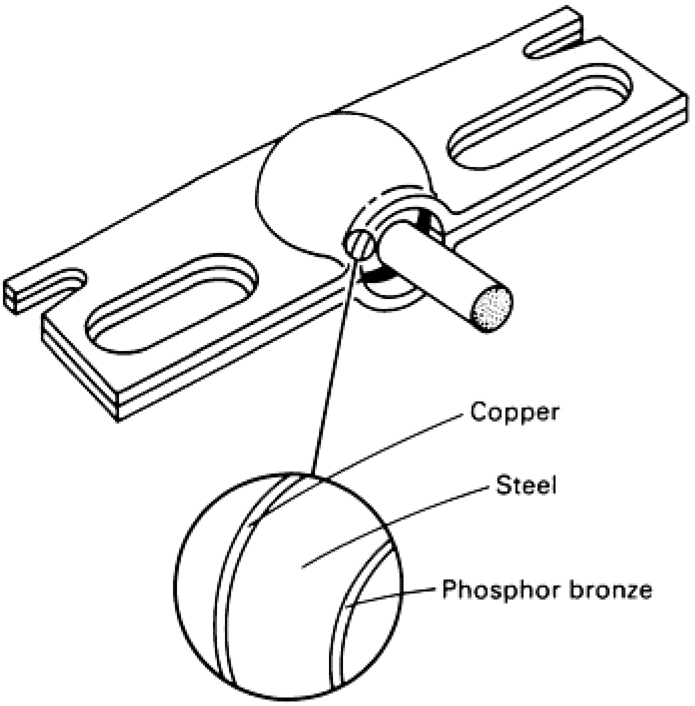


Fig. 21 Clad metal windshield wiper socket, which consists of copper-clad, steel-clad phosphor bronze

References cited in this section

45. L.M. Smith, Engineering with Clad Steel, NiDI Technical Series No. 10,064, Nickel Development Institute, 1992
46. R.G. Delati, "Designing with Clad Metals," Metallurgical Materials Division of Texas Instruments, Inc.
47. Stainless Steel Cladding and Weld Overlays, in *ASM Specialty Handbook: Stainless Steels,* J.R. Davis, Ed., ASM International, to be published in the Fall of 1994

Organic Coatings

Paint is applied to a steel sheet or a part for one or both of the following reasons: enhancement of the aesthetic value of the product and/or preservation of structural integrity. The former goal is a consideration for the designer and will receive no further discussion in this section. The latter goal, however, will be discussed as it applies to prepainted steel.

This section will describe how paints deter corrosion, the prepainting process, the primary differences between prepaint paint formulations and postpaint formulations, considerations about part design, and selection criteria for the appropriate paint system. More detailed information on organic coating materials can be found in Ref 48 and the articles "Painting" and "Elastomeric Coatings and Linings" in this Volume.

How Paint Films Deter Corrosion. In the presence of water and oxygen, iron corrodes to form iron oxides and hydroxides. The corrosion rate is accelerated when electrolytic solutes, such as the chloride or sulfate salts of alkali metals, are present. Of course, temperature also increases the corrosion rate, and where possible, decreasing the service temperature will increase the service life of the part. However, because little can usually be done to change service temperature, the exclusion of one or more of the principal reactants (oxygen, water, or electrolytes) from the steel surface will help deter corrosion. Such exclusion of reactants is the purpose of the paint film.

There are primarily three methods of protection: barrier, passivation, and galvanic. In barrier protection, the paint film retards the diffusion of water, oxygen, or salts to the steel substrate. It has been demonstrated that the flow of water and oxygen through the film is rapid; therefore, the contribution of the coating to lowering the corrosion rate is the addition of a high electrolytic resistance (Ref 49). Flake-shaped pigment particles that leaf (overlap) can increase the path length a reactant must traverse before reaching the surface; this increases the effectiveness of the barrier film. Some aluminum and stainless steel pigments protect in this fashion. The reactivity of the steel surface can be decreased when the paint film contains passivating pigments such as chromate salts. As described below in the section on "Painting With Zinc-Rich Paints," paints are also often pigmented with zinc for both barrier and galvanic protection. The zinc loading must be sufficiently high for interparticle contact, a condition that requires that the critical pigment volume be exceeded; that is, the pigment particles are not completely wetted by the paint vehicle. Although some galvanic protection is afforded, most of the protection is provided by the barrier formed by zinc corrosion products (Ref 50).

Prepaint Processing. Much of the painted steel used today is prepainted in coil form (coil coated) before shipment to fabricators. Modern, high-speed paint lines can process bare or coated steel strip, and can be used to apply a wide variety of organic coatings.

After decoiling, the first step in the prepaint process is to clean the steel strip with an alkaline detergent. The steel strip is then brushed with an abrasive roll to remove mill oils and grime and to reduce the level of an amorphous form of surface carbon indigenous to steel strip processing. High levels of surface carbon lower corrosion resistance (Ref 51). Cleaning is usually more effective on flat strip than on a formed part. Next, the strip is rinsed and pretreated to improve paint adhesion and to reduce corrosion. A prepaint treatment may consist of phosphate coating or an organic pretreatment known as wash primer or etch primer. Such pretreatments are described in the article "Painting" in this Volume. Following pretreatment, a paint is then applied and cured in an oven. Depending on the paint formulation and the paint line, the dwell time in the oven is generally between 20 and 50 s. A second coat may then be applied and cured.

Differences Between Prepaint and Postpaint. In formulating a paint designed for a prepaint application, the forming step must be considered. Aside from steel consideration, successful forming of the part will depend on the flexibility and the abrasion resistance of the coating. The paint film must be flexible enough to withstand the strains induced from bending without crazing, which may compromise corrosion resistance. In addition, in the forming stages, the bend radii are often more severe than in the final part.

The coating must also withstand the abrasive forces of handling and forming. For a given coating type, the harder the coating, the more abrasion resistant the coating will be. Unfortunately, flexibility and hardness are inversely related; that is, the more flexible the coating, the softer the coating.

A method for overcoming the problems associated with coating flexibility is covered in the discussion on part design considerations in this section. Flexibility and hardness are considerations only for the end use of postpainted parts, while forming and handling are also factors of concern in the formulation of a paint designed for precoating a steel strip.

The final dried paint thickness, or dry-film thickness, on a prepainted steel strip is usually no more than 0.25 mm (1 mil). Plastisols and organosols are the major exceptions. Therefore, the prepaint dry-film thickness is much less than the typical dry-film thickness on a postpainted part. However, because of the method of application, the film is more evenly distributed; this results in significantly fewer areas of low dry-film thickness and the elimination of many of the appearance defects observed on finished postpainted parts. Many areas on postpainted parts will receive little or no paint because of the part shape. The formulations for prepaints are engineered to account for the lower dry-film thicknesses.

Part Design Considerations. When designing a part to be fabricated from prepainted steel, the maximum bend radius, the forming equipment, and the joining method must be considered. As mentioned earlier, the maximum bend radius is often smaller than that specified on the blueprint of the part. This radius should be as generous as the structural and decorative criteria will allow. In considering the part shape, the avoidance of catchment areas, where possible, will decrease failures due to corrosion.

The forming equipment should be well maintained to avoid marring the surface. Where possible, roll forming is preferable to stamping. In cases in which hard finishes in conjunction with tight radii (high flexibility) are required, the prepainted strip can be warm formed. In warm forming, the paint is heated into or above its glass transition temperature range. In this temperature range, the paint is softer and more flexible, thus allowing tighter radii to be achieved during forming. After cooling, the paint becomes harder and more abrasion resistant.

Lastly, the part may require joining. Welding and mechanical fastening damage the paint film. Therefore, it is necessary to touch up the scars to restore corrosion resistance. Adhesive bonding eliminates the need for touch up of these damage areas. Taking these factors into account, prepainted steel has been successfully fabricated into finished or semifinished (requiring a post finish coat operation) parts in many automotive, appliances, or office furniture manufacturing plants. Prepainted parts have been produced on lines designed for their use and on existing lines, sometimes with no modification to the line.

Selection Guideline. As an aid to understanding the evaluation process, Table 29 compares various common coatings in several categories of performance. Changes in pigmentation and resin source for the vehicle can influence the rating by a factor of one or more. Table 29 is merely a guideline to the performance of these coatings. Comments from technical personnel at a paint company should be sought before making any decision on paint selection.

Table 29 Relative hardness rankings of various coatings in different performance categories

Category key: A, hardness; B, flexibility; C, humidity resistance; D, corrosion resistance to industrial atmospheres; E, salt spray; F, exterior durability, pigmented film; G, exterior durability, clear film; H, paint cure temperature, in °C (°F); I, cost guide. Ratings key: 1, excellent; 2, good; 3, fair; 4, poor; H, high cost; M, moderate cost; L, low cost

Type	A	B	C	D	E	F	G	H	I
Silicone acrylic	1	3	2	2	2	2	1	230 (450)	H
Thermoset acrylic	2	2	1	2	1	2	2	220 (430)	M
Amine-alkyd	2	3	2	2	3	2	3	170 (340)	L
Silicone alkyd	2	3	2	2	2	1	2	215 (420)	H

Vinyl-alkyd	2	2	1	2	2	3	3	170 (340)	M
Straight epoxy	1	2	1	1	1	4	4	205 (400)	H
Epoxy-ester	2	2	1	2	1	4	4	205 (400)	M
Organosol	2	1	1	1	1	2	3	175 (350)	L
Plastisol	3	1	1	1	1	2	3	175 (350)	L
Polyester (oil-free)	1	2	1	2	1	2	3	205 (400)	M
Silicone polyester	2	2	1	2	1	1	2	230 (450)	H
Polyvinyl fluoride	2	1	1	1	1	1	1	230 (450)	H
Polyvinyl idene fluoride	2	1	1	1	1	1	1	230 (450)	H
Solution vinyl	2	1	1	2	1	2	3	150 (300)	M

The columns in Table 29 are self-explanatory, with the exception of those involving exterior durability and salt spray. Exterior durability is the resistance to weathering, particularly the resistance to ultraviolet light. Ultraviolet light causes some coatings to chalk. Proper pigmentation will prevent this phenomenon for some coatings, and this can be determined by comparing the columns for pigmented and clear films.

Salt spray is not a predictor of service life and coatings cannot be compared for end use on this basis. However, salt spray does detect coating defects and can be put to good use for detecting induced flaws by comparing results for flat panels with those of panels with coating defects induced, for example, by forming or abrasion.

The first step in the evaluation is the selection of a steel mill and/or paint company that is willing and able to help evaluate the needs of the final product. These needs can be categorized as either preservice or service. The preservice conditions involve forming, handling, and joining. The service conditions are those to which the customer exposes the product: humidity, temperature, corrosive agents, sunlight, and abrasion. Of course, the preservice conditions can affect the service life of the final product, and these effects should be evaluated.

The next step is the experimental design. The test program compares candidate materials to the current product, if possible. Evaluation in actual service conditions is often not possible because of time limitations. Therefore, accelerated and laboratory tests are needed (see the article "Corrosion Testing" in this Volume). From these results, acceptable candidates are identified and are included in the next level of tests. A set of suitable parts is identified for testing the candidates. After the parts are fabricated, they are inspected to determine whether coating damage occurred and whether corrosion resistance was compromised. In general, one material will not be superior in all aspects. Therefore, the desirable properties must be prioritized.

Advantages of Prepainted Steels. Although the above evaluation sequence may seem formidable, many manufacturers have found the use of prepainted steel to be productive and economical. The use of prepainted steel reduces or eliminates the problems of the waste treatment of the emissions from paint lines. The postpainting line is often the slow step in the process, and using prepainted steel increases output. Although the material cost of prepainted steel is higher than the bare metal, the final part cost is lower because of increased productivity and the reduction of other costs,

such as emissions control. Although prepainted steel cannot replace postpainted steel in every application, prepainted steel has demonstrated its productive and economic advantages.

References cited in this section

48. K.B. Tator, Organic Coatings and Linings, *Corrosion,* Vol 13, *ASM Handbook* (formerly 9th ed., *Metals Handbook*), ASM International, 1987, p 399-418
49. J.E.O. Mayne, *Anti-corros.,* Oct 1973, p 3-8
50. N.C. Fawcett, *Polymer Mater. Sci. Eng.,* Vol 53, 1985, p 855-859
51. R.A. Iezzi and H. Leidheiser, Jr., *Corrosion,* Vol 37, 1981, p 28

Painting With Zinc-Rich Paints

Zinc-rich coatings, often called zinc-rich primers, are a unique class of cross-linked coatings that provide galvanic protection to a ferrous substrate. As the name implies, the binder is highly loaded with a metallic zinc dust pigment. After the coating is applied to a thoroughly cleaned substrate, the binder holds the metallic zinc particles in contact with the steel and with each other. Thus, metal-to-metal contact of two dissimilar metals is made, resulting in a galvanic cell. In this couple, zinc becomes the anode and sacrifices itself to protect the underlying cathodic steel.

The major advantage of corrosion protection using zinc-rich coatings is that localized pitting corrosion and subfilm corrosion are eliminated, even at voids, pinholes, scratches, and abrasions in the coating system. This cannot be said of any other type of protective coating, and it is this protective capability that makes zinc-rich coatings unique and widely used.

This advantage, however, comes with certain disadvantages. The underlying steel substrate must be cleaned of all rust, old paint, and other contaminants that may interfere with metal-to-metal contact. Thus, the degree of surface preparation must be quite thorough: blast cleaning should produce a Commercial Blast Cleaning minimum and, for immersion service, a White or Near-White surface. The Steel Structures Painting Council (SSPC), NACE, and other organizations issue standards for the surface preparation of metals for organic coatings: these are discussed in more detail in Ref 48 and also mentioned below.

Zinc Dust/Zinc Oxide Coatings

Zinc dust/zinc oxide paints, also known as metallic zinc paints, contain a pigmentation of approximately 80% zinc dust, 20% ZnO, and approximately 80% pigment by weight. These paints offer excellent rust-inhibitive properties, adhesion, film distensibility, and abrasion resistance. Because they adhere tightly to zinc and other metals, they are ideal for prime and finish coat applications and may be used as a primary first coat even over partially rusted surfaces.

Zinc dust/zinc oxide paints are used for the protection of many types of steel structures under a variety of service conditions. They are particularly well suited to use on galvanized steel; are highly satisfactory for priming steel for atmospheric and underwater exposure; and can be used on many outdoor structures, such as bridges, water tanks, and dams, where rusting must be prevented.

In accordance with Federal Specification TT-P-641 which covers primer paints and zinc dust/zinc oxides for galvanized surfaces, there are three types of zinc dust/zinc oxide paints:

- *Type I:* zinc dust/zinc oxide linseed oil for outdoor exposure, recommended as a primer or finish coat for broad, general use, especially when there is widespread rusting of the steel surfaces; should be air dried only
- *Type II:* zinc dust/zinc oxide alkyd resin paint, a heat-resistant paint sometimes sold as a stack paint, may also be used for outdoor exposures where rust is not severe; quick drying; can be air dried or baked at temperatures to 150 °C (300 °F)
- *Type III:* zinc dust/zinc oxide phenolic resin paint; used for water immersion and other severe moisture conditions; may be air dried or baked at temperatures to 150 °C (300 °F)

These paints, when properly formulated and prepared, can be applied by brushing, dipping, or spraying. Although the presence of ZnO prevents rapid or hard settling, adequate agitation of the paint in the dip tank is necessary to ensure the coating homogeneity necessary for maximum metal protection. Pressure equipment should be used when spraying, and the distance between the paint reservoir and the spray gun should be as short as possible to ensure the proper rate of feed to the nozzle. Again, some agitation of the paint in the reservoir is recommended.

Zinc dust/zinc oxide paints possess high covering power and can hide backgrounds of almost any color when spread at the rate of approximately 20 m^2/L (800 ft^2/gal). However, because the protection afforded by a paint coating is directly related to its thickness, the necessary protection cannot be guaranteed unless the dry film is thick enough for the specific environmental conditions. Therefore, care must be taken to avoid spreading the paints too thin. The natural blue-gray color of zinc dust/zinc oxide paints provides an aesthetic appearance, but if another color is desired, red, buff (orange-yellow), and green can be obtained by varying the pigment.

To prepare surfaces for zinc dust/zinc oxide paints, rust (or scale) and any accumulation of leaves, dirt or other foreign materials should be removed. This may be accomplished on large structures by sandblasting and on small structures or areas with a deck or wire brush.

Zinc-Rich Coatings

In recent years, a number of paints have been developed that will deposit a film of metallic zinc having many properties in common with zinc coatings applied by hot-dip galvanizing, electroplating, thermal spraying, and mechanical plating. Such paint films will protect the underlying steel sacrificially if they contain 92 to 95% metallic zinc in the dry film and if the film is in electrical contact with the steel surface at a sufficient number of points. They are effective where steel is subjected to high humidity and water immersion. Under normal conditions, zinc-rich coatings are long lasting and most effective where a regular maintenance program may be difficult. In applications in which steel is immersed in brackish or salt water, zinc-rich coatings, along with a suitable top coat, should be used. Most zinc-rich paints are of the air-drying type although oven-cured primers containing a high content of zinc dust are available.

The type of zinc dust used is a heavy powder, light blue-gray in color, with spherically shaped particles having an average diameter of approximately 4 mm. Such powder normally contains 95 to 97% free metallic zinc with a total zinc content exceeding 99%.

Surface Preparation. Zinc-rich primers must be applied over clean steel surfaces to provide the metal-to-metal contact essential to successful performance of the coating. Abrasive blasting is the most effective method of cleaning steel. Although white metal blast-cleaning (NACE No. 1) is preferred, near-white SSPC-SP-10 or Commercial Blast Cleaning SSPC-SP-6 is acceptable (Ref 52).

Where the zinc is supplied as a separate component, it should be added slowly to the vehicle with constant agitation. After a homogeneous mix is obtained, the primer may be applied with air spray. Airless spray may also be used, but the nozzles may wear quickly. Because zinc settles rapidly, continuous agitation of the paint is essential during application, and fluid lines should be kept as short as possible.

To obtain a wet coat, the gun should be kept within 30 cm (1 ft) of the surface. Uneven film thickness due to brushing or rolling may result in mudcracking in the thick portions. Zinc-rich primers should be applied at a dry film thickness of 0.06 to 0.08 mm (2.5 to 3.5 mils).

The Nature of the Zinc-Rich Coating. Depending on the binder, zinc-rich coatings fall into two classes: organic and inorganic. The inorganic solvent-base types are derived from organic alkyl silicates, which become totally inorganic upon curing. Each offers particular protection characteristics, and each requires different preparation of the steel surface. The following comparisons should be helpful in selecting the most useful binder system.

The organic zinc-rich coatings are formed by using zinc dust as a pigment in an organic binder. This binder may be any of the well-known coating vehicles, such as chlorinated rubber and epoxy. The zinc dust must be in sufficient concentration so that the zinc particles are in particle-to-particle contact throughout the film. Thus, zinc provides cathodic protection. In the case of the organic binder, there is no reaction with the underlying surface other than for the organic vehicle to wet the steel surface thoroughly and to obtain mechanical adhesion.

Organic zinc-rich coatings do not require a white blast preparation of the steel surface, although a commercial blast should be included if the application is heavy service. For mild-service applications, the organic coating can be applied to a well-hand-cleaned surface, even if traces of rust are present.

Some proponents feel that maintaining proper humidity during surface preparation, application, and curing is not necessary. Because this type of coating is more flexible than inorganic coatings, exacting surface preparation for bonding to a substrate is not required. Finally, although organic coatings are more compatible with top coats, they are somewhat less abrasion resistant than the inorganic types.

As to the advantages of these coatings, organic zinc-rich coatings require less critical surface preparation, allow greater variation in application techniques, are less sensitive to varying climatic conditions during application and curing, and are more flexible and more resistant to chemical environments. Their disadvantages include flammability, blistering, harmful solvent effects, sensitivity to atmospheric influences, and relatively low heat resistance.

For better resistance against continuous exposure to salt water and to acid or alkali chemical fumes, zinc-rich coatings should be top coated with organic topcoats to provide a totally organic system, with optimum intercoat compatibility. A top coating may also be applied to provide color or to prevent gradual erosion of the zinc coating. Although zinc-rich coatings vary in application characteristics, they can be applied by brush or spray, and depending on the specific formulation, one coat can vary in thickness from 0.05 to 0.2 mm (2 to 7 mils).

Inorganic Zinc-Rich Coatings. Many inorganic zinc-rich coatings use water solutions of alkali silicates as vehicles. Others use phosphates, silicones, and modifications of these groups.

Self-cured coatings are two-component materials consisting of zinc dust and a vehicle; they are mixed immediately before application. Postcured coatings are three-component materials that consist of zinc dust, the vehicle to be mixed with it before application, and a curing agent that is applied on top of the coating.

The inorganic zinc coating forms its film and its adhesion to the steel surface by methods quite different from those of the organics. The coating system is a chemically reactive system, and the chemical activity is similar for either the water- or the solvent-base inorganic. Zinc is the principal reactive element in the inorganic coating systems and is primarily responsible for the development of initial insolubility. Depending on the formulation, other metal ions may be present in the system that also react and aid in the insolubilization of the coating. The silicate vehicle can also react with the underlying iron surface to form a chemical bond with the iron or steel substrate.

Inorganic zinc-rich coatings commonly require a white metal blast as preparation for the steel surface. Because inorganic coatings generally have limited flexibility and tend to break or crack upon bending or impact, careful preparation of the steel surface is required to ensure a good bond between the coating and the steel. However, despite the difficulties of preparation, these inorganic coatings are unaffected by solvents, oils, petroleum products, aliphatics, aromatics, ketones, and alcohols. They do not chalk, peel, or lose thickness over long periods of time. Also, they are easier to weld through and have excellent abrasion resistance and surface hardness.

Inorganic zinc-rich coatings offer good conductivity; good adhesion to clean steel; excellent resistance to weather, sunlight, and variations in temperature; resistance to radiation, heat, and abrasion; and reduced undercutting. Conversely, these coatings require unusually good surface preparation, display a lack of distensibility and adhesion to some metals other than steel and zinc, require moderate temperatures and atmospheric humidity for cure, and exhibit unsatisfactory durability under conditions of continuous immersion in electrolytes, and a lack of resistance to strong acids and alkalies.

Zinc Dust/Zinc Oxide Paint Versus Zinc-Rich Coating

Whether to use a zinc dust/zinc oxide paint or a zinc-rich coating depends on a number of factors, including cost of surface preparation, paint application, and anticipated length of surface. Zinc dust/zinc oxide coatings are ideal for rural or semi-industrial atmospheres. They are particularly effective on galvanized surfaces.

The widely used zinc dust/zinc oxide primers based on ordinary drying oil media do not give general electrolytic protection against corrosion and therefore do not fall in the category of zinc-rich paints.

Zinc-rich coatings are preferred for the protection of steel or galvanized steel structures exposed to marine environments or immersed in seawater. Applications include interiors of floating roof tanks, cooling tower piping, pipe racks and

exterior piping in refineries, stacks, chemical plant maintenance, offshore drilling platforms, aboveground pipelines, structural steel before erection, exterior of pressure vessels, ammonia tanks, ship holds, and air conditioning equipment.

A top coat finish may be necessary in aggressive atmospheres. The top coat must adapt to the environment and must guarantee compatibility with, and adhesion to, the zinc-rich primer.

Advantages and Limitations of Zinc-Rich Paints. Zinc-rich primers offer a more versatile form for applying zinc to steel than galvanization; large, continuous complex shapes and fabricated new or existing structures can be easily coated at manufacturing shops or in the field. Their performance has earned them a prominent place in the field of corrosion protection coatings. However, the limitations of zinc-rich paints include cost, difficulty in applying, and the requirement of clean steel surfaces. They must be top coated in severe environments (pH under 6.0 and over 10.5).

References cited in this section

48. K.B. Tator, Organic Coatings and Linings, *Corrosion,* Vol 13, *ASM Handbook* (formerly 9th ed., *Metals Handbook*), ASM International, 1987, p 399-418

52. *Zinc Coatings for Corrosion Protection,* Zinc Institute, 1978, p 14

Porcelain Enameling

Porcelain enamels are glass coatings applied primarily to products made of steel sheet, cast iron, or aluminum to improve appearance and protect the metal surface from corrosion. Porcelain enamels are distinguished from other ceramic coatings by their predominantly vitreous nature and the types of applications for which they are used, and from paint by their inorganic composition and the fusion of the coating matrix to the substrate metal. Porcelain enamels of all compositions are matured at 425 °C (800 °F) or above.

Several basic methods are used to apply porcelain enamels to the base metal. These include dipping, flow coating, electrodeposition, manual spray, electrostatic spray, and dry-powder spray. The best method of application for a particular part is determined by quantity and quality requirements, the type of material being applied, units produced per hour, capital investment, labor cost, and, ultimately, part cost. Details on application techniques for porcelain enameling are provided in the article "Porcelain Enameling" in this Volume.

Coating Materials The frits for porcelain enamel are designed and manufactured to meet specific end-use applications and processing requirements. Porcelain enamel frits for sheet steel are classified as either ground coat or cover coat types. Ground coat enamels contain metallic oxides that promote adherence to the steel substrate and may be used as a single functional coat or as a base coat for additional cover coats. Table 30 gives the composition of a typical ground coat enamel. Cover coat enamels (Table 31) are normally applied over ground coats for appearance and/or to improve the chemical and physical properties of the coating. Cover coats may also be applied directly to properly prepared decarburized steel substrates.

Table 30 Melted-oxide compositions of frits for ground coat enamels for sheet steel

Constituent	Composition, %			
	Regular blue-black enamel	Alkali-resistant enamel	Acid-resistant enamel	Water-resistant enamel
SiO_2	33.74	36.34	56.44	48.00
B_2O_3	20.16	19.41	14.90	12.82
Na_2O	16.74	14.99	16.59	18.48

K_2O	0.90	1.47	0.51	. . .
Li_2O	. . .	0.89	0.72	1.14
CaO	8.48	4.08	3.06	2.90
BaO	9.24	8.59	. . .	. . .
ZnO	. . .	2.29	. . .	. . .
Al_2O_3	4.11	3.69	0.27	. . .
ZrO_2	. . .	2.29	. . .	8.52
TiO_2	. . .	. . .	3.10	3.46
CuO	. . .	. . .	0.39	. . .
MnO_2	1.43	1.49	1.12	0.52
NiO	1.25	1.14	0.03	1.21
Co_3O_4	0.59	1.00	1.24	0.81
P_2O_5	1.04	. . .	. . .	0.20
F_2	2.32	2.33	1.63	1.94

Table 31 Melted oxide compositions of frits used for cover coat enamels for sheet steel

Constituent	**Composition, wt%**		
	Titania white enamel	**Semi-opaque enamel**	**Clear enamel**
SiO_2	44.67	44.92	54.26
B_2O_3	14.28	16.40	12.38
Na_2O	8.27	8.67	6.55

K_2O	6.99	8.12	11.32
Li_2O	0.98	0.45	1.14
ZnO	. . .	0.74	. . .
ZrO_2	1.98	3.34	1.40
Al_2O_3	0.31	0.16	. . .
TiO_2	18.49	13.05	10.04
P_2O_5	1.32	0.88	. . .
MgO	0.5	. . .	. . .
F_2	2.21	3.27	2.91

Because all porcelain enamels are variations of borosilicate glass, they are characterized by end use and not by chemical composition. Some common designations for those with particular characteristics are acid-resistant, alkali-resistant, heat-resistant, glossy, low-gloss, and matte.

Steel Substrates. Typical compositions of the various grades of low-carbon sheet iron or steel that are commercially available for porcelain enameling are listed in Table 32. Cold-rolled sheet steels used for porcelain enameling can be divided into three groups:

- Extra-low carbon steels (a maximum of 0.008% C), including HSLA steels in which the carbon is stabilized by the addition of titanium or niobium
- Low-carbon steels containing about 0.02% C (these steels are suitable for ground or two-coat enameling)
- Conventional cold-rolled sheets with higher carbon contents of about 0.06% (such sheets have a tendency toward primary boiling and sagging and are used in less critical ground coat and two-coat enameling applications)

Table 32 Compositions of low-carbon steels used for porcelain enameling

Type of steel	Composition, %[(a)]							
	C	Mn	P	S	Al	Ti	Nb	B
Replacement steel for enameling iron	0.02-0.05	0.15-0.3	0.015[(b)]	0.015[(b)]	0.03-0.07	. . .	. . .	0.006
Decarburized	0.005	0.2-0.3	0.01	0.02	[(c)]	. . .	. . .	. . .

Titanium-stabilized	0.05	0.30	0.01	0.02	0.05	0.30	. . .	. . .
Interstitial-free	0.005	0.20	0.01	0.02	. . .	0.04	0.09	. . .
Cold-rolled	0.06	0.35	0.01	0.02	(c)	. . .	. . .	. . .

(a) All compositions contain balance of iron.

(b) Maximum.

(c) Some steels may be supplied as aluminum-killed products. Data from Porcelain Enamel Institute

Hot-rolled steels are generally used for porcelain enameled water heater tanks and for other applications where thickness and strength requirements dictate their use. When hot-rolled steels are used, components should be coated on one side only to minimize processing defects such as fishscales.

Coating Properties. Porcelain enamel is used extensively because of its resistance to household chemicals and foods. Mild alkaline or acid environments are generally involved in household applications. Special enamels or glass compositions are available to resist most acids--except for hydrofluoric or concentrated phosphoric--to temperatures of 230 °C (450 °F). Compositions may be formulated to resist alkali concentrations up to a pH of 12 at temperatures as high as 95 °C (200 °F).

The hardness of porcelain enamels ranges from 3.4 to 6.0 on the Moh's scale. Porcelain enamels show a high degree of abrasion resistance. Abrasion resistance can be increased by adding crystalline particles to the enamel composition by a devitrification heat treatment.

Thermal Spray Coatings

Thermal spray coatings are surface coatings engineered to provide original equipment with resistance to wear, erosion, abrasion, corrosion, and oxidation. Thermal spraying is also used to repair and upgrade in-service equipment. In general, thermal spray coatings can be applied to a range of substrate materials, including metals, ceramics, plastics, and polymer composites. Such coatings often are used instead of paint because of their predictable service life, increased effectiveness, and lower life-cycle costs.

Thermal spray processes deposit finely divided metallic or nonmetallic feedstock surfacing material in a molten or semimolten condition onto a properly prepared, grit-blasted substrate to form a coating. The thermal spray feedstock material (wire, cored wire, ceramic rod, or powder) is heated to its plastic or molten state by combustion (flame, high-velocity oxygen fuel, or detonation) or by electric (arc or plasma) processes. The material is then accelerated toward the substrate. The particles or droplets strike the surface, flatten, and form thin platelets (splats) that conform, adhere, and interlock with roughened surface irregularities and with each other. As the sprayed particles impinge on the substrate, they cool and build up, particle by particle, into a lamellar-structured coating. Figure 7 in the preceding article "Surface Engineering of Cast Irons" in this Volume shows the lamellar structure of particle splats, oxide inclusions, and unmelted particles in a cross section of a typical thermal spray coating. In general, the substrate temperature can be kept at 200 °C (390 °F) or below to prevent metallurgical changes in the substrate material. Details of the thermal spray process can be found in Ref 53 and the article "Thermal Spray Coatings" in this Volume.

The properties of a thermal spray coating depend on such factors as its porosity, the cohesion between particles, adhesion to the substrate (including interface integrity), and the chemistry of the coating material. The particles bond to the substrate mechanically (the primary mechanism), metallurgically, or chemically. Particle impact velocity, particle size, substrate roughness, particle temperature, and substrate temperature influence bond strength.

Aluminum and zinc thermal spray coatings have a long history of corrosion protection in structural steel work, including:

- Buildings
- Bridges
- Towers
- Radio and TV antenna masts
- Steel gantry structures
- High-power search radar aerials
- Overhead walkways
- Railroad overhead line support columns
- Electrification masts
- Tower cranes
- Traffic island posts
- Street and bridge railings

Corrosion Protection by Thermal Spraying. Thermal spray coatings are used extensively for the corrosion protection of steel and iron in a wide range of environments. Their long-term effectiveness (20 years or more) in rural, industrial, and marine environments is well documented (Ref 54, 55, 56, 57).

The selection of a thermal spray coating depends on the service environment, desired service life, operating duty cycle, and available maintenance and repair support. Tables 33 and 34 give current service-life information for thermal spray coatings in various service environments, and Fig. 22 and 23 plot the corresponding required thickness specifications. The service-life estimates for 85Zn-15Al alloy and 90Al-10MMC (metal-matrix composite) coatings--introduced in the late 1970s and 1980s, respectively--are based on accelerated laboratory tests and service applications through 1992. In a marine environment, powder spray coatings with higher aluminum contents exhibit improved corrosion resistance (Ref 55). Where resistance to wear and/or abrasion is required in addition to corrosion protection, 90Al-10MMC coatings should be considered. The 90Al-10MMC wire is composed of 90 vol% Al and 10 vol% Al_2O_3.

Table 33 Service life estimates for 85Zn-15Al thermal spray coatings in selected corrosive environments

Type of exposure	Coating thickness required for indicated service life							
	5-10 years		10-20 years		20-40 years		>40 years	
	μm	in.	μm	in.	μm	in.	μm	in.
Rural atmosphere	. . .	. . .	75-125	0.003-0.005	125-175	0.005-0.007	250-300	0.010-0.012
Industrial atmosphere	. . .	. . .	150-200	0.006-0.008	300-375	0.012-0.015	350-400	0.014-0.016
Marine atmosphere	. . .	. . .	250-300	0.010-0.012	300-375	0.012-0.015	350-400	0.014-0.016
Freshwater immersion	150-200	0.006-0.008	250-350	0.010-0.014	300-375	0.012-0.015	. . .	. . .
Saltwater immersion	250-300	0.010-0.012	350-400	0.014-0.016	. . .	. . .	. . .	. . .

Table 34 Service-life estimates for aluminum and 90Al-10MMC (vol%) thermal spray coatings

Type of exposure	Coating thickness required for indicated service life[a]

	5-10 years		10-20 years		20-40 years		>40 years	
	µm	**in.**	**µm**	**in.**	**µm**	**in.**	**µm**	**in..**
Rural atmosphere	. . .	. . .	. . .	. . .	150-200	0.006-0.008	. . .	. . .
Industrial atmosphere	. . .	. . .	150-200	0.006-0.008	250-300	0.010-0.012	250-375	0.010-0.015
Marine atmosphere	150-200	0.006-0.008	200-250	0.008-0.010	250-300	0.010-0.012	250-375	0.010-0.015
Freshwater immersion	150-200	0.006-0.008	200-250	0.008-0.010	250-300	0.010-0.012	. . .	. . .
Saltwater immersion	200-250	0.008-0.010	250-300	0.010-0.012	300-350	0.012-0.014	. . .	. . .
High-temperature (100-540 °C, or 210-1000 °F)	150-200	0.006-0.008	200-250	0.008-0.010	250-300	0.010-0.012	. . .	. . .
Wear, abrasion, erosion, and impact (90/10 MMC preferred)	150-200	0.006-0.008	250-300	0.010-0.012	. . .	. . .	. . .	. . .

(a) With exception of wear abrasion, erosion, and impact properties, data for aluminum and 90Al-10MMC thermal spray coatings are identical.

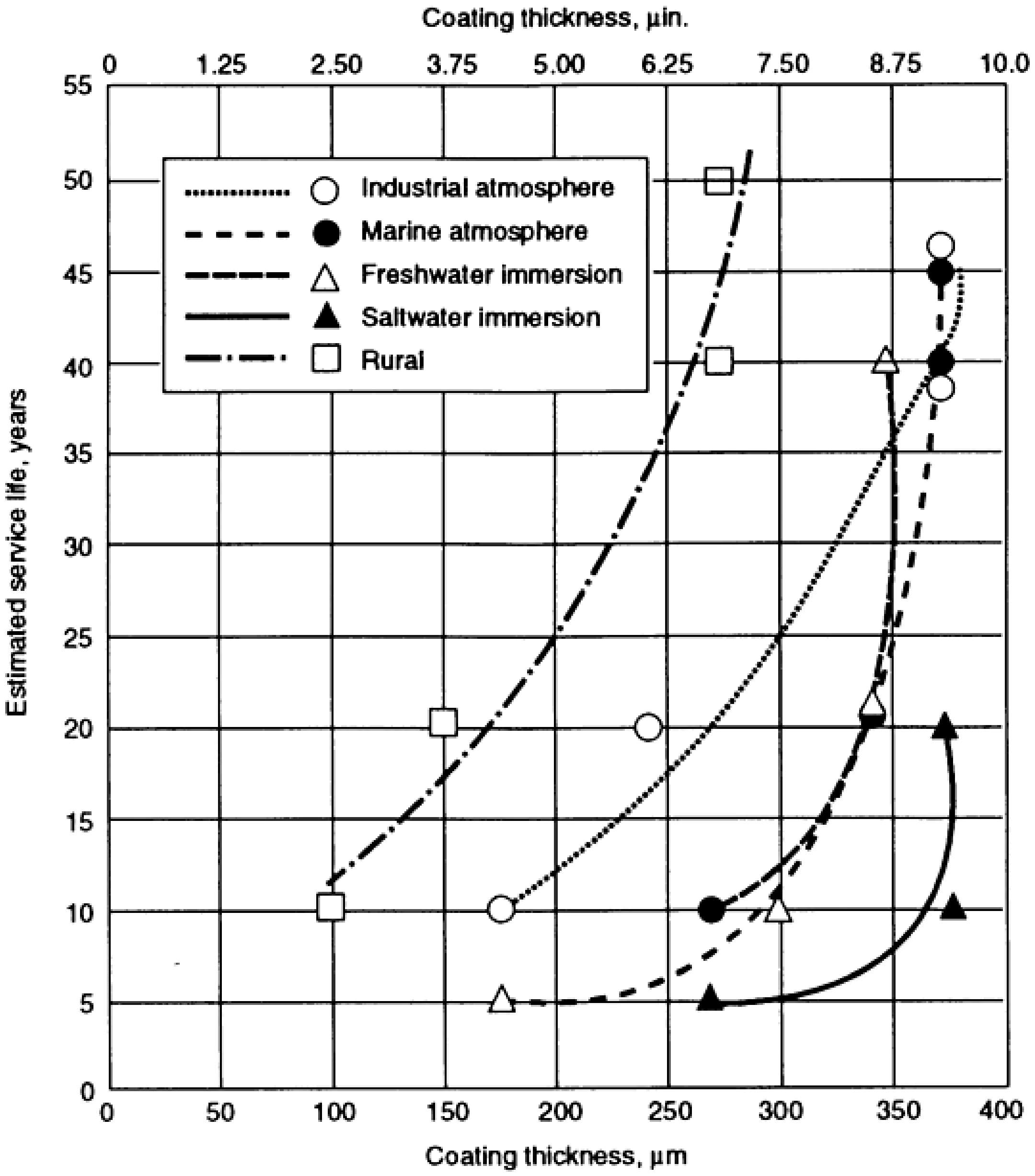


Fig. 22 Plot of service life versus coating thickness as a function of environment for an 85Zn-15Al thermal spray coating

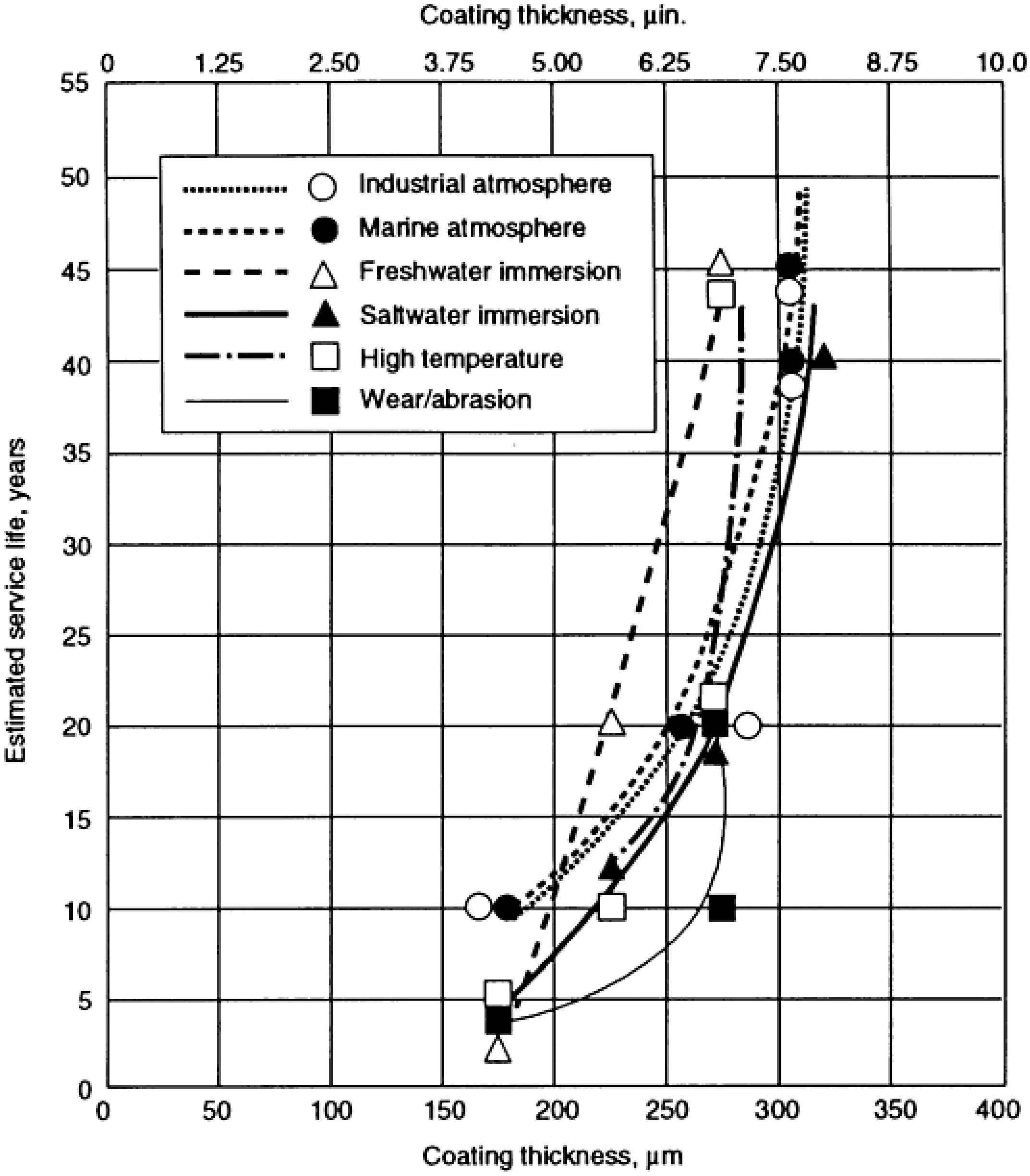


Fig. 23 Plot of service life versus coating thickness as a function of environment for a 90Al-10MMC (vol%) thermal spray coating

Coatings of aluminum, zinc, and their alloys and composites provide broad atmospheric protection. Aluminum and zinc are anodic to steel and protect the ferrous substrate in electrolytic solutions. When applied sufficiently thick to prevent through-porosity, they provide both barrier and cathodic protection. When applied too thinly or when cut through to expose the underlying steel, these coatings provide galvanic protection. Aluminum corrodes less rapidly than zinc in highly acidic conditions, while zinc performs better in alkaline conditions. Aluminum thermal spray coatings immediately oxidize to form a loosely adherent Al_2O_3 protective film that prevents further oxidation. Thus, there is no advantage to applying aluminum coatings in a thickness greater than that which prevents through-porosity (150 to 200 μm, or 0.006 to 0.008 in.) unless wear or abrasion resistance is required in addition to corrosion resistance. Aluminum thermal spray coatings have greater wear, abrasion, and erosion resistance than zinc coatings.

Zinc alloyed with aluminum forms an effective corrosion-resistant coating, combining the attributes of both elements. The greater electrochemical activity of zinc provides greater galvanic protection than aluminum. Aluminum, with its lower electrochemical activity and a loosely adherent aluminum oxide film, provides long-term protection even when the coating is porous and gives better wear, abrasion, and erosion resistance than zinc.

Aluminum and aluminum composite thermal spray coatings can be used where the temperature is greater than 200 °C (390 °F). Aluminum composite coatings are used when resistance to wear, abrasion, and erosion is required beyond that provided by aluminum and zinc.

Wear coatings applied by thermal spraying are used to resist abrasion, erosion, cavitation, and fretting, and to reduce friction. These coatings consist of a wide range of metals and their alloys, ceramics, cermets, carbides, and even low-friction plastics. Typical coating hardness ranges from 20 to 70 HRC. Table 35 lists friction and wear (hardfacing) applications for various thermal spray materials.

Table 35 Thermal spray coatings used for hardfacing applications

Type of wear	Coating material	Coating process[(a)]	Applications
Adhesive wear	Aluminum bronze	OFW, EAW, OFP, PA, HVOF	Babbitt bearings, hydraulic press sleeves, thrust bearing shoes, piston guides, compressor crosshead slippers
	Soft bearing coatings:		
	Tobin bronze	OFW, EAW	
	Babbitt	OFW, EAW, OFP	
	Tin	OFW,EAW, OFP,	
	Hard bearing coatings:		
	Mo/Ni-Cr-B-Si blend	PA	Bumper crankshafts for punch press, sugar cane grinding roll journals, antigalling sleeves, rudder bearings, impeller shafts, pinion gear journals, piston ring (internal combustion); fuel pump rotors
	Molybdenum	OFW,EAW, PA	
	High-carbon steel	OFW, EAW	
	Alumina/titania	OFP, PA	
	Tungsten carbide	OFP, PA, HVOF	
	Co-Mo-Cr-Si	PA, HVOF	
	Fe-Mo-C	PA	

Abrasive wear	Aluminum oxide	PA	Slush-pump piston rods, polish rod liners, and sucker rod couplings (oil industry); concrete mixer screw conveyors; grinding hammers (tobacco industry); core mandrels (dry-cell batteries); buffing and polishing fixtures; fuel-rod mandrels
	Chromium oxide	PA	
	Tungsten carbide	PA, HVOF	
	Chromium carbide	PA, HVOF	
	Ni-Cr-B-SiC/WC (fused)	OFP, HVOF	
	Ni-Cr-B-SiC (fused)	OFP, HVOF	
	Ni-Cr-B-SiC (unfused)	HVOF	
Surface fatigue wear			
Fretting: Intended motion applications	Molybdenum	OFW, PA	Servomotor shafts, lathe and grinder dead centers, cam followers, rocker arms, piston rings (internal combustion), cylinder liners
	Mo/Ni-Cr-B-SiC	PA	
	Co-Mo-Cr-Si	PA, HVOF	
Fretting: Small amplitude oscillatory displacement applications:			
Low temperature (<540 °C, or 1000 °F)	Aluminum bronze	OFW, EAW, PA, HVOF	Aircraft flap tracks (air-frame component); expansion joints and mid-span supports (jet engine components)
	Cu-Ni-In	PA, HVOF	
	Cu-Ni	PA, HVOF	
High temperature (>540 °C or 1000 °F)	Co-Cr-Ni-W	PA, HVOF	Compressor air seals, compressor stators, fan duct segments and stiffeners (all jet engine components)
	Chromium carbide	PA, HVOF	
Erosion	Chromium carbide	PA,HVOF	Exhaust fans, hydroelectric valves, cyclone dust collectors, dump valve plugs and seats, exhaust valve seats

	Tungsten carbide	PA, HVOF	
	WC/Ni-Cr-B-Si-C(fused)	OFP, HVOF	
	WC/Ni-Cr-B-SiC (unfused)	OFP, HVOF	
	Chromium oxide	PA	
Cavitation	Ni-Cr-B-SiC-Al-Mo	PA	Wear rings (hydraulic turbines), water turbine buckets, water turbine nozzles, diesel engine cylinder liners, pumps
	Ni-Al/Ni-Cr-B-SiC	PA	
	Type 316 stainless steel	PA	
	Ni-Cr-B-SiC (fused)	OFP, HVOF	
	Ni-Cr-B-SiC (unfused)	HVOF	
	Aluminum bronze	PA, HVOF	
	Cu-Ni	PA, HVOF	

(a) OFW, oxyfuel wire spray; EAW, electric arc wire spray;OFP, oxyfuel powder spray; PA, plasma arc spray; HVOF, high-velocity oxyfuel powder spray

Oxidation Protection. Thermal spray coatings are extensively used by industry to protect steel components and structures from heat oxidation at surface temperatures to 1095 °C (2000 °F). By ensuring long-term protection, thermal spray coatings show real economic advantages during the service lives of such items. Coatings such as pure aluminum, aluminum-iron, nickel-chromium, and MCrAlY are particularly effective in protecting low-alloy and carbon steels.

References cited in this section

53. J.R. Davis, Hardfacing, Weld Cladding, and Dissimilar Metal Joining, *Welding, Brazing, and Soldering,* Vol 6, *ASM Handbook,* ASM International, 1993, p 789-829
54. "Corrosion Tests of Flame-Sprayed Coated Steel, 19-Year Report," C2.14-74, American Welding Society, 1974
55. R.M. Kain and E.A. Baker, Marine Atmospheric Corrosion Museum Report on the Performance of Thermal Spray Coatings on Steel, *Testing of Metallic and Inorganic Coatings,* STP 947, ASTM, 1987

56. "Code of Practice for Protective Coating of Iron and Steel Structures against Corrosion," BS 5493, British Standards Institution, 1977; available from the American National Standards Institute
57. "Sprayed Metal Coatings for Atmospheric Corrosion Protection," G 189-1966, Canadian Standards Association, 1966; reaffirmed 1980

Hardfacing

Hardfacing may be broadly defined as the application of a wear-resistant material, in depth, to the vulnerable (or worn) surfaces of a component by a weld overlay or thermal spray process. This discussion deals with the weld overlay materials used to resist wear; the thermal spray materials are covered in the previous section in this article. More detailed information on hardfacing process and alloy selection can be found in Ref 47 and 53.

Welding processes used to apply hardfacing materials range from the traditional (for example, oxyacetylene torch) to the new and sophisticated (for example, plasma-transferred arc, PTA, and laser methods). To accommodate these different overlay processes, the hardfacing materials are available in a variety of forms. The most popular processes, and the forms most commonly associated with each process, are listed in Table 36.

Table 36 Characteristics of welding processes used in hardfacing

Welding process	Mode of application	Form of hardfacing alloy	Weld-metal dilution, %	Deposition		Minimum thickness[a]		Deposit efficiency, %
				kg/h	lb/h	mm	in.	
OAW	Manual	Bare cast rod, tubular rod	1-10	0.5-2	1-4	0.8	$\frac{1}{32}$	100
	Manual	Powder	1-10	0.5-2	1-4	0.8	$\frac{1}{32}$	85-95
	Automatic	Extra-long bare cast rod, tubular wire	1-10	0.5-7	1-15	0.8	$\frac{1}{32}$	100
SMAW	Manual	Flux-covered cast rod, flux-covered tubular rod	10-20	0.5-5	1-12	3.2	$\frac{1}{8}$	65
Open arc	Semiautomatic	Alloy-cored tubular wire	15-40	2-11	5-25	3.2	$\frac{1}{8}$	80-85
	Automatic	Alloy-cored tubular wire	15-40	2-11	5-25	3.2	$\frac{1}{8}$	80-85
GTAW	Manual	Bare cast, tubular rod	10-20	0.5-3	1-6	2.4	$\frac{1}{32}$	98-100
	Automatic	Various forms(b)	10-20	0.5-5	1-10	2.4	$\frac{1}{32}$	98-100

SAW	Automatic, single wire	Bare tubular wire	30-60	5-11	10-25	3.2	$\frac{1}{8}$	95
	Automatic, multiwire	Bare tubular wire	15-25	11-27	25-60	4.8	$\frac{3}{16}$	95
	Automatic, series arc	Bare tubular wire	10-25	11-16	25-35	4.8	$\frac{3}{16}$	95
PAW	Automatic	Powder(c)	5-15	0.5-7	1-15	0.8	$\frac{1}{32}$	85-95
	Manual	Bare cast rod, tubular rod	5-15	0.5-4	1-8	2.4	$\frac{3}{32}$	98-100
	Automatic	Various forms(b)	5-15	0.5-4	1-8	2.4	$\frac{3}{32}$	98-100
GMAW	Semiautomatic	Alloy-cored tubular wire	10-40	0.9-5	2-12	1.6	$\frac{1}{16}$	90-95
	Automatic	Alloy-cored tubular wire	10-40	0.9-5	2-12	1.6	$\frac{1}{16}$	90-95
Laser	Automatic	Powder	1-10	(d)	(d)	0.13	0.005	85-95

(a) Recommended minimum thickness of deposit.

(b) Bare tubular wire; extra-long (2.4 m, or 8 ft) bare cast rod; tungsten carbide powder with cast rod or bare tubular wire.

(c) With or without tungsten carbide granules.

(d) Varies widely depending on powder feed rate and laser input power

Hardfacing materials fall into six categories:

- Build-up alloys
- Metal-to-metal wear alloys
- Metal-to-earth abrasion alloys
- Tungsten carbides (for extreme earth sliding and cutting wear)
- Nonferrous alloys

- Stainless steels

The build-up alloys are not designed to resist wear but to return a worn part back to, or near, its original dimensions and to provide adequate support for subsequent layers of true hardfacing materials. However, these alloys are sometimes used as wear-resistant materials under mild wear conditions.

The build-up alloys fall into two categories: alloy steels and austenitic manganese steels. The alloy steel build-up materials are used with carbon steel and alloy steel substrates; the austenitic manganese steels are used for the joining, repair, and/or protection of manganese steel components. Specific build-up alloy compositions and properties are given in Table 37. Typical examples of applications where build-up alloys are used include tractor rails, railroad rail ends, steel mill table rolls, and large slow-speed gear teeth.

Table 37 Composition, hardness, and abrasion data for build-up alloys and metal-to-metal wear alloys

Alloy	**Composition, wt%**							**Hardness, HRC**	**Abrasion, volume loss**			
									Low-stress[c]		**High-stress[d]**	
	Fe	**Cr**	**C**	**Si**	**Mn**	**Mo**	**Ni**		**mm^3**	**$in.^3 \times 10^{-3}$**	**mm^3**	**$in.^3 \times 10^{-3}$**
Build-up weld overlay												
EFe1[a]	bal	2	0.1	1.0	1	1.5	. . .	37	88	5.4	49	3.0
EFeMn-C[a]	bal	4	0.8	1.3	14	. . .	4	18	65	4.0	57	3.5
EFeMn-Cr[a]	bal	15	0.5	1.3	15	2.0	1	24	93	5.7	46	2.8
Metal-to-metal weld overlay												
EFe2[a]	bal	3	0.2	1.0	1	1.0	1	48	54	3.3	66	4.0
EFe3[b]	bal	6	0.7	1.0	1	1.0	. . .	59	60	3.7	68	4.1

(a) Two-layer SMA deposit process.

(b) Two-layer SAW deposit process.

(c) Dry sand/rubber wheel test (ASTM G 65, Procedure B): Load 13.6 kg (30 lb); 200 rev.

(d) Slurry/steel wheel test (ASTM B 611, modified): load 22.7 kg (50 lb); 250 rev

Alloys in the metal-to-metal category (commonly referred to as machinery hardfacing alloys) are martensitic, air-hardening steels that can be applied several layers thick and can be finish machined (although with some difficulty) if adequate equipment is used. They are recommended for wearing, industrial, heavy-duty, nonlubricated parts. These materials are also sometimes referred to as "super build-up" alloys. If a machined finish is required, three layers are generally applied, with the assumption that the top layer will be removed during machining. A single layer is usually adequate because of the effects of substrate/overlay intermixing (dilution).

Typical compositions and properties of metal-to-metal wear alloys are listed in Table 37. In hostile environments, a higher chromium content is beneficial. ER420 (American Welding Society, AWS, classification), and modified versions containing nickel, molybdenum, and niobium (or vanadium), are therefore the natural choice when high temperatures and mildly corrosive environments are encountered. For applications using steel mill hot-work rolls (which demand considerable hot hardness, resistance to oxidation, and resistance to thermal fatigue) both ER420 and EFe3 have been found suitable. Other applications for the metal-to-metal wear alloys in Table 37 include tractor rollers and crane wheels (EFe2), pincer guide shoes (EFe3), and blast furnace bells (ER420).

Most of the materials in the metal-to-earth, carbide, and nonferrous alloy categories consist of hard particles within a metallic matrix, and, for many, it is the hard constituent that provides resistance to wear. The primary function of the metal-to-earth abrasion alloys and tungsten carbides is abrasion resistance. The metal-to-earth alloys are high-chromium white irons in which chromium carbides are formed during alloy solidification. The tungsten carbides are actually composite materials, and their use involves the transfer of discrete tungsten carbide particles (which in the welding consumable forms are encased in a steel tube) across the welding arc and into the molten weld pool, where they are subsequently "frozen" into the overlay structure by the matrix formed from the melting of the steel tube. Typical applications for these material types include shovel teeth, rock crusher parts, plowshares, and auger flights.

The nonferrous hardfacing alloys are used in environments that are too aggressive for the ferrous hardfacing alloys or where high resistance to a specific type of wear (other than abrasion) is required. They are classified as follows:

- Cobalt-base/carbide type
- Cobalt- and nickel-base/Laves type
- Nickel-base/boride type
- Bronze type

Whereas the ferrous hardfacing alloys and tungsten carbide composites find extensive use in agriculture, mining, construction, and the steel industry, the nonferrous alloys are typically used in the chemical processing, power, automotive, and oil industries, all of which require resistance to a hostile environment in addition to resistance to wear. The cobalt-base alloys are especially resistant to deformation and chemical attack at high temperatures (500 °C < $T \leq 900$ °C, or 930 °F < $T \leq 1650$ °F) and are used to protect dies and guide rolls in the steel industry. Other common applications of the nonferrous hardfacing alloys include valve seating surfaces (both control valves and diesel exhaust valves), pump parts, extrusion screw flights, rock bit bearings, marine bearings, and glass molding hardware.

The stainless steel weld overlays include both cobalt-free and cobalt-containing austenitic stainless steels. The cobalt-free grades, which contain nominally 0.8% C, 25% Cr, 4.5% Mn, 3.0% Si, 7.0% Ni, 2.0% Mo, and 0.1% N, have been developed to replace cobalt-base hardfacing alloys in nuclear power plant applications (valve overlays). The cobalt-containing grades, which contain nominally 0.2% C, 17% Cr, 9.5% Mn, 2.5% Si, 9% Co, and 0.2% N, have been developed for the repair of the cavitation erosion damage of turbines used in hydroelectric power plants.

References cited in this section

47. Stainless Steel Cladding and Weld Overlays, in *ASM Specialty Handbook: Stainless Steels,* J.R. Davis, Ed., ASM International, to be published in the Fall of 1994
53. J.R. Davis, Hardfacing, Weld Cladding, and Dissimilar Metal Joining, *Welding, Brazing, and Soldering,* Vol 6, *ASM Handbook,* ASM International, 1993, p 789-829

Vapor-Deposited Coatings

Vapor-deposited coatings are sometimes used for the protection of steel, although the cost of such coatings can be prohibitive. In vapor deposition, whether it be physical vapor deposition (PVD) or chemical vapor deposition (CVD), the coating material is transported to the substrate in the form of individual atoms or molecules. A wide range of coating materials can be applied by vapor deposition. If applied to a sufficient thickness, the coating is essentially pore free and dense, thus providing excellent barrier protection. Processing details for various PVD/CVD coating methods can be found in the articles contained in the Section entitled "Vacuum and Controlled-Atmosphere Coating and Surface Modification Processes" in this Volume.

Ion plating of aluminum coatings on steel is used by the aircraft industry to protect high-strength steel components, such as landing gear, and as a fastener coating to reduce the galvanic effects of steel fasteners inserted in an aluminum structure. Ion plating has several advantages over other aluminum coating processes. The aluminum deposit is very adherent and passes the bend-to-break test. The deposit does not affect the mechanical properties of the substrate and can be applied with precise thickness control on a wide range of shapes. Both the coating and the coating process are nontoxic and do not contribute to pollution. Because of these advantages, ion plating of aluminum can be used in a wide range of applications and is particularly effective as a replacement for cadmium coatings, which can cause hydrogen embrittlement of high-strength steels. Vapor deposition of aluminum does not produce hydrogen; therefore, it does not cause embrittlement. Vapor-deposited aluminum protects against stress-corrosion cracking (SCC) and has a temperature limit of 495 °C (925 °F). It is less expensive than most other barrier coatings. Vapor deposition is also replacing hot dipping of aluminum on steel in some applications. During immersion in hot dipping, a brittle intermetallic compound layer of iron-aluminum is formed; this limits the formability of the steel. In addition, the coating contains iron impurities, which may be a severe shortcoming in highly corrosive environments (Ref 58).

Another important application area for vapor-deposited coatings on ferrous alloys is the use of PVD coatings to enhance the service life of high-speed tool steels. Examples of increased tool life obtained when using TiN and/or TiC PVD coated tools are described in the article "Surface Engineering of Specialty Steels" in this Volume.

Reference cited in this section

58. F. Dunbar, "Aluminum Coated Steels: Past, Present and Future," Paper 8201-037, presented at the ASM Metals Congress, St. Louis, MO, American Society for Metals, Oct 1982

Surface Modification

Surface modification processes, which involve altering the surface composition or structure of a material by the use of high-energy or particle beams, include ion implantation and laser surface processing. Although used far less on steels than the coating processes described previously in this article, surface modification techniques can significantly improve the wear and corrosion resistance of steel substrates.

Ion Implantation

Ion implantation is the process of modifying the physical or chemical properties of the near surface of a solid by embedding appropriate atoms into it from a beam of ionized particles. The use of accelerated electron beams can produce penetration into a substrate surface on the order of 0.1 to 0.2 μm (1000 to 2000 Å) at 100 kV, and with higher accelerating voltages the potential for depth of penetration is increased. Surfaces may be treated by ion implantation to produce an effective alloyed surface layer where the composition varies as a function of depth.

Although virtually any element in the periodic table can be injected into near-surface regions of a solid using ion implantation, the ions that improve the properties of steels include:

- Adhesive and abrasive wear: Ni, Ti + C, Y, and Ta + C
- Fatigue wear: B, N, and Ti
- Corrosion and oxidation wear: Cr, Ta, and Y
- Friction: Ti, Ti + C, Ag, Sn, and Au

The most common use of ion implantation for improving the properties of ferrous alloys involves tool steels used in metalworking and machining applications (see the article "Surface Engineering of Specialty Steels" in this Volume). Other end-use applications of ion implantation include improved wear, corrosion, and rolling contact fatigue in bearing alloys such as type 440C stainless steel and 52100 bearing steel (Ref 59, 60).

Laser Surface Processing

Lasers with continuous outputs of 0.5 to 10 kW can be used to modify the metallurgical structure of a surface and to tailor the surface properties without adversely affecting the bulk properties. Surface modification of steels via lasers can take the following four forms:

- Laser transformation hardening
- Laser surface melting
- Laser surface alloying
- Laser cladding (hardfacing)

Figure 24 shows typical ranges of conditions for various processes. The laser power, power density, and interaction time are the primary variables. Other variables, such as the composition of the atmosphere during treatment or the rate of material addition, are determined by the details of the processing--for example, the necessity of shielding against oxidation and the desired thickness, composition, and structure of the surface layer.

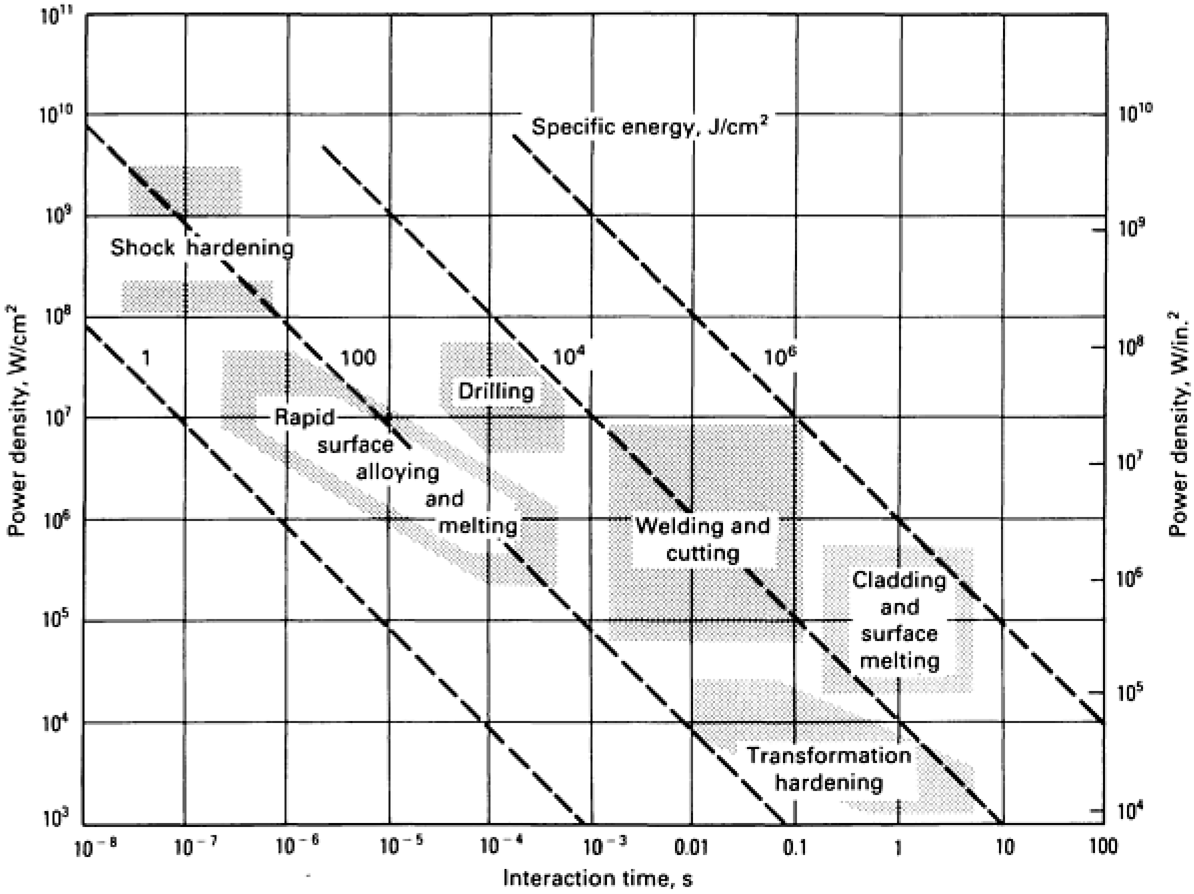


Fig. 24 Interaction times and power densities necessary for various laser surface modification processes

The laser beam modified layer can range in thickness from 0.01 to 5 mm (0.4 to 200 mils), depending on the processing variables, although thicknesses of 0.05 to 1 mm (2 to 40 mils) are more common. The longer the interaction time of the laser beam with the material, the deeper the processed layer will be. Of the processes shown in Fig. 24, the area labeled

"Cladding and surface melting" delineates process parameters that typically affect the material to depths from 0.5 to 5 mm (20 to 200 mils) and result in metallurgical structures similar to welded structures. The parameters designated "Rapid surface alloying and melting" affect a surface layer only 0.02 to 0.6 mm (0.8 to 24 mils) thick, but result in quench rates to 10^7 K/s and therefore allow for the production of novel metallurgical structures and alloys. Because laser transformation hardening is the most commercially viable (with regard to steels) of the laser processing methods listed above, it will be described further below. Additional information on laser surface processing can be found in Ref 61. Laser cladding, or laser hardfacing, is also described in Ref 53.

Laser surface heat treatment is widely used to harden localized areas of steel machine components such as gears and bearings. The heat generated by the absorption of the laser light is controlled to prevent melting, and therefore is used to selectively austenitize local surface regions which transform to martensite as a result of rapid cooling by the conduction of heat into the bulk of the workpiece. This process is referred to as laser transformation hardening to differentiate it from laser surface melting and alloying phenomena (Fig. 24). There is no chemistry change produced by laser surface heat treating of steels.

Laser heat treatment produces thin surface zones which are heated and cooled very rapidly, resulting in very fine martensitic microstructures, even in steels with relatively low hardenability. High hardness and good wear resistance with less distortion result from this process.

Steels which have been successfully laser surface hardened include plain carbon steels (1040, 1045, 1050, 1070) and alloy steels (4140, 4340, 52100) (Ref 62, 63). Typical case depths for steels range from 0.75 to 1.3 mm (0.030 to 0.050 in.) depending on the laser power range (Fig. 25). Hardness values as high as 60 HRC are routinely achieved using laser surface hardening.

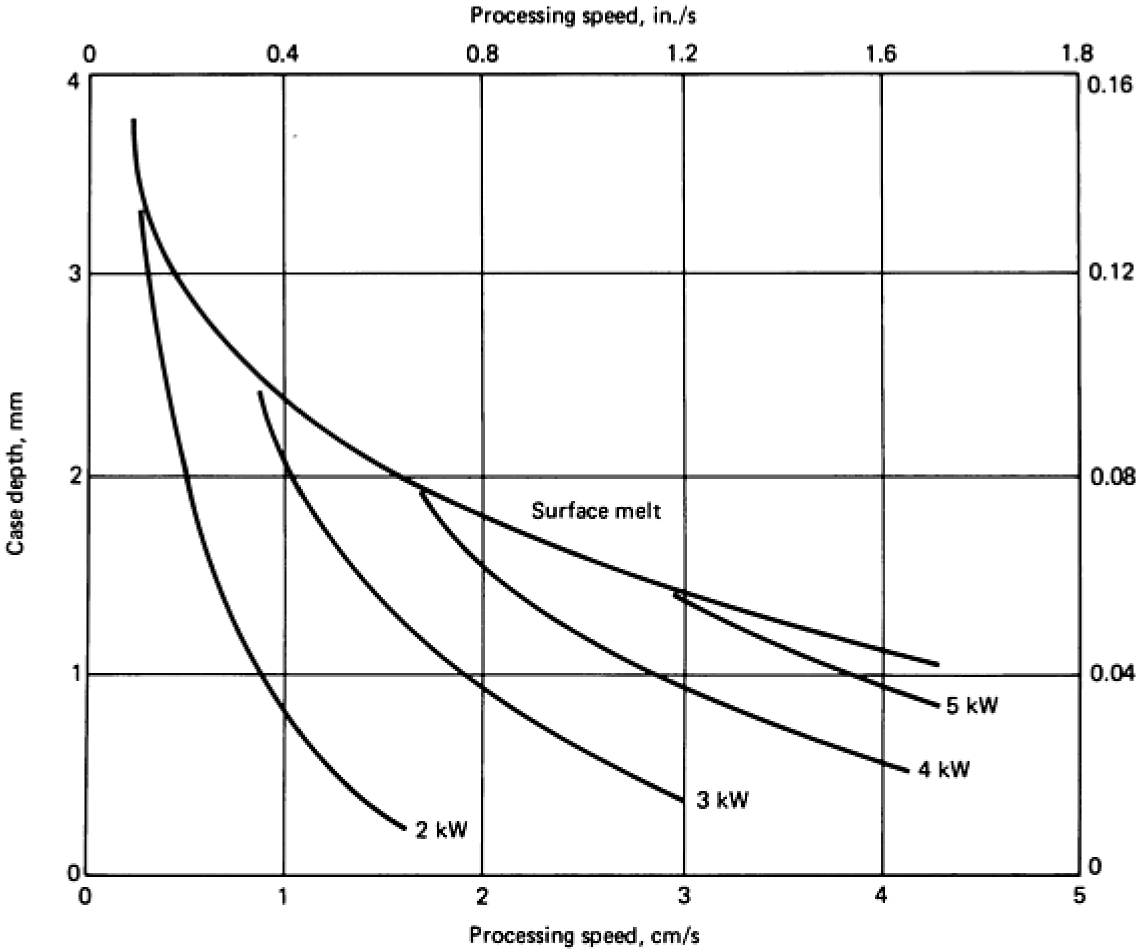


Fig. 25 Effect of laser processing speed and power output on case depth thickness of laser hardened 1078 carbon steel

References cited in this section

53. J.R. Davis, Hardfacing, Weld Cladding, and Dissimilar Metal Joining, *Welding, Brazing, and Soldering,* Vol 6, *ASM Handbook,* ASM International, 1993, p 789-829
59. D.L. Williamson, F.M. Kustas, and D.F. Fobare, *J. Appl. Phys.,* Vol 60, 1986, p 1493
60. F.M. Kustas, M.S. Misra, and P. Sioshensi, in *Ion Implantation and Ion Beam Processing of Materials,* G.K. Hubler, O.W. Holland, and C.R. Clayton, Ed., MRS Symposia Proceedings, 27, 1984, p 675
61. K.P. Cooper, Laser Surface Processing, *Friction, Lubrication, and Wear Technology,* Vol 18, *ASM Handbook,* ASM International, 1992, p 861-872
62. P.A. Molian, Engineering Applications and Analysis of Hardening Data for Laser Heat Treated Ferrous Alloys, *Surf. Eng.,* Vol 2, 1986, p 19-28
63. O. Sandven, Laser Surface Hardening, *Heat Treating,* Vol 4, *ASM Handbook,* ASM International, 1991, p 286-296

Surface Hardening (Ref 64)

Surface hardening is used to extend the versatility of certain steels by producing combinations of properties not readily attainable in other ways. For many applications, wear and the most severe stresses act only on the surface of a part. Therefore, the part may be fabricated from a formable low- or medium-carbon steel, and is surface hardened by a final heat treatment after all other processing has been accomplished. Surface hardening also reduces distortion and eliminates cracking that might accompany through hardening, especially in large sections. While an extensive review is beyond the scope of this article, two major approaches to surface hardening will be described below. One approach does not change composition and consists of hardening the surface by flame, induction, laser, or electron beam heating. The other approach changes surface composition and includes the applications of such diffusion techniques as carburizing, nitriding, and carbonitriding. Table 38 compares the relative benefits of the five most common surface hardening processes. More detailed information on surface hardening of steels can be found in *Heat Treating,* Volume 4 of the *ASM Handbook.*

Table 38 Relative benefits of five common surface-hardening processes

Process	Benefits
Carburizing	Hard, highly wear-resistant surface (medium case depth); excellent capacity for contact load; good bending fatigue strength; good resistance to seizure; excellent freedom from quench cracking; low-to-medium-cost steels required; high capital investment required
Carbonitriding	Hard, highly wear-resistant surface (shallow case depths); fair capacity for contact load; good bending fatigue strength; good resistance to seizure; good dimensional control possible; excellent freedom from quench cracking; low-cost steels usually satisfactory; medium capital investment required
Nitriding	Hard, highly wear-resistant surface (shallow case depths); fair capacity for contact load; good bending fatigue strength; excellent resistance to seizure; excellent dimensional control possible; good freedom from quench cracking (during pretreatment); medium-to-high-cost steels required; medium capital investment required
Induction hardening	Hard, highly wear-resistant surface (deep case depths); good capacity for contact load; good bending fatigue strength; fair resistance to seizure; fair dimensional control possible; fair freedom from quench cracking; low-cost steels usually satisfactory; medium capital investment required
Flame hardening	Hard, highly wear-resistant surface (deep case depths); good capacity for contact load; good bending fatigue strength; fair resistance to seizure; fair dimensional control possible; fair freedom from quench cracking; low-cost steels usually satisfactory; low capital investment required

Flame, Induction, and High-Energy Beam Methods

Flame hardening consists of austenitizing the surface of a steel by heating with an oxyacetylene or oxyhydrogen torch and immediately quenching with water. The result is a hard surface layer of martensite over a softer interior core with a ferrite-pearlite structure. There is no change in composition, and therefore the flame-hardened steel must have adequate carbon content for the desired surface hardness. The rate of heating and the conduction of heat into the interior appear to be more important in establishing case depth than the use of a steel of high hardenability.

Flame-heating equipment may be a single torch with a specially designed head or an elaborate apparatus that automatically indexes, heats, and quenches parts. Large parts such as gears and machine tool ways, with sizes or shapes that would make furnace heat treatment impractical, are easily flame hardened. With improvements in gas-mixing equipment, infrared temperature measurement and control, and burner design, flame hardening has been accepted as a reliable heat-treating process that is adaptable to general or localized surface hardening for small or medium-to-high production requirements.

Induction heating is an extremely versatile heating method that can perform uniform surface hardening, localized surface hardening, through hardening, and tempering of hardened pieces. Heating is accomplished by placing a steel part in the magnetic field generated by high-frequency alternating current passing through an inductor, usually a water-cooled copper coil. The depth of heating produced by induction is related to the frequency of the alternating current: The higher the frequency, the thinner or more shallow the heating. Therefore, deeper case depths and even through hardening are produced by using lower frequencies. The electrical considerations involve the phenomena of hysteresis and eddy currents. Because secondary and radiant heat are eliminated, the process is suited for production line areas.

High-energy beam methods for surface hardening include laser surface transformation hardening described earlier and electron beam (EB) hardening. Electron beam hardening, like laser treatment, is used to harden the surfaces of steels. The EB heat-treating process uses a concentrated beam of high-velocity electrons as an energy source to heat selected surface areas of ferrous parts. Electrons are accelerated and are formed into a directed beam by an electron beam gun. After exiting the gun, the beam passes through a focus coil, which precisely controls beam density levels (spot size) at the workpiece surface and then passes through a deflection coil. To produce an electron beam, a high vacuum of 10^{-5} torr (1.3×10^{-3} Pa) is needed in the region where the electrons are emitted and accelerated. This vacuum environment protects the emitter from oxidizing and avoids scattering of the electrons while they are still traveling at a relatively low velocity.

Like laser beam hardening, the EB process eliminates the need for quenchants but requires a sufficient workpiece mass to permit self-quenching. A mass of up to eight times that of the volume to be EB hardened is required around and beneath the heated surfaces.

Diffusion Methods

As previously mentioned, surface hardening by diffusion involves the chemical modification of a surface. The basic process used is thermochemical because some heat is needed to enhance the diffusion of hardening species into the surface and subsurface regions of a part.

Methods of hardening by diffusion include several variations of hardening species (such as carbon or nitrogen) and of the process method used to handle and transport the hardening species to the surface of the part. Process methods for exposure involve the handling of hardening species in forms such as gas, liquid, or ions. These process variations naturally produce differences in typical case depth and hardness. Table 39 compares the characteristics of various diffusion treatments.

Table 39 Typical characteristics of diffusion treatments

Process	Nature of case	Process temperature, °C (°F)	Case hardness, Typical case depth	HRC	Typical base metals	Process characteristics
Carburizing						
Pack	Diffused carbon	815-1090	125 μm-1.5 mm (5-60	50-	Low-carbon steels, low-	Low equipment costs, difficult to

		(1500-2000)	mils)	63[(a)]	carbon alloy steels	control case depth accurately
Gas	Diffused carbon	815-980 (1500-1800)	75 µm-1.5 mm (3-60 mils)	50-63[(a)]	Low-carbon steels, low-carbon alloy steels	Good control of case depth, suitable for continuous operation, good gas controls required, can be dangerous
Liquid	Diffused carbon and possibly nitrogen	815-980 (1500-1800)	50 µm-1.5 mm (2-60 mils)	50-65[(a)]	Low-carbon steels, low-carbon alloy steels	Faster than pack and gas processes, can pose salt disposal problem, salt baths require frequent maintenance
Vacuum	Diffused carbon	815-1090 (1500-2000)	75 µm-1.5 mm (3-60 mils)	50-63[(a)]	Low-carbon steels, low-carbon alloy steels	Excellent process control, bright parts, faster than gas carburizing, high equipment costs
Nitriding						
Gas	Diffused nitrogen, nitrogen compounds	480-590 (900-1100)	125 µm-0.75 mm (5-30 mils)	50-70	Alloy steels, nitriding steels, stainless steels	Hardest cases from nitriding steels, quenching not required, low distortion, process is slow, is usually a batch process
Salt	Diffused nitrogen, nitrogen compounds	510-565 (950-1050)	2.5 µm-0.75 mm (0.1-30 mils)	50-70	Most ferrous metals including cast irons	Usually used for thin hard cases <25 µm (1 mil), no white layer, most are proprietary processes
Ion	Diffused nitrogen, nitrogen compounds	340-565 (650-1050)	75 µm-0.75 mm (3-30 mils)	50-70	Alloy steels, nitriding steels, stainless steels	Faster than gas nitriding, no white layer, high equipment costs, close case control
Carbonitriding						
Gas	Diffused carbon and nitrogen	760-870 (1400-1600)	75 µm-0.75 mm (3-30 mils)	50-65[(a)]	Low-carbon steels, low-carbon alloy steels, stainless steel	Lower temperature than carburizing (less distortion), slightly harder case than carburizing, gas control critical
Liquid (cyaniding)	Diffused carbon and nitrogen	760-870 (1400-1600)	2.5-125 µm (0.1-5 mils)	50-65[(a)]	Low-carbon steels	Good for thin cases on noncritical parts, batch process, salt disposal problems
Ferritic nitrocarburizing	Diffused carbon and nitrogen	480-590 (900-1090)	2.5-25 µm (0.1-1 mil)	40-60[(a)]	Low-carbon steels	Low-distortion process for thin case on low-carbon steel, most processes are proprietary

Source: Ref 64

(a) Requires quench from austenitizing temperature.

Carburizing is the addition of carbon to the surface of low-carbon steels at temperatures (generally between 850 and 950 °C, or 1560 and 1740 °F) at which austenite, with its high solubility for carbon, is the stable crystal structure. Hardening is accomplished when the high-carbon surface layer is quenched to form martensite so that a high-carbon martensite case with good wear and fatigue resistance is superimposed on a tough, low-carbon steel core. Carburizing steels for case hardening usually have base-carbon contents of about 0.2%, with the carbon content of the carburized layer generally being controlled at between 0.8 and 1% C.

Carburizing methods include:

- Gas carburizing
- Vacuum carburizing
- Plasma carburizing
- Salt bath carburizing
- Pack carburizing

These methods introduce carbon by the use of gas (atmospheric-gas, plasma, and vacuum carburizing), liquids (salt bath carburizing), or solid compounds (pack carburizing). All of these methods have advantages and limitations, but gas carburizing is used most often for large-scale production because it can be accurately controlled and involves a minimum of special handling.

Nitriding is a surface-hardening heat treatment that introduces nitrogen into the surface of steel at a temperature range of 500 to 550 °C (930 to 1020 °F) while it is in the ferritic condition. Thus, nitriding is similar to carburizing in that surface composition is altered but different in that nitrogen is added into ferrite instead of austenite. Because nitriding does not involve heating into the austenite phase field and a subsequent quench to form martensite, nitriding can be accomplished with a minimum of distortion and with excellent dimensional control. Process methods for nitriding include gas, liquid (salt bath), and plasma (ion) nitriding.

Nitrided steels are generally medium-carbon (quenched and tempered) steels that contain strong nitride-forming elements such as aluminum, chromium, vanadium, and molybdenum. The most significant hardening is achieved with a class of alloy steels (nitralloy type) that contain about 1% Al. When these steels are nitrided, the aluminum forms AlN particles, which strain the ferrite lattice and create strengthening dislocations. Titanium and chromium are also used to enhance case hardness, although case depth decreases as alloy content increases. The microstructure also influences nitridability because ferrite favors the diffusion of nitrogen and because a low carbide content favors both diffusion and case hardness. Usually alloy steels in the heat-treated (quenched and tempered) state are used for nitriding.

Carbonitriding is a surface-hardening heat treatment that introduces carbon and nitrogen in the austenite of steel. This treatment is similar to carburizing in that the austenite composition is changed and high surface hardness is produced by quenching to form martensite. However, because nitrogen enhances hardenability, carbonitriding makes possible the use of low-carbon steel to achieve surface hardness equivalent to that of high-alloy carburized steel without the need for drastic quenching, resulting in less distortion and reducing the danger of cracking the work. To some extent, hardening is also dependent on nitride formation.

Although the process of carbonitriding can be performed with gas atmospheres or salt baths, the term carbonitriding often refers solely to treatment in a gas atmosphere. Basically, carbonitriding in a salt bath is the same as cyanide bath hardening. In both processes, nitrogen enhances hardenability and case hardness but inhibits the diffusion of carbon.

Ferritic nitrocarburizing involves the diffusion of carbon and nitrogen into the ferrite phase and the formation of a thin white layer of carbonitrides. The diffusion of nitrogen into the substrate is necessary for fatigue resistance. The case depths are thin (Table 39), but have a reduced tendency to spall, compared to the white layer formed during conventional nitriding. Ferritic nitrocarburizing, which is used to improve the anti-skuffing properties of steels, can be carried out by gas or plasma (ion) methods.

Reference cited in this section

64. S. Lampman, Introduction to Surface Hardening of Steels, *Heat Treating,* Vol 4, *ASM Handbook,* ASM International, 1991, p 259-267

Surface Engineering of Stainless Steels

J.R. Davis, Davis & Associates

Introduction

STAINLESS STEELS are iron-base alloys that contain a minimum of approximately 11% Cr, the amount needed to prevent the formation of rust in unpolluted atmospheres (hence the designation "stainless"). Few stainless steels contain more than 30% Cr or less than 50% Fe. They achieve their stainless characteristics through the formation of an invisible and adherent chromium-rich oxide surface film. This oxide forms and heals itself in the presence of oxygen. Other elements added to improve particular characteristics include nickel, molybdenum, copper, titanium, aluminum, silicon, niobium, nitrogen, sulfur, and selenium. Carbon is normally present in amounts ranging from less than 0.03% to over 1.0% in certain martensitic grades.

Although stainless steel is naturally passivated by exposure to air and other oxidizers, additional surface treatments often are needed to prevent corrosion. Passivation, pickling, electropolishing, and, in some cases, mechanical cleaning are important surface treatments for the successful performance of stainless steel used for piping, pressure vessels, tanks, and machined parts in a wide variety of applications, including pulp mills, nuclear power plants, hospital sterilization systems, food processing equipment, biotechnology processing plants, breweries, electronic-chip washing facilities, swimming pool hardware, water treatment plants, and chemical process plants.

Following a brief overview of the various types of stainless steels, this article will describe the various cleaning, finishing, and coating processes associated with engineered stainless steel surfaces. Determining which treatment should be used for specific applications is sometimes confusing. A good place to start is with ASTM A 380 (Ref 1), which is an excellent resource document for the cleaning and descaling of stainless steel parts, equipment, and systems, although it does not cover electropolishing.

Reference

1. "Standard Practice for Cleaning and Descaling Stainless Steel Parts, Equipment, and Systems," A 380, *Annual Book of ASTM Standards,* ASTM, 1988

Designations for Stainless Steels

In the United States, wrought grades of stainless steels are generally designated by the American Iron and Steel Institute (AISI) numbering system, the Unified Numbering System (UNS), or by the proprietary name of the alloy. In addition, designation systems have been established by most of the major industrial nations. Of the two institutional numbering systems used in the U.S., AISI is the oldest and most widely used. Most of the grades have a three-digit designation; the 200 and 300 series are generally austenitic stainless steels, whereas the 400 series are either ferritic or martensitic. Some of the grades have a one- or two-letter suffix that indicates a particular modification of the composition.

The UNS system is a broader-based system that comprises a list of all metallic materials, including stainless steel. This system includes a considerably greater number of stainless steels than AISI, because it incorporates all of the more recently developed stainless steels. The UNS designation for a stainless steel consists of the letter S, followed by a five-digit number. For those alloys that have an AISI designation, the first three digits of the UNS designation usually correspond to an AISI number. When the last two digits are 00, the number designates a basic AISI grade. Modifications of the basic grades use two digits other than zeroes.

Table 1 provides the compositional limits for select stainless steels, listed by UNS and AISI type designations and separated into the basic families described below. Where AISI type designations are not available, common trade names

are listed. These names, the third commonly used identification of stainless steels, have often become the popular means of identifying a particular alloy.

Table 1 Composition of selected standard and special stainless steels

UNS designation	AISI type	Composition, wt% max									
		C	Mn	Si	P	S	Cr	Ni	Mo	N	Others
Ferritic alloys											
S40500	405	0.08	1.00	1.00	0.040	0.030	11.50-14.50	. . .	. . .	. . .	0.10-0.30 Al
S40900	409	0.08	1.00	1.00	0.045	0.045	10.50-11.75	0.50	. . .	. . .	6 × C-0.75 Ti
S43000	430	0.12	1.00	1.00	0.040	0.030	16.00-18.00	. . .	. . .	. . .	. . .
S43020	430F	0.12	1.25	1.00	0.060	0.15[(a)]	16.00-18.00	. . .	0.60	. . .	. . .
S43023	430FSe	0.12	1.25	1.00	0.060	0.060	16.00-18.00	. . .	. . .	. . .	0.15 min Se
S43400	434	0.12	1.00	1.00	0.040	0.030	16.00-18.00	. . .	0.75-1.25	. . .	. . .
S44200	442	0.20	1.00	1.00	0.040	0.030	18.00-23.00	. . .	. . .	. . .	. . .
S44300	443[(b)]	0.20	1.00	1.00	0.040	0.030	18.00-23.00	0.50	. . .	. . .	0.90-1.25 Cu
S44400	444[(b)]	0.025	1.00	1.00	0.040	0.030	17.50-19.50	1.00	1.75-2.50	0.025	[0.20 + 4 (C + N)]-0.80 Ti + Nb
S44600	446[(b)]	0.20	1.50	1.00	0.040	0.030	23.00-27.00	. . .	. . .	0.25	. . .
S18200	18-2FM[(c)]	0.08	1.25-2.50	1.00	0.040	0.15[(a)]	17.50-19.50	. . .	1.50-2.50	. . .	. . .
Martensitic alloys											
S40300	403	0.15	1.00	0.50	0.040	0.030	11.50-	. . .	. . .	. . .	. . .

UNS designation	AISI type	Composition, wt% max									
		C	Mn	Si	P	S	Cr	Ni	Mo	N	Others
							13.00				
S41000	410	0.15	1.00	1.00	0.040	0.030	11.50-13.00	. . .	. . .	. . .	. . .
S41400	414	0.15	1.00	1.00	0.040	0.030	11.50-13.50	1.25-2.50	. . .	. . .	. . .
S41600	416	0.15	1.25	1.00	0.060	0.15[a]	12.00-14.00	. . .	0.60	. . .	. . .
S41610	416 Plus X[d]	0.15	1.50-2.50	1.00	0.060	0.15[a]	12.00-14.00	. . .	0.60	. . .	. . .
S41623	416Se	0.15	1.25	1.00	0.060	0.060	12.00-14.00	. . .	. . .	. . .	0.15 min Se
S42000	420	0.15[a]	1.00	1.00	0.040	0.030	12.00-14.00	. . .	. . .	. . .	. . .
S42010	TrimRite[e]	0.15-0.30	1.00	1.00	0.040	0.030	13.50-15.00	0.25-1.00	0.40-1.00	. . .	. . .
S42020	420F	0.15[a]	1.25	1.00	0.060	0.15[a]	12.00-14.00	. . .	0.60	. . .	. . .
S42023	420FSe[b]	0.30-0.40	1.25	1.00	0.060	0.060	12.00-14.00	. . .	0.60	. . .	0.15 min Se; 0.60 Zr or Cu
S43100	431	0.20	1.00	1.00	0.040	0.030	15.00-17.00	1.25-2.50	. . .	. . .	. . .
S44002	440A	0.60-0.75	1.00	1.00	0.040	0.030	16.00-18.00	. . .	0.75	. . .	. . .
S44003	440B	0.75-0.95	1.00	1.00	0.040	0.030	16.00-18.00	. . .	0.75	. . .	. . .
S44004	440C	0.95-1.20	1.00	1.00	0.040	0.030	16.00-18.00	. . .	0.75	. . .	. . .
S44020	440F[b]	0.95-1.20	1.25	1.00	0.040	0.10-0.35	16.00-18.00	0.75	0.40-0.60	0.08	. . .

UNS designation	AISI type	Composition, wt% max									
		C	Mn	Si	P	S	Cr	Ni	Mo	N	Others
S44023	440FSe[(b)]	0.95-1.20	1.25	1.00	0.040	0.030	16.00-18.00	0.75	0.60	0.08	0.15 min Se
Austenitic alloys											
S20100	201	0.15	5.50-7.50	1.00	0.060	0.030	16.00-18.00	3.50-5.50	. . .	0.25	. . .
S20161	Gall-Tough[(e)]	0.15	4.00-6.00	3.00-4.00	0.040	0.040	15.00-18.00	4.00-6.00	. . .	0.08-0.20	. . .
S20300	203EZ[(f)]	0.08	5.00-6.50	1.00	0.040	0.18-0.35	16.00-18.00	5.00-6.50	0.50	. . .	1.75-2.25 Cu
S20910	22-13-5[(c)]	0.06	4.00-6.00	1.00	0.040	0.030	20.50-23.50	11.50-13.50	1.50-3.00	0.20-0.40	0.10-0.30 Nb; 0.10-0.30 V
S21000	SCF19[(e)]	0.10	4.00-7.00	0.60	0.030	0.030	18.00-23.00	16.00-20.00	4.00-6.00	0.15	2.00 Cu
S21300	15-15LC[(e)]	0.25	15.00-18.00	1.00	0.050	0.050	16.00-21.00	3.00	0.50-3.00	0.20-0.80	0.50-2.00 Cu
S21800	Nitronic 60[(g)]	0.10	7.00-9.00	3.50-4.50	0.040	0.030	16.00-18.00	7.00-9.00	. . .	0.08-0.20	. . .
S21904	21-6-9LC[(e)]	0.04	8.00-10.00	1.00	0.060	0.030	19.00-21.50	5.50-7.50	. . .	0.15-0.40	. . .
S24100	18-2Mn[(c)]	0.15	11.00-14.00	1.00	0.060	0.030	16.50-19.50	0.50-2.50	. . .	0.20-0.45	. . .
S28200	18-18 Plus[(e)]	0.15	17.00-19.00	1.00	0.045	0.030	17.00-19.00	. . .	0.50-1.50	0.40-0.60	0.50-1.50 Cu
. . .	Nitronic 30[(g)]	0.10	7.00-9.00	1.00	. . .	. . .	15.00-17.00	1.50-3.00	. . .	0.15-0.30	1.00 Cu
S30100	301	0.15	2.00	1.00	0.045	0.030	16.00-18.00	6.00-8.00	. . .	. . .	. . .
S30200	302	0.15	2.00	1.00	0.045	0.030	17.00-	8.00-	. . .	. . .	. . .

UNS designation	AISI type	Composition, wt% max									
		C	Mn	Si	P	S	Cr	Ni	Mo	N	Others
							19.00	10.00			
S30300	303	0.15	2.00	1.00	0.20	0.15[(a)]	17.00-19.00	8.00-10.00	0.60	. . .	. . .
S30310	303 Plus X[(d)]	0.15	2.50-4.50	1.00	0.20	0.25[(a)]	17.00-19.00	7.00-10.00	0.75	. . .	. . .
S30323	303Se	0.15	2.00	1.00	0.20	0.060	17.00-19.00	8.00-10.00	. . .	. . .	0.15 min Se
S30330	303 Cu[(b)]	0.15	2.00	1.00	0.15	0.10[(a)]	17.00-19.00	6.00-10.00	. . .	. . .	2.50-4.00 Cu; 0.10 Se
S30400	304	0.08	2.00	1.00	0.045	0.030	18.00-20.00	8.00-10.50	. . .	. . .	. . .
S3043	304L	0.03	2.00	1.00	0.045	0.030	18.00-20.00	8.00-12.00	. . .	. . .	. . .
S30430	302 HQ[(b)]	0.10	2.00	1.00	0.045	0.030	17.00-19.00	8.00-10.00	. . .	. . .	3.00-4.00 Cu
S30431	302 HQ-FM[(e)]	0.06	2.00	1.00	0.040	0.14	16.00-19.00	9.00-11.00	. . .	. . .	1.30-2.40 Cu
S30452	304 HN[(b)]	0.08	2.00	1.00	0.045	0.030	18.00-20.00	8.00-10.50	. . .	0.16-0.30	. . .
S30500	305	0.12	2.00	1.00	0.045	0.030	17.00-19.00	10.00-13.00	. . .	. . .	. . .
S30900	309	0.20	2.00	1.00	0.045	0.030	22.00-24.00	12.00-15.00	. . .	. . .	. . .
S30908	309S	0.08	2.00	1.00	0.045	0.030	22.00-24.00	12.00-15.00	. . .	. . .	. . .
S31000	310	0.25	2.00	1.50	0.045	0.030	24.00-26.00	19.00-22.00	. . .	. . .	. . .
S31008	310S	0.08	2.00	1.50	0.045	0.030	24.00-26.00	19.00-22.00	. . .	. . .	. . .

UNS designation	AISI type	Composition, wt% max									
		C	Mn	Si	P	S	Cr	Ni	Mo	N	Others
S31600	316	0.08	2.00	1.00	0.045	0.030	16.00-18.00	10.00-14.00	2.00-3.00	. . .	. . .
S31603	316L	0.030	2.00	1.00	0.045	0.030	16.00-18.00	10.00-14.00	2.00-3.00	. . .	. . .
S31620	316F	0.08	2.00	1.00	0.20	0.10[a]	17.00-19.00	12.00-14.00	1.75-2.50	. . .	. . .
S31700	317	0.08	2.00	1.00	0.045	0.30	18.00-20.00	11.00-15.00	3.00-4.00	. . .	. . .
S31703	317L	0.030	2.00	1.00	0.045	0.030	18.00-20.00	11.00-15.00	3.00-4.00	. . .	. . .
S32100	321	0.08	2.00	1.00	0.045	0.030	17.00-19.00	9.00-12.00	. . .	. . .	5 × C min Ti
S34700	347	0.08	2.00	1.00	0.045	0.030	17.00-19.00	9.00-13.00	. . .	. . .	10 × C min Nb
S34720	347F[b]	0.08	2.00	1.00	0.045	0.18-0.35	17.00-19.00	9.00-12.00	. . .	. . .	10 × C-1.10 Nb
S34723	347FSe[b]	0.08	2.00	1.00	0.11-0.17	0.030	17.00-19.00	9.00-12.00	. . .	. . .	10 × C-1.10 Nb; 0.15-0.35 Se
S38400	384	0.08	2.00	1.00	0.045	0.030	15.00-17.00	17.00-19.00	. . .	. . .	. . .
N08020	20Cb-3[e]	0.07	2.00	1.00	0.045	0.035	19.00-21.00	32.00-38.00	2.00-3.00	. . .	8 × C-1.00 Nb; 3.00-4.00 Cu
Duplex alloys											
S31803	2205[c]	0.030	2.00	1.00	0.030	0.020	21.0-23.0	4.50-6.50	2.50-3.50	0.08-0.20	. . .
S32550	Alloy 255[c]	0.04	1.50	1.00	0.04	0.03	24.0-27.0	4.50-6.50	2.00-4.00	0.10-0.25	1.50-2.50 Cu
S32900	329	0.20	1.00	0.75	0.040	0.030	23.00-	2.50-	1.00-	. . .	. . .

UNS designation	AISI type	Composition, wt% max									
		C	Mn	Si	P	S	Cr	Ni	Mo	N	Others
							28.00	5.00	2.00		
S32950	7-Mo Plus(e)	0.03	2.00	0.60	0.035	0.010	26.0-29.0	3.50-5.20	1.00-2.50	0.15-0.35	. . .
Precipitation-hardenable alloys											
S13800	PH13-8 Mo(g)	0.05	0.20	0.10	0.010	0.008	12.25-13.25	7.50-8.50	2.00-2.50	0.01	0.90-1.35 Al
S15500	15-5PH(g)	0.07	1.00	1.00	0.040	0.030	14.00-15.50	3.50-5.50	. . .	. . .	0.15-0.45 Nb; 2.50-4.50 Cu
S15700	15-7PH(g)	0.09	1.00	1.00	0.040	0.030	14.00-16.00	6.50-7.25	2.00-3.00	. . .	0.75-1.50 Al
S17400	17-4PH(g)	0.07	1.00	1.00	0.040	0.030	15.50-17.50	3.00-5.00	. . .	. . .	0.15-0.45 Nb; 3.00-5.00 Cu
S17700	PH 17-7(g)	0.09	1.00	1.00	0.040	0.040	16.00-18.00	6.50-7.75	. . .	. . .	0.75-1.50 Al
S35000	633(b)	0.07-0.11	0.50-1.25	0.50	0.040	0.030	16.00-17.00	4.00-5.00	2.50-3.25	0.07-0.13	. . .
S35500	634(b)	0.10-0.15	0.50-1.25	0.50	0.040	0.030	15.00-16.00	4.00-5.00	2.50-3.25	0.07-0.13	. . .
S45000	Custom 450(e)	0.05	1.00	1.00	0.030	0.030	14.00-16.00	5.00-7.00	0.50-1.00	. . .	8 × C min; 1.25-1.75 Cu
S45500	Custom 455(e)	0.05	0.50	0.50	0.040	0.030	11.00-12.50	7.50-9.50	0.50	. . .	0.10-0.50 Nb; 1.50-2.50 Cu 0.80-1.40 Ti
S66286	A286(c)	0.08	2.00	1.00	0.040	0.030	13.50-16.00	24.0-27.0	1.00-1.50	. . .	0.35 Al; 0.0010-0.010 B 1.90-2.35 Ti; 0.10-0.50 V

Note: All compositions include Fe as balance.

(a) Minimum, rather than maximum wt%.

(b) Designation resembles AISI type, but is not used in that system.

(c) Common trade name, rather than AISI type.

(d) Trade name of Crucible Inc.

(e) Trade name of Carpenter Technology Corporation.

(f) Trade name of Al-Tech Corp.

(g) Trade name of Armco Inc.

Classification of Stainless Steels

Stainless steels can be divided into five families. Four are based on the characteristic crystallographic structure/microstructure of the alloys in the family: ferritic, martensitic, austenitic, or duplex (austenitic plus ferritic). The fifth family, the precipitation-hardenable alloys, is based on the type of heat treatment used, rather than microstructure.

Ferritic stainless steels are so named because their body-centered-cubic (bcc) crystal structure is the same as iron at room temperature. These alloys are magnetic and cannot be hardened by heat treatment. In general, ferritic stainless steels do not have particularly high strength. Their annealed yield strengths range from 275 to 350 MPa (40 to 50 ksi), and their poor toughness and susceptibility to sensitization limit their fabricability and the usable section size. Their chief advantages are their resistance to chloride stress-corrosion cracking, atmospheric corrosion, and oxidation, at a relatively low cost.

Ferritic stainless steels contain between 11 and 30% Cr, with only small amounts of austenite-forming elements, such as carbon, nitrogen, and nickel. Their general use depends on their chromium content.

The low-chromium (11%) alloys (S40500 and S40900, the latter being the most widely used ferritic stainless steel), have fair corrosion and oxidation resistance and good fabricability at low cost. They have gained wide acceptance for use in automotive exhaust systems.

The intermediate-chromium (16 to 18%) alloys (S43000 and S43400) are used for automotive trim and cooking utensils. These alloys are not as readily fabricated as the lower chromium alloys, because of their poor toughness and weldability.

The high-chromium (19 to 30%) alloys (S44200 and S44600), which are often referred to as superferritics, are used for applications that require a high level of corrosion and oxidation resistance. These alloys often contain either aluminum or molybdenum and have a very low carbon content. Their fabrication is possible because of special melting techniques that can achieve very low carbon, as well as very low nitrogen contents. Stabilizing elements, like titanium and niobium, can be added to prevent sensitization and to improve as-welded properties.

Austenitic stainless steels constitute the largest stainless family, in terms of number of alloys and usage. Like the ferritic alloys, they cannot be hardened by heat treatment. However, their similarity ends there. The austenitic alloys are nonmagnetic, and their structure is face-centered-cubic (fcc), like high-temperature (900 to 1400 °C, or 1650 to 2550 °F) iron. They possess excellent ductility, formability, and toughness, even at cryogenic temperatures. In addition, they can be substantially hardened by cold work.

Although nickel is the chief element used to stabilize austenite, carbon and nitrogen are also used, because they are readily soluble in the fcc structure. A wide range of corrosion resistance can be achieved by balancing the ferrite-forming elements, such as chromium and molybdenum, with austenite-forming elements.

Austenitic stainless steels can be subdivided into two categories: chromium-nickel alloys, such as S30400 and S31600, and chromium-manganese-nitrogen alloys, such as S20100 and S24100. The latter group generally contains less nickel and maintains the austenitic structure with high levels of nitrogen. Manganese (5 to 20%) is necessary in these low-nickel alloys to increase nitrogen solubility in austenite and to prevent martensite transformation. The addition of nitrogen also increases the strength in austenitic alloys. Typical chromium-nickel alloys have tensile yield strengths from 200 to 275 MPa (30 to 40 ksi) in the annealed condition, whereas the high-nitrogen alloys have yield strengths up to 500 MPa (70 ksi).

As previously mentioned, austenitic alloys can be substantially hardened by cold working. The degree of work hardening depends on the alloy content, with increasing alloy content decreasing the work-hardening rate. Austenitic stainless steels that have a low alloy content, such as S20100, S20161, S30100, and S30400, often become magnetic because of the transformation to martensite when sufficiently cold worked or heavily deformed in machining or forming operations. The rapid work hardening of S20161 is a major advantage in sliding wear. In S30430, copper is intentionally added to lower the work-hardening rate for enhanced headability in the production of fasteners.

Another property that depends on alloy content is corrosion resistance. Molybdenum is added to S31700 and S31600 to enhance corrosion resistance in chloride environments. High-chromium grades (S30900 and S31000) are used in oxidizing environments and high-temperature applications, whereas a high-nickel grade (N08020) is used in severe reducing acid environments. To prevent intergranular corrosion after elevated-temperature exposure, titanium or niobium is added to stabilized carbon in S32100 or S34700. Also, lower-carbon grades (AISI L or S designations), such as S30403 (type 304L), have been established to prevent intergranular corrosion. Highly alloyed materials (the superaustenitics) containing 20 to 26% Cr, 18 to 26% Ni, 6% Mo, and 0.1 to 0.2% N have been developed for enhanced resistance to chloride stress-corrosion cracking. Some of the more corrosion-resistant alloys, such as N08020 (20Cb-3), have nickel levels high enough (32 to 38% Ni) to rate classification as nickel-base alloys.

Martensitic stainless steels are similar to iron-carbon alloys that are austenitized, hardened by quenching, and then tempered for increased ductility and toughness. These alloys are magnetic, and their heat-treated structure is body-centered tetragonal (bct). In the annealed condition, they have a tensile yield strength of about 275 MPa (40 ksi) and are generally machined, cold formed, and cold worked in this condition.

The strength obtained by heat treatment depends on the carbon content of the alloy. Increasing carbon content increases strength, but decreases ductility and toughness. The most commonly used alloy in this family is S41000, which contains about 12% Cr and 0.1% C. This alloy is tempered to a variety of hardness levels, from 20 to 40 HRC. Both chromium and carbon contents are increased in alloys S42000, S44002, S44003, and S44004. The first of these contains 14% Cr and 0.3% C and has a hardness capability of 50 HRC. The other three alloys contain 16% Cr and from 0.6 to 1.1% C. These alloys are capable of 60 HRC, and a tensile yield strength of 1900 MPa (280 ksi). The amount of primary carbides increases with increased carbon content in these three alloys.

Wear resistance for martensitic stainless steels is very dependent on carbon content. S44004 (1.1% C) has excellent adhesive and abrasive wear, similar to tool steels, whereas S41000 (0.1% C) has relatively poor wear resistance. The key to adhesive wear resistance is a high hardness. Abrasive wear resistance requires both high hardness and primary carbides. Molybdenum and nickel can be added to martensitic stainless steel to improve corrosion and toughness properties. Nickel also serves to maintain the desired microstructure, preventing excessive free ferrite when higher chromium levels are used to improve corrosion resistance. However, the addition of these elements is somewhat restricted, because higher amounts result in a microstructure that is not fully martensitic.

Precipitation-hardenable (PH) stainless steels are chromium-nickel grades that can be hardened by an aging treatment. These grades are classified as austenitic (such as S66286), semi-austenitic (such as S17700), or martensitic (such as S17400). The classification is determined by their solution-annealed microstructure. The semi-austenitic alloys are subsequently heat treated, so that the austenite transforms to martensite. Cold work is sometimes used to facilitate the aging reaction. Various alloying elements, such as aluminum, titanium, niobium, or copper, are used to achieve aging. They generally form intermetallic compounds, but in S17400, fine copper precipitates are formed.

Like the martensitic stainless steels, PH alloys can attain high tensile yield strengths, up to 1700 MPa (250 ksi). Cold working prior to aging can result in even higher strengths. The PH grades generally have good ductility and toughness with moderate-to-good corrosion resistance. A better combination of strength and corrosion resistance is achieved than with the martensitic alloys. These improved properties are related to their higher chromium, nickel, and molybdenum contents, as well as their restricted carbon (0.040 max) levels. The low carbon content of the martensitic PH stainless

steels is especially critical for toughness and good ductility. However, this low carbon content reduces the wear resistance of these alloys.

The most well-known precipitation-hardenable stainless steel is S17400. It contains chromium and nickel, as do all precipitation-hardenable stainless steels, with copper for age hardening and niobium for stabilizing the carbon. The age-hardening agents used in other alloys include titanium (S45500), aluminum (S13800), and niobium (S45000). Molybdenum can be added to improve mechanical properties or corrosion resistance. Both molybdenum and copper are added for corrosion resistance in S45000. Carbon is normally restricted, except in semiaustenitic alloys such as S35500, which require it to provide the desired phase transformations.

Duplex stainless steels are chromium-nickel-molybdenum alloys that are balanced to contain a mixture of austenite and ferrite, and are magnetic, as well. Their duplex structure results in improved stress-corrosion cracking resistance, compared with the austenitic stainless steels, and improved toughness and ductility, compared with the ferritic stainless steels. They are capable of tensile yield strengths ranging from 550 to 690 MPa (80 to 100 ksi) in the annealed condition, which is approximately twice the strength level of either phase alone.

The original alloy in this family was the predominantly ferritic S32900. The addition of nitrogen to duplex alloys, such as S32950 and S31803, increases the amount of austenite to nearly 50%. In addition, nitrogen improves as-welded corrosion properties, chloride corrosion resistance, and toughness. The improvement in toughness is probably related to the higher amount of austenite present, which makes it possible to produce heavier product forms, such as plates and bars.

Stainless Steel Mill Finishes (Ref 2)

The standard industry designations for stainless steel finishes are classified by mill form, as there are separate finishes (or conditions) for sheet, strip, plate, bar, rod, wire, and tubing. Table 2 classifies the various stainless steel product forms. More detailed information on stainless steel product forms can be found in Ref 3.

Table 2 Classification of stainless steel product forms

Item	Description	Thickness		Width		Diameter or size	
		mm	in.	mm	in.	mm	in.
Sheet	Coils and cut lengths:						
	Mill finishes No. 1, 2D, and 2B	<5	$< \frac{3}{16}$	≥ 610	≥ 24	. . .	. . .
	Polished finishes No. 3, 4, 6, 7, and 8	<5	$< \frac{3}{16}$	All widths		. . .	. . .
Strip	Cold finished, coils, or cut lengths	<5	$< \frac{3}{16}$	<610	<24	. . .	. . .
Plate	Flat rolled or forged	≥ 5	$\geq \frac{3}{16}$	>25	>10	. . .	. . .
Bar	Hot-finished rounds, squares, octagons, and hexagons	. . .	. . .	. . .	. . .	≥ 6	$\geq \frac{1}{4}$

	Hot-finished flats	≥ 3	$\geq \frac{1}{8}$	6-25	$\frac{1}{4}$-10	. . .	. . .
	Cold-finished rounds, squares, octagons, and hexagons	. . .	. . .	. . .	. . .	>13	$> \frac{1}{2}$
	Cold-finished flats	. . .	. . .	≥ 9.5	$\geq \frac{3}{8}$	. . .	. . .
Wire	Cold finished only: round, square, octagon, hexagon, flat wire	0.25 to <5	0.010 to $< \frac{3}{16}$	1.6 to <9.5	$\frac{1}{16}$ to $< \frac{3}{8}$	≤ 13	$\leq \frac{1}{2}$
Pipe and tubing	Several different classifications, with differing specifications, are available. For information on standard sizes, consult Committee of Stainless Steel Producers, AISI.						
Extrusions	Not considered "standard" shapes, but of potentially wide interest. Currently limited in size to approximately 165 mm ($6\frac{1}{2}$ in.) diam circle, or structurals to 125 mm (5 in.) diam.						

Source: Ref 2

Sheet Finishes

Stainless steel sheets are produced on continuous mills or hand mills. The steel is usually cast in ingot form and rolled on a slabbing or a blooming mill to slabs or sheet bars. Alternatively, the steel may be cast directly in slab form ready for finish hot rolling.

Sheets produced on continuous mills from slabs are rolled into coils and are further processed by annealing, descaling, and cold reducing to specified thickness, then further annealing and descaling. Coils or lengths cut from coils may then be subjected to light cold rolling for finish on dull or bright rolls.

Sheet finishes (Table 3) are designated by a system of numbers: No. 1, 2D, and 2B for rolled (unpolished) finishes; and No. 3, 4, 6, 7, and 8 for polished finishes.

Table 3 Standard mechanical sheet finishes

Finish	Description
Unpolished or rolled finishes	
No. 1	A rough, dull surface that results from hot rolling to the specified thickness followed by annealing and descaling
No. 2D	A dull finish that results from cold rolling followed by annealing and descaling, and may perhaps get a final light roll pass through unpolished rolls. A 2D finish is used where appearance is of no concern.
No.	A bright, cold-rolled finish resulting in the same manner as No. 2D finish, except that the annealed and descaled sheet receives a

2B	final light roll pass through polished rolls. This is the general-purpose cold-rolled finish that can be used as is, or as a preliminary step to polishing.
Polished finishes	
No. 3	An intermediate polished surface obtained by finishing with a 100-grit abrasive. Generally used where a semifinished polished surface is required. A No. 3 finish usually receives additional polishing during fabrication.
No. 4	A polished surface obtained by finishing with a 120 to 150-mesh abrasive, following initial grinding with coarser abrasives. This is a general-purpose bright finish with a visible "grain" that prevents mirror reflection.
No. 6	A dull satin finish having lower reflectivity than No. 4 finish. It is produced by tampico brushing the No. 4 finish in a medium of abrasive and oil. It is used for architectural applications and ornamentation where a high luster is undesirable, and to contrast with brighter finishes.
No. 7	A highly reflective finish that is obtained by buffing finely ground surfaces but not to the extent of completely removing the grit lines. It is used chiefly for architectural and ornamental purposes.
No. 8	The most reflective surface, which is obtained by polishing with successively finer abrasives and buffing extensively until all grit lines from preliminary grinding operations are removed. It is used for applications such as mirrors and reflectors.

Source: Ref 2

No. 1 is a very dull finish produced by first hot rolling the steel on hand sheet mills to the specified thickness and then annealing and descaling. It is used in industrial applications for resistance to heat or corrosion, where a smooth finish is not of particular importance.

No. 2D is a dull finish produced on either hand sheet mills or continuous mills by cold rolling to the specified thickness, annealing, and descaling. The dull finish may result from the descaling operation or may be developed by a final light cold roll pass on dull rolls. This finish is favorable to the surface retention of lubricants in deep drawing operations. It generally is used in forming deep-drawn articles that may be polished after fabrication.

No. 2B is a bright, cold-rolled finish commonly produced in the same way as No. 2D, except that the annealed and descaled sheet receives a final light cold-roll pass on polished rolls. It is a general-purpose finish used for all but exceptionally difficult deep drawing applications. This finish is more readily polished than No. 1 or 2D.

No. 3 is an intermediate polished finish for use where a semifinished polished surface is required and a further finishing operation follows fabrication. For sheets or articles that will not be subject to additional finishing or polishing, No. 4 finish is recommended.

No. 4 is a general-purpose polished finish widely used for architectural panels and trim, and for dairy, restaurant, and kitchen equipment. Following initial grinding with coarser abrasives, sheets are finally finished with lubricated 120- to 150-mesh abrasive belts.

No. 6 is a dull satin finish having lower reflectivity than No. 4. It is produced by tampico brushing No. 4 finished sheets in a medium of abrasive and oil and is used for architectural applications and ornamentation where a high luster is undesirable. It also is used to contrast with brighter finishes.

No. 7 is a finish with a high degree of reflectivity, produced by buffing a finely ground surface without removing the grit lines. It is used chiefly for architectural and ornamental purposes.

No. 8 is the most reflective finish and is obtained by polishing with successively finer abrasives and buffing extensively with very fine buffing rouges. The surface is essentially free of grit lines from preliminary grinding operations. This finish

is most widely used for press plates, as well as for small mirrors and reflectors. Sheets can be produced with one or both sides polished. When polished on one side only, the other side may be rough ground in order to obtain the necessary flatness. The relationship between abrasive grit numbers and surface roughness in terms of microinches is sometimes a basis for specification. The values are approximately as follows:

Abrasive grit no.	Surface roughness	
	μm	μin.
500	0.10 to 0.25	4 to 10
320	0.15 to 0.38	6 to 15
240	0.20 to 0.51	8 to 20
180	0.64 max	25 max
120	1.14 max	45 max

Strip Finishes

Hot-rolled stainless steel strip is a semifinished product obtained from the hot rolling of slabs or billets and is produced for conversion by cold rolling. Cold-rolled stainless steel strip is manufactured from hot-rolled, annealed, and pickled strip by cold rolling on polished rolls. Depending on the thickness desired, the cold rolling requires various numbers of passes through the mill to effect the necessary reduction and to secure the desired surface characteristics and mechanical properties. Only three rolled (unpolished) finishes (No. 1, No. 2, and bright annealed) and one polished finish (mill buffed) are commonly supplied on stainless steel strip.

No. 1 finish is produced by cold rolling, annealing, and pickling. Appearance varies from dull gray matte to fairly reflective, depending largely on stainless steel type. This finish is used for severely drawn or formed parts, as well as for applications where the brighter No. 2 finish is not required, such as parts to be used at high temperatures. No. 1 finish for strip approximates No. 2D finish for sheet in corresponding chromium-nickel or chromium-nickel-manganese types.

No. 2 finish is produced by the same treatment used for No. 1 finish, followed by a final light cold-rolling pass, which generally is done using highly polished rolls. This final pass produces a smoother and more reflective surface, the appearance of which varies with stainless steel type. No. 2 finish for strip is a general-purpose finish widely used for household appliances, automotive trim, tableware, and utensils. No. 2 finish for strip approximates No. 2B finish for sheet in corresponding chromium-nickel or chromium-nickel-manganese stainless steels.

Bright annealed finish is a bright, cold-rolled, highly reflective finish retained by final annealing in a controlled-atmosphere furnace. The purpose of atmosphere control is to prevent scaling or oxidation during annealing. The atmosphere usually consists of either dry hydrogen or dissociated ammonia. Bright annealed strip is used most extensively for automotive trim.

Mill-buffed finish is a highly reflective finish obtained by subjecting either No. 2 or bright annealed coiled strip to a continuous buffing pass. The purpose of mill buffing is to provide a finish uniform in color and reflectivity. It also can

provide a surface receptive to chromium plating. This type of finish is used chiefly for automotive trim, household trim, tableware, utensils, fire extinguishers, and plumbing fixtures.

Grade Limitations. Not all of the standard compositions of stainless steel strip are available in each of the standard mill finishes. Surface finishes of these products depend on end use rather than any restriction imposed by the supplier. Table 4 lists the finishes most often applied to sheet and strip of a number of standard grades of austenitic, martensitic, and ferritic steels.

Table 4 Mill finishes available on stainless steel sheet and strip

See text for explanation of numerical designations of finishes

Type	Sheet		Strip
	Unpolished	Polished	
Austenitic steels[(a)]			
201	2D, 2B	[(b)]	1, 2
202	2D, 2B	3, 4	1, 2
301	2D, 2B	[(b)]	1, 2
302	2D, 2B	3, 4, 6, 7	1, 2
302B	2D	[(b)]	. . .
304	2D, 2B	3, 4, 6, 7	1, 2
304L	2D, 2B	4	1, 2
305	2D, 2B	[(b)]	1, 2
309, 309S	2D	[(b)]	1, 2
310	2D	[(b)]	1, 2
316	2D, 2B	4	1, 2
316L	2D, 2B	[(b)]	1, 2
321	2D, 2B	[(b)]	1, 2
347	2D, 2B	[(b)]	1, 2

348	2D, 2B	(b)	1, 2
Martensitic steels			
403	2D, 2B	(b)	1, 2
410	2D, 2B	(b)	1, 2
420	(c)	(c)	1, 2
440A, B, and C	(c)	(c)	(d)
Ferritic steels[a]			
430	2D, 2B	3, 4	1, 2
446	2D, 2B	(b)	1, 2

(a) All grades listed, in both sheet and strip form, are regularly available in the smooth rolled and bright annealed condition.

(b) Usually not polished.

(c) Not available in sheet form.

(d) Material available in strip form on special order only; finish negotiated with supplier

Plate Finishes

Stainless steel plates usually are produced by hot rolling from slabs, which have been directly cast or rolled from ingots; some plates may be produced by direct rolling from the ingot. Plates are generally produced in the annealed condition and are either blast cleaned or pickled. When blast cleaned, the plates are subjected to further cleaning in appropriate acids to remove possible iron contamination. Stainless steel plate can be produced in the conditions and surface finishes shown in Table 5.

Table 5 Conditions and surface finishes for stainless steel plate

Condition and finish	**Description and remarks**
Hot rolled	Scale not removed; not heat treated; plate not recommended for final use in this condition[a]
Hot or cold rolled, annealed or heat treated	Scale not removed; use of plate in this condition generally confined to heat-

	resisting applications; scale impairs corrosion resistance.[(a)]
Hot or cold rolled, annealed or heat treated, blast cleaned or pickled	Condition and finish commonly preferred for corrosion-resisting and most heat-resisting applications
Hot or cold rolled, annealed, descaled, and temper passed	Smoother finish for specialized applications
Hot rolled, annealed, descaled, cold rolled, annealed, descaled, optionally temper passed	Smooth finish with greater freedom from surface imperfections than any of the above
Hot or cold rolled, annealed or heat treated, surface cleaned and polished	Polished finishes similar to the polished finishes on sheet

Source: Ref 2

(a) Surface inspection is not practicable for plate that has not been pickled or otherwise descaled.

Table 5 indicates that polished finishes similar to those for sheet are available for plate. Technically speaking, there is no No. 4 finish for plate, nor is there a No. 8 finish. However, arrangements can be made either with a mill or an independent polisher to grind and polish plate in the same manner as sheet. This work should be specified on the basis of submitted samples.

Plate commonly is conditioned by localized grinding to remove surface imperfections on either or both surfaces; ground areas are well flared and the thickness is not reduced below the allowable tolerance in any of these areas.

Bar Finishes

Hot-finished bars are commonly produced by hot rolling, forging, or pressing ingots to intermediate-size blooms or billets, which are subsequently hot rolled, forged, or extruded to final dimensions. (In some mills, the process starts with continuous cast sections.) The selection of rolling, forging, or extruding as the finishing method depends on several factors, including the composition of the steel and the final size. It is common practice to process bars in straight lengths, although smaller bars produced by rolling may be coiled.

Following hot rolling or forging, hot-finished bars may be subjected to various operations, including annealing or other heat treating; cleaning by pickling, blast cleaning, or other methods of descaling; rough turning; and machine straightening. When only improved surface is required, as for bars intended for forging, bars can be turned or ground.

Cold-finished bars are produced from hot-finished bars by additional operations to give close tolerance, improved surface finish, or specific mechanical properties.

Stainless steel bar is produced in the conditions and surface finishes given in Table 6. It is important that both condition and finish be specified, because each finish is applicable only to certain conditions.

Table 6 Conditions and surface finishes for stainless steel bar

Condition	**Surface finish**
Hot worked only	Scale not removed (except for spot conditioning)

	Rough turned[a][b]
	Blast cleaned
Annealed or otherwise heat treated	Scale not removed (except for spot conditioning)
	Rough turned[a]
	Pickled or blast cleaned and pickled
	Cold drawn or cold rolled
	Centerless ground[a]
	Polished[a]
Annealed and cold worked to high tensile strength[c]	Cold drawn or cold rolled
	Centerless ground[a]
	Polished[a]

Source: Ref 2

(a) Applicable to round bar only.

(b) Bar of 400-series stainless steels that are highly hardenable, such as types 414, 420, 420F, 431, 440A, 440B, and 440C, are annealed before rough turning. Other hardenable types, such as types 403, 410, 416, and 416Se, also may require annealing, depending on composition and size.

(c) Produced only in mill orders; made predominantly in types 301, 302, 303Se, 304, 304N, 316, and 316N.

The finish on stainless steel bar is generally the result of processes used to size the bar or to improve the surface and usually not for purposes of achieving a certain surface appearance. Turning, for instance, improves the surface by removing undesirable defects. It is difficult, if not impossible, to obtain a hot-rolled surface that the customer can use without removal of a portion of the "skin." Turning is accomplished by passing the bar through a turning machine or lathe, using one or more passes depending on the amount of material to be removed.

Sometimes the final surface or dimension of round bar can be achieved only by centerless grinding. Centerless grinding differs from turning in that a grinding wheel is used for metal removal instead of a cutting tool, and more accurate dimensions and better surface finish are obtained. The centerless grinding machine is constructed so that the bar is supported under the greater portion of its length as well as under the grinding wheel, other than at the ends.

In some cases, a highly polished bar is desired rather than the standard centerless ground finish. In this case, centerless ground bars are passed through a polishing or lapping machine that imparts a higher degree of polish. Flat or shaped bars cannot be centerless ground, so any finish requirements are achieved by methods similar to those used for strip.

Wire Finishes

Stainless steel wire is a product derived by cold finishing a coiled hot-rolled and annealed rod for the purpose of obtaining desired size with dimensional accuracy, improved surface, and specific mechanical properties. Wire is produced in a number of tempers and finishes. The finishes on wire are usually applied to meet the requirements of further processing, such as drawing, forming into parts, or coiling into springs.

Oil- or grease-drawn finish is a special bright finish for wire intended for uses such as racks and handles, where the finish supplied is to be the final finish of the end product. In producing this finish, lower drawing speeds are necessary and additional care in processing is needed to provide a surface with few scratches and with only a very light residue of lubricant.

Diamond-drawn finish is a very bright finish generally limited to wet-drawn stainless steel wire in fine sizes. Drawing speeds are necessarily reduced to obtain the desired brightness.

Copper-coated wire is supplied when a special finish is required for lubrication in an operation such as spring coiling or cold heading. Generally, copper-coated wire is drawn after the coating, the amount depending on the desired cold-worked temper of the wire.

Tinned wire is coated by passing single strands through a bath of molten tin. Tinned wire is used in soldering applications. The temper of the finished wire is controlled by processing prior to tinning.

Lead-coated wire is coated by passing single strands through, or immersing bundles of wire in, a bath of molten lead. The wire is then drawn to final size, with the lead forming a thin coating over the entire surface. This coating is useful on wire for coil springs, where it serves as a lubricant during coiling operations.

Tubing and Pipe Finishes

Hot-finished tubular products produced by the seamless processes have a surface finish comparable to hot-rolled bars. Welded tubular products produced from hot-rolled sheets, strip, or plate retain the general surface finish of those flat rolled products. Thin-wall tubular products, due to greater reduction during the rolling operation and the lower finishing temperatures, may have a smoother surface than those with heavy walls.

Stainless steel tubular products are cold worked to improve dimensional limits or--in the case of welded tubing--to control the weld bead on the inside, or to condition the weld for grain refinement during the annealing operation. Cold finishing may include cold drawing, tube reducing, or swaging. Tubes may also be rough turned (machined) or honed, such as for hydraulic cylinders.

Tubular products may be polished, but instead of "typical" finish designations, the polished finishes for tubing are usually indicated by the grit size, such as 80, 120, 180, or 320 grit. Note that for the exterior surface of round tubing, grit lines are longitudinal. Tubing may be specified polished on the outside, the inside, or both surfaces. Welded and cold-finished seamless tubing is suitable for grinding or polishing and is produced in sizes up to 168 mm ($6\frac{5}{8}$ in.) OD with polished outside surfaces. It is not practical to polish interior surfaces or tubes with an inner diameter of less than 19 mm ($\frac{3}{4}$ in.).

Preservation of Mill Finishes

In making a finished part, the original mill finish may be retained with little or no modification, depending on fabrication requirements. If this finish is satisfactory, no additional finishing operations are necessary. Therefore, every effort should be made to preserve the mill finish while the steel is in storage or being processed. The following preventive measures will serve to minimize additional cleaning and polishing:

- Steel should be kept in original containers or wrappers until fabrication actually begins.
- Steel should be stored indoors, on clean racks, shelves, or platforms, and should be covered wherever possible.
- Storage areas should be kept free of shop dirt, pickling or plating fumes, particles of scale from steel fabrication, and other contaminants.
- Storage areas should not be located beneath line shafting from which lubricating oils and grease may fall.
- Fabricating equipment should be cleaned of all residues before being used for a new operation on stainless steel.
- Steel should be handled with clean gloves or cloths, to avoid fingerprints.
- Only marking materials that leave no permanent blemishes on work should be used.
- Whenever feasible, paper or other protective covering should be placed on all surfaces between processes.
- Chips should not be removed by compressed air, which may contain oil or other contaminants.

References cited in this section

2. *Finishes for Stainless Steel,* Publ. 201-683-14M-EB, American Iron and Steel Institute, 1983
3. Metallurgy and Properties of Wrought Stainless Steels, in *ASM Specialty Handbook: Stainless Steels,* J.R. Davis, Ed., ASM International, to be published in the Fall of 1994

Abrasive Blast Cleaning

Aspects of abrasive blast cleaning that apply particularly or exclusively to stainless steel include sandblasting, shot blasting, and wet blasting. For more complete information, see the article "Mechanical Cleaning Systems" in this Volume.

Sandblasting is effective for rapidly removing heavy or tightly adhering scale before acid pickling. Applied to stainless steel, it is not a complete cleaning procedure. Types of work for which it is frequently used include heavily scaled plate sections, forgings and castings, and parts made of straight chromium steel that have developed a tightly adhering scale during annealing. It is fast and economical when used in conjunction with a final pickling treatment.

Only clean silica sand should be used. If the sand is iron-bearing or becomes contaminated with scale, minute particles of these contaminants can become embedded in the metal. The only sure way to remove such contaminants and to produce a thoroughly clean, rust-free surface is to follow the blasting with an acid pickling treatment.

Sandblasting should not be used on materials that are too light to stand the blast pressure, because distortion results from the local stretching caused by impingement of the sand. The blast should be kept moving to avoid excessive cutting at localized points.

Shot Blasting. The use of carbon steel shot, steel wire, or iron grit as blasting media is not recommended as they may cause particles of iron to become embedded and seriously detract from the corrosion resistance of stainless steel surfaces. Unless these contaminants are completely removed by acid pickling, they can rust and begin pitting.

The use of stainless steel shot or grit reduces the danger of rusting, but it cannot eliminate the possibility of residual oxide scale. Final pickling is mandatory for maximum corrosion resistance of surfaces so treated.

Stainless steels, and particularly those of the 300 series, work harden when they are subjected to cold working. Therefore, if work hardening of the surface is undesirable for a particular application, shot blasting should not be used.

Wet blasting is adaptable for use with stainless steel. Various abrasives conveyed in liquid carriers are discharged at the work by compressed air. A variety of finishes can be obtained through selection of abrasives and adjustment of pressures. Finishes that are much smoother than those resulting from blasting with dry sand and that are similar in appearance to a No. 6 (tampico-brushed) finish may be obtained by wet blasting. As in sandblasting, a final pickling treatment and water washing are required.

Acid Descaling (Pickling)

Acid descaling, or pickling, is the removal of heavy, tightly adherent oxide films resulting from hot-forming operations, thermal treatments (such as annealing or hardening), or welding (Ref 4). Because most stainless steel products received from the producing mill have been pickled, descaling is required only as a result of subsequent manufacturing operations.

In evaluating the different methods for removing scale, it should be kept in mind that scale on stainless steel is far more complex than scale formed on plain carbon steel. The scale on stainless steel consists of oxides of chromium, nickel, and/or other alloying elements--in addition to iron--and the ease by which it can be removed depends on base metal composition and the thermal treatment to which it is exposed. The problem may be further complicated by the presence of lubricants. Lubricants and other contamination should be removed before thermal treatment.

When the metal is exposed to hot gases containing oxygen, a heavy scale is formed. A heavy scale, because it is readily exposed to the oxygen only near the surface, may be oxygen rich at the surface and metal rich near the base metal. Most oxygen-rich scale is readily soluble in common pickling acids, but the metal-rich scale may require acids aggressive to the base metal itself. For this reason, pickling is sometimes preceded by a preconditioning step, such as an alkaline salt bath, or scale removal by mechanical means, such as shot blasting.

The final step, however, involves elimination of scale and other surface defects through removal of the normal, protective oxide layer and 25 to 40 μm (0.001 to 0.0015 in.) of the substrate metal by pickling the surface in a nitric-hydrofluoric acid (HNO_3-HF) bath. The protective film then reforms in air over the freshly cleaned surface. This oxide film is uniform and leaves the stainless surface in its normal passive condition.

Although pickling is not strictly a passivating treatment, it provides many of the same benefits. Pickling is most useful for localized cleaning of welded areas, but also can be used to improve the corrosion resistance of mechanically cleaned surfaces.

Disposal of pickle liquor is a growing problem that tends to limit pickling by immersion to those fabricator and chemical cleaning contractors who have pickle tanks and approved arrangements for disposal.

Pickling at the steel mill removes the oxide scale that forms during annealing. Mill pickling also removes manganese sulfides or other inclusions in the surface and removes surface layers that may have been depleted of chromium during annealing.

ASTM A 380 (Ref 1) lists three pickling solutions for stainless steel (Table 7). Fabricated austenitic stainless steels can be pickled by immersion in a standard 10% HNO_3, 2% HF bath at 50 °C (120 °F). For localized pickling or if the fabricated component is too large to be immersed, commercial HNO_3-HF pickle pastes can be just as effective. Pickle paste can be applied with a paint roller or nylon brush.

Table 7 Acid descaling (pickling) of stainless steel

Alloy[(a)]	Condition[(b)]	Code	Treatment			Time[(e)], min
			Solution, vol%[(c)]	Temperature		
				°C	°F	
200, 300, and 400 series, precipitation hardening, and maraging alloys (except free-machining alloys)	Fully annealed only	A	H_2SO_4 (8-11)[(d)] Follow by treatment D or F, Annex A2 (ASTM A 380), as appropriate	66-82	150-180	5-45 max
200 and 300 series; 400 series containing 16% Cr or more; precipitation-hardening alloys (except	Fully annealed only	B	HNO_3 (15-25%) plus HF (1-8%)[(f)(g)]	21-60 max	70-140 max	5-30

free-machining alloys)						
All free-machining alloys and 400 series containing less than 16% Cr	Fully annealed only	C	HNO_3 (10-15%) plus HF ($\frac{1}{2}$-1 $\frac{1}{2}$%)[f][g]	20 (up to 60 with caution)	70 (up to 140 with caution)	5-30

Source: Ref 1

(a) This table is also applicable to the cast grades equivalent to the families of wrought materials listed.

(b) Other heat treatments may be acceptable if proven by experience: see sections 5.2.1, A2.4, and A2.5 of ASTM A 380 for further information.

(c) Solution prepared from reagents of following weight percent: H_2SO_4, 98; HNO_3, 67; HF, 70.

(d) Tight scale may be removed by a dip in this solution for a few minutes followed by water rinse and HNO_3-HF treatment as noted.

(e) Minimum contact times necessary to obtain the desired surface should be used in order to prevent overpickling. Tests should be made to establish correct procedures for specific applications.

(f) For reasons of convenience and handling safety, commercial formulations containing fluoride salts may be found useful in place of HF for preparing HNO_3-HF solutions.

(g) After pickling and water rinsing, an aqueous caustic permanganate solution containing 10% NaOH and 4 wt% $KMnO_4$, 71 to 82 °C (160 to 180 °F), 5 to 60 min, may be used as a final dip for removal of smut, followed by thorough water rinsing and drying.

Paste must be washed off within 15 to 30 min of application, or corrosion will initiate. Personnel need protective clothing and training in safe handling procedures.

Although postfabrication pickling improves the performance of stainless steels in a variety of applications, until recently there has been very little research data to support field experience. Quantitative data on the increase in critical pitting temperature in ferric chloride ($FeCl_3$) (ASTM G 48) shows that pickling provides a 2.5 to 10 °C (4.5 to 18 °F) improvement in performance (Fig. 1). While not large, the improvements in lightly ground surfaces and glass-bead-blasted surfaces are uniformly positive, indicating that pickling provides benefits beyond those obtained with the best controlled mechanical treatments. Additional information on acid pickling of stainless steels can be found in the article "Pickling and Descaling" in this Volume.

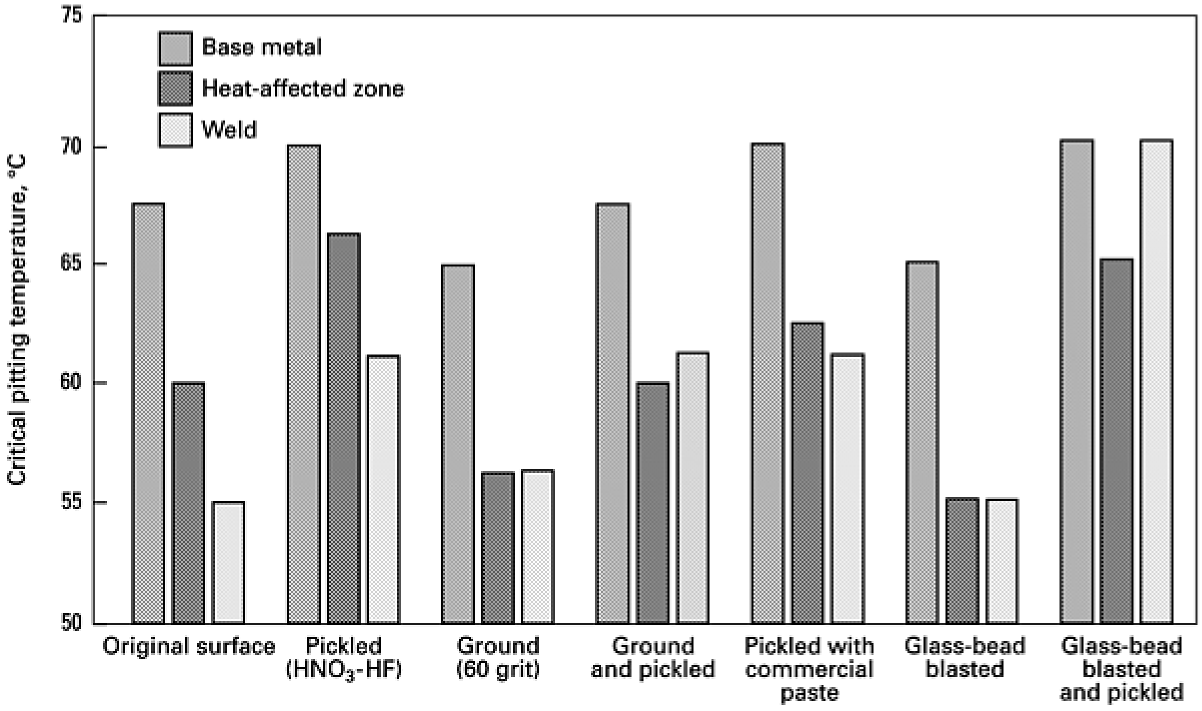


Fig. 1 Pickling of stainless steel increases the critical pitting temperature in $FeCl_3$ in the base metal, heat-affected zone, and weld areas. Mechanical cleaning treatments that are performed without a subsequent pickling treatment decrease the critical pitting temperature. Source: Ref 5

References cited in this section

1. "Standard Practice for Cleaning and Descaling Stainless Steel Parts, Equipment, and Systems," A 380, *Annual Book of ASTM Standards,* ASTM, 1988
4. *Cleaning and Descaling Stainless Steels,* No. 9001, American Iron and Steel Institute, 1982 (reprinted by Nickel Development Institute, 1988)
5. A.H. Tuthill and R.E. Avery, Specifying Stainless Steel Surface Treatments, *Advanced Materials & Processes,* Vol 142 (No. 6), Dec 1992, p 34-38

Salt Bath Descaling

The removal of oxide scale can be accelerated by using baths of molten sodium hydroxide (NaOH) to which certain reagents are added. These baths can be used with virtually all grades of stainless steel. Salt bath descaling has several advantages:

- It acts only on the scale and does not result in metal loss or etching.
- It does not preferentially attack areas in which intergranular carbides are present.
- It is particularly useful in descaling the straight chromium grades without the preliminary sandblasting that is frequently required prior to acid descaling.

Use of molten salts is not recommended for those stainless steels that precipitation harden at the operating temperature of the bath. Procedures and equipment for descaling in molten salt are described in the article "Molten Salt Bath Cleaning" in this Volume.

Sequence of Descaling Methods

Usually, more than one method of cleaning is used to remove scale from stainless steel. For instance, in mill processing sheet, salt bath descaling and acid pickling often are used for a cold-rolled product and abrasive blast cleaning and acid pickling for a hot-rolled product.

In a continuous annealing and pickling line, multistep cleaning usually occurs twice in producing stainless steel sheet. The sequence of operations is: hot roll, anneal, descale, pickle, cold reduce 30 to 50%, anneal, descale, and pickle. As shown in Fig. 2, salt descaling is used for cold-rolled sheet, whereas the salt is bypassed and abrasive blast cleaning is used when a hot-rolled product is being cleaned. Salt also can be eliminated on low-chromium cold-rolled sheet.

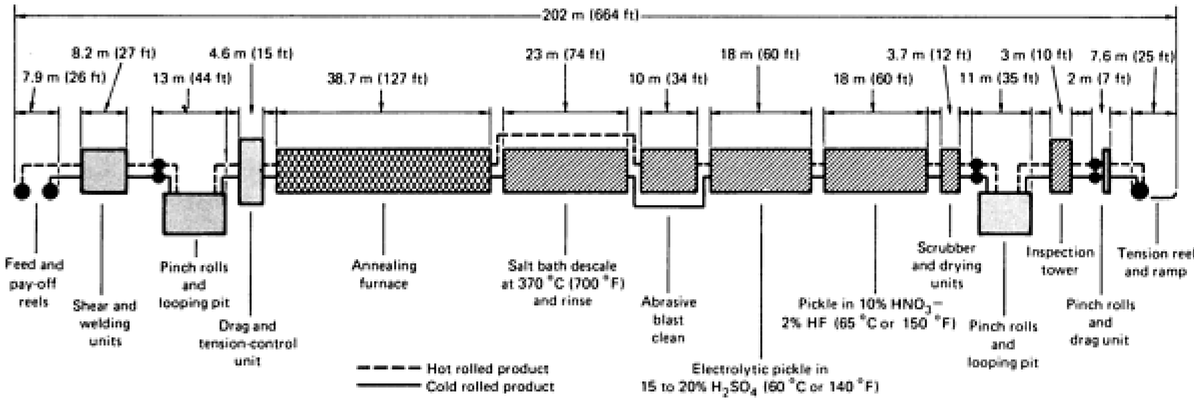


Fig. 2 Sequence of annealing and scale-removing operations in mill processing of stainless steel sheet

Cold-rolled sheet is left in the salt bath 10 to 15 min. Oxides are not removed from the surface. The rack of hot sheet is transferred to a water bath, and the violent reaction that results on immersion blasts much of the scale from the steel. The surface is essentially free of scale, but quite dull and dirty. To remove the last remnants of oxide, the rack is transferred to a 10 to 15% sulfuric acid (H_2SO_4) solution at 70 °C (160 °F) for 3 to 5 min. After removal from the H_2SO_4 tank, the rack of sheet steel is rinsed and then immersed for 1 to 2 min in HNO_3-HF (8 to 10% HNO_3, 1 to 2% HF) at 60 °C (140 °F). This removes all smut and residue and produces a white finish. The sheet is finally rinsed, removed from the rack, scrubbed, and dried with an air blast.

Cleaning Stainless Steels

Cleaning includes all operations necessary for the removal of surface contaminants from metals to ensure maximum corrosion resistance of the metal, prevention of product contamination, and achievement of desired appearance (Ref 1). Selection of cleaning processes is influenced mainly by the type of contaminant to be removed, the required degree of cleanliness, and cost.

Dirt deposits on stainless steel, which include accumulated dust and dirt, finger marks, and identification markings, are easily removed (Ref 4). Frequently, warm water with or without detergent is sufficient. Next in order are mild nonscratching abrasive powders such as typical household cleaners. These can be used with warm water, bristle brushes, stainless steel brushes, sponges, or clean cloths. Ordinary carbon steel brushes or steel wool should be avoided as they may leave particles embedded on surfaces which can lead to rusting. For slightly more aggressive cleaning, a small amount of vinegar can be added to the scouring powder. Cleaning should always be followed by rinsing in clean hot water. When water is known to contain mineral solids, which leave water spots, it is good practice to wipe the surfaces completely with dry towels. Some companies use oil impregnated cloths to remove water spots and enhance appearance. Commercial metal cleaners may also be considered, but it is important to make certain that they can be used on stainless steels.

Finger marks are probably the most troublesome of unwanted marks on stainless steel (Ref 4). They not only detract from overall appearance of smoothly polished or bright finishes, but they also can "burn in" quite deeply during annealing or other thermal treatments, leaving permanent marks which can be removed only by grinding. Fortunately, they can be easily prevented through the use of clean gloves, or they can be removed by gentle rubbing with a paste of soda ash (sodium carbonate) and water applied with a soft rag. Again, this should be followed by a thorough warm water rinse.

Most inspection stamps and identification marks applied at the mill are ink, which can be removed by applying a solvent on a rag and rubbing (Ref 4). Selection of solvent is determined by the type of ink used. Solvents should be rinsed from the stainless steel with warm water, repeating the treatment if necessary.

Commonly used methods for the removal of greases, drawing compounds, and machining oils include:

- Alkaline cleaning
- Emulsion cleaning
- Solvent cleaning
- Vapor degreasing
- Ultrasonic cleaning
- Acid cleaning

Each of these are described briefly below and in greater detail in the articles contained in the Section "Surface Cleaning" in this Volume. Additional information can also be found in ASTM Standard A 380 (Ref 1).

Alkaline cleaning is used to remove soils from the surface of metals. Soils removed through alkaline cleaning include oil, grease, waxy solids, metallic particles, dust, carbon particles, and silica. Alkaline cleaners are applied by immersion or spray, and the metal is cleaned by emulsification, dispersion, saponification, or combinations of these mechanisms. The cleaning step is usually followed by a water rinse and a drying stage. Alkaline cleaner compositions are discussed in the article "Alkaline Cleaning" in this Volume.

Emulsion cleaning is a process for removing oily deposits and other common contaminants from metals by solution with the aid of a soap or other emulsifying agent (an emulsifying agent is one which increases the stability of a dispersion of one liquid in another). It is effective for removing a wide variety of contaminants including pigmented and unpigmented drawing compounds and lubricants, cutting fluids, and residues resulting from liquid penetrant inspection. Emulsion cleaning is used when rapid, superficial cleaning is required and when a light residual film of oil is not objectionable. Depending on the solvent used, cleaning is done at temperatures from 10 to 80 °C (50 to 180 °F). Compositions and operating temperatures for emulsion cleaners are described in the article "Emulsion Cleaning" in this Volume.

Solvent cleaning is a process for removing contaminants from metal surfaces by immersion or by spraying or swabbing with common organic solvents such as the aliphatic petroleums, chlorinated hydrocarbons, or blends of these two classes of solvents. Cleaning is usually performed at, or slightly above, room temperature. Parts are cleaned by being immersed and soaked in the solvent, with or without agitation. Parts that are too large to be immersed are sprayed or wiped with the solvent. Properties of cleaning solvents are described in the article "Solvent Cold Cleaning and Vapor Degreasing" in this Volume.

Vapor degreasing is a generic term applied to a cleaning process that uses the hot vapors of a chlorinated or fluorinated solvent to remove soils, particularly oils, greases, and waxes. The cleanliness and chemical stability of the degreasing solvent are critical factors in the efficiency of the vapor and possible chemical attack of the metal. Water in the degreasing tank or on the item being cleaned may react with the solvent to form hydrochloric acid, which may be harmful to the metal. No water should be present in the degreasing tank or on the item being cleaned. Acids, oxidizing agents, and cyanides must also be prevented from contaminating the solvent. Vapor degreasing systems and procedures are described in the article "Solvent Cold Cleaning and Vapor Degreasing" in this Volume.

Ultrasonic Cleaning. Ultrasonic transducers, which convert electrical energy into ultrasonic vibrations, can be used in conjunction with some solvent cleaning systems to loosen and remove contaminants from deep recesses and other difficult to reach areas, particularly in small workpieces. Cavitation in the liquid produced by the high-frequency sound causes microagitation of the solvent in even tiny recesses of the workpiece, making the method especially desirable for cleaning parts or assemblies having an intricate configuration. More detailed information can be found in the article "Ultrasonic Cleaning" in this Volume.

Acid cleaning is a process in which a solution of a mineral acid, organic acid, or acid salt, in combination with a wetting agent and detergent, is used to remove oxide, shop soil, and similar contaminants from metal surfaces, with or without application of heat. Acid cleaning is not generally effective for removal of oils, greases, and waxes. Surfaces

should be precleaned to remove oils and greases before acid cleaning. Common techniques for acid cleaning are immersion, swabbing, and spraying. Maximum surface quality is best achieved by using a minimum cleaning time at a given acid concentration and temperature. After acid cleaning the surfaces must be thoroughly rinsed with clean water to remove all traces of the acid and thoroughly dried after the final water rinse. To minimize staining, surfaces must not be permitted to dry between successive steps of the acid cleaning and rinsing procedure. A neutralizing treatment may be required under some conditions; if used, neutralization must be followed by repeated water rinsing to remove all trace of the neutralizing agent followed by thorough drying after the final water rinse. Suggested solutions, contact times, and solution temperatures for acid cleaning of stainless steels are given in ASTM A 380. Additional information can also be found in the section "Passivation Treatments" in this article and in the article "Acid Cleaning" in this Volume.

References cited in this section

1. "Standard Practice for Cleaning and Descaling Stainless Steel Parts, Equipment, and Systems," A 380, *Annual Book of ASTM Standards*, ASTM, 1988
4. *Cleaning and Descaling Stainless Steels*, No. 9001, American Iron and Steel Institute, 1982 (reprinted by Nickel Development Institute, 1988)

Mass Finishing

Mass finishing provides methods that can be advantageously used for surface treating stainless steels include barrel finishing, vibratory finishing, and centrifugal barrel finishing. Mass finishing methods are adaptable to removal of burrs, scale, and residual flux, and they also can be used for light surface treatment, such as cleaning, burnishing, or coloring. For more information, see the article "Mass Finishing Methods" in this Volume.

Post-Treatments. Once a mass finishing treatment is completed, stainless steel parts are rinsed thoroughly in water and dipped in a 20 vol% solution of HNO_3 at 50 °C (120 °F) for 10 to 15 min. This is followed by another water rinse. If any oxide scale remains on the work after mass finishing, it must be removed by acid pickling.

Finishing Methods

This section deals with the finishing of stainless steels as practiced by the fabricator or manufacturer--specifically, grinding (used here to mean metal removal for the purpose of altering surface finish, not to achieve close dimensional tolerances), polishing, and buffing. Table 8 summarizes the sequence of operations for the grinding, polishing, and buffing of stainless steels.

Table 8 Sequence of grinding, polishing, and buffing operations for stainless steels

Operation	Stage	Wheels	Grit size	Abrasive	Method	Purpose
Grinding	Rough	Solid wheels; rubber or bakelite bonded, soft body	20-30	Manufactured types, such as Al_2O_3 or SiC	Dry	For rough work on castings, forgings, and weld beads that may require it. Castings usually sandblasted initially
Grinding	Finish	Same as above; or setup disk wheels or abrasive belts	36-80	Manufactured types, such as Al_2O_3 or SiC	Dry	For subsequent operations on the above and also preliminary to polishing operations on hot-rolled plate. May also be employed for touch-up work (removing deep scratches and tool marks prior to polishing)
Polishing	Rough	Setup disk canvas	80-100	Manufactured types,	Grease stick	To produce a rough polished finish and to remove imperfections left

		compress wheels or abrasive belts		such as Al_2O_3 or SiC		by hand wheel grinding. Also use as a preparatory operation for a final polish corresponding to standard No. 4 mill finish. This is the usual starting on cold-rolled sheet.
Polishing	No. 4 finish	Setup disk canvas compress wheels or abrasive belts	120-150	Manufactured types, such as Al_2O_3 or SiC	Grease stick	To provide a finish similar to standard No. 4 mill finish. Variations in fineness of finish should be expected with variations in condition of grit as between a new or worn belt.
Polishing	No. 6 finish (tampico)	Tampico brush type	Start with No. 4 finish	. . .	Pumice pastes made up on the job, or commercially available manufactured compositions	To provide a finish corresponding to standard No. 6 mill finish
Polishing	Pre-No. 7 finish	Made-up cloth wheels or abrasive belts	180	Manufactured types	Grease stick	To provide a finish preparatory to buffing for standard No. 7 finish. May be used as final finish on drawn parts and architectural trim
Polishing	Pre-No. 8 finish	Made-up cloth wheels or abrasive belts	240 to flour	Manufactured types or Turkish emery	Grease stick	To provide a final polished finish preliminary to a mirror finish
Polishing	Satin finishing	Full disk buffs, loose or concentric sewed		Greaseless compounds applied to the wheel as required. These are available in many grit sizes.	. . .	A method of producing satin finishes. Fineness of finish varies with composition employed.
Buffing	Cutting	Bias-type, sewed piece, or fill disk buffs		Use stainless steel cutting compound on buff.	. . .	Apply as needed to remove any residual polishing lines or other imperfections prior to color buffing for high-luster finishes such as No. 7. May be applied directly to bright cold-rolled strip
Buffing	Coloring	Full disk or bias-type buff		Use stainless steel coloring compound.	. . .	For final coloring to bright lusters such as No. 7 and mirror. High speeds for brightness (approximately 50 m/s, or 10,000 sfm). Lower speeds for satinlike finish (approximately 20 to 30 m/s, or 3500 to 6000 sfm)

Source: Ref 2

Before discussing each of these processes, it is useful to review the inherent characteristics of stainless steels that set these materials apart from other metals, and to emphasize the ever-present need to avoid any practices that may result in a loss

in corrosion resistance or a reduction in mechanical property values. For example, stainless steels, as a group, are characterized by:

- *High tensile strength.* This fact determines the power necessary for efficient metal removal in grinding and polishing.
- *High surface hardness.* This governs the selection of abrasive materials and their cutting behavior.
- *Low heat conductivity.* This requires attention to precautionary measures that will prevent rapid or excessive rise in temperature, which can cause heat tint discoloration and, possibly, a reduction in corrosion resistance.
- *Rapid work hardening.* This necessitates proper grinding techniques, especially of austenitic grades in which residual stresses at the metal surface may affect in-service corrosion resistance.
- *Need for cleanliness.* This means attention must be given to grinding and polishing media to keep it clean and free of iron particles, which can be picked up if used with carbon or alloy steel products.

Grinding

Grinding is used for preliminary surface conditioning before polishing, and as a means of removing excess metal from weld beads and flash from forgings and castings. It also is used for dressing gas-cut welding edges. These operations usually require coarse or rough grinding. However, as the refinement of the surface increases with the use of finer abrasives, grinding begins to approach polishing; the dividing line between fine grinding and polishing is seldom clear cut.

Solid wheels are used for coarse grinding and include the vitreous and rubber-bonded or plastic-bonded types. They should be free-cutting to avoid loading and glazing. Abrasives frequently used are aluminum oxide (Al_2O_3) and silicon carbide (SiC), in grit sizes ranging from 20 to 36 (for initial or coarse cutting) to 60 (for subsequent finishing work). Surface speeds for solid wheels usually range between 25.5 and 30 m/s (5000 and 6000 sfm). For safety, wheels should never be operated above their maximum permissible speed. To realize the maximum cutting efficiency of which they are capable, they should not be run at less than recommended speeds.

Wheel Operation. Grinding wheels should never be forced; forcing causes excessive wheel breakdown and localized high temperature in the workpiece. In addition, the wheel should not be allowed to ride on the workpiece with insufficient pressure, because this causes rapid glazing of the wheel.

The elimination of heat buildup in localized zones is of major importance with stainless steel. The low thermal conductivity of stainless steel contributes to increased thermal distortion. This applies particularly to the chromium-nickel grades, of which the coefficients of thermal expansion are relatively high. Holding the metal at low temperature avoids heat tinting, which becomes evident at 230 to 260 °C (445 to 500 °F) and above. Marked increases in metal temperature can reduce the hardness of heat-treated grades and precipitate carbides in the unstabilized chromium-nickel grades, which are susceptible to intergranular corrosion.

Rough surfaces on weldments, castings, and forgings are cut down to the general finish contour with a solid wheel of either Al_2O_3 or SiC of grit size from 20 to 40, and with a bond loose enough to allow the wheel to remain open and free-cutting without excessive wheel wear. Again, it is important to prevent local overheating, which can cause either mechanical or metallurgical damage, and to avoid excessive metal removal, allowing sufficient material for further finishing. Surface contamination is not important at this stage of finishing.

The next roughing operation, which in many applications may replace the solid-wheel operation, requires the use of a portable disk grinder, powered by air or electricity, using abrasive disks coated with Al_2O_3 ranging in grit size from 80 to 120. Localized overheating may be prevented by applying a small stream of water or water-soaked rags to the side not being ground.

Weld Beads. Excess metal in weld beads ordinarily is removed by grinding, although an initial cut may be made with a cold chisel when the size of the bead warrants. Grinding procedures and precautions conform to those previously described, except that the width of weld beads precludes right-angle cutting with successive grit sizes. Usually, a raised bead will take a fairly coarse grit at the outset. Canting of wheels must be avoided; otherwise, grooves may be cut parallel to the bead and undesirable thinness will result. Limiting stops attached to portable grinders may be installed to prevent canting and excessive metal removal.

When grinding is to be followed by polishing, as for weld joints on polished sheet, the grinding operation must terminate sufficiently above the level of the base metal to allow enough metal for final polishing to finish flush, without a ridge or groove. Limiting stops on grinding machines are helpful.

For economic reasons, grinding of weld joints in cold-rolled or polished sheet should be held to a minimum by using welding procedures that avoid high beads of excess metal. The grinding step can often be eliminated, allowing the workpiece to go directly into the polishing operations where finer abrasives are used.

Metal adjacent to beads that are being ground should be protected from flying bits of metal cuttings by shields of material such as paper. Wet rags may be laid on the workpiece to absorb heat and reduce thermal distortion, particularly on thin-gage material.

Progressive Grinding. To remedy an existing surface condition, such as removing scale patterns or indentations from hoisting clamps on an annealed plate, a series of wheels of decreasing grit size is often needed. The initial grit size is selected on the basis of which coarseness is needed to remove the major portion of the unwanted condition. After the workpiece has been partly dressed down, the operation is completed by using a graduated series of successively finer wheels until the desired final finish is attained. The use of a relatively soft plastic wheel impregnated with fine, sharp grit makes it possible to reduce the number of finishing operations, because of the combination of free cutting and wheel resilience for ease in blending.

The direction of wheel traverse across the work is changed by 90° with each change in grit size to remove residual grinding lines. As each change is made, workpiece surfaces should be brushed thoroughly to remove any particles of the preceding abrasive or of metal cuttings that mar the performance of the finer grit to follow. The progression from coarse to fine grit size may be made in steps of 20 to 40 mesh.

When using a flat disk grinder, with which cutting is performed against the face (instead of the rim) of the wheel, a rotary or circular traversing motion is most frequently used. This eliminates the need for reversing the direction of grinding with each change of grit size.

Belt Grinding. Belts carrying abrasives of various grit sizes are widely used for grinding and polishing stainless steel surfaces. Although many complex shapes can be belt ground, a simple projection may make belt grinding impossible; for example, the studs welded to a cookware pot or pan to which the handle is affixed. In this application, the finishing operations, from grinding to color buffing, must be completed before the studs are welded in place. Grit sizes and belt speeds for abrasive grit roughing and polishing are given in Table 9.

Table 9 Grit sizes and belt speeds for abrasive belt roughing and polishing of stainless steels[a]

Product	Roughing				Rough polishing			Polishing			
	Obstruction or roughness removed	Grit size, mesh	Belt speed		Grit size, mesh	Belt speed		Grit size for for successive stages, mesh	Belt speed		Polishing aid[b]
			m/s	sfm		m/s	sfm		m/s	sfm	
Billets, alloy or stainless steel	. . .	. . .	. . .	. . .	50	17.9	3500	. . .	. . .	. . .	G
Cutlery, stainless steel											
Blades--tapering	. . .	50	28	5500	80	28	5500	180	28	5500	G

Forks or knives	. . .	. . .	. . .	. . .	80	26.5	5200	1500	26.5	5200	G
Spoons	. . .	. . .	. . .	. . .	. . .	. . .	. . .	150, 220	26.5	5200	G
Hypodermic needles, stainless steel	. . .	. . .	. . .	. . .	. . .	. . .	. . .	320[c], 400[c]	23.5	4600	WSO
Jet blades, stainless steel											
Airfoil	. . .	. . .	. . .	. . .	50	28	5500	120	28	5500	O
Longitudinal	. . .	. . .	. . .	. . .	. . .	. . .	. . .	80, 100, 120, 150, 180	[d]	[d]	O
Stainless steel											
Coil (series 300)	Pits	60	17.3	3400	80	17.3	3400	120, 150	17.3	3400	O
Pots and pans	Wrinkles	80	25.5	5000	. . .	. . .	. . .	220, 320[c]	25.5	5000	G
Press plates	Scratches	80	20.4	4000	100	20.4	4000	120, 150, 180, 240, 320	20.4	4000	G
Sheets, No. 3 finish	. . .	. . .	. . .	. . .	80	20.4	4000	100	20.4	4000	G
Sheets, No. 4 finish	Inclusions	100	20.4	4000	120	20.4	4000	150[c]	20.4	4000	G
Sheets, No. 7 finish	Inclusions	100	20.4	4000	150	20.4	4000	180[c], 240[c], 280[c]	20.4	4000	G
Tubes	. . .	. . .	. . .	. . .	150	17.9	3500	220, 280, 320	23	4500	O
Turbine nozzles and buckets	. . .	. . .	. . .	. . .	80	25.5	5000	120	23	4500	G

Source: Ref 2

(a) Abrasive belts coated with Al_2O_3, unless grit size is footnoted to indicate otherwise.

(b) G, grease; O, oil; WSO, water-soluble oil.

(c) Silicon carbide.

(d) Fixture abrasive, reciprocating.

Mechanized Belt Grinding. In mechanized belt grinding, longer belts provide a longer belt life and dissipate heat more effectively. Thus, longer belts frequently are operated without a coolant, eliminating a post-grinding cleaning operation.

In belt grinding of rectangular stainless steel sinks, for example, it was necessary to use short belts to reach all internal surfaces. Each sink was ground in a machine with four grinding heads indexing about the main column of the machine while the sink was held in a cradle that rotated in a horizontal plane. A narrow belt ground the radii between the bottom and the side walls of the sink. Wider belts were used to grind the side walls; these belts were comparatively short and required the use of a coolant. Belt abrasives varied in grit size from 80 to 220 mesh, depending on the desired finish.

On a typical grinding machine using a 2200 mm (86 in.) wide abrasive belt and powered by a 250-hp ac motor, a positive hydraulic reciprocating drive permits instantaneous variations in table speed; belt speed is fixed at 25.5 m/s (5000 sfm). The 2200 mm (86 in.) belt travels over a conventional vertical-head assembly consisting of a dynamically balanced upper idler roll of steel and a rubber-covered serrated lower contact roll. A pneumatic belt-centering device ensures positive tracking of the abrasive belt and is adjustable to compensate for belts of different widths. Incorporated into the entire worktable is a 2200 mm (86 in.) wide vacuum chuck 4.9 m (16 ft) long. To produce single or compound tapers, a worktable can be tilted to any angle, for either right-hand or left-hand tapered sheets.

Belt life is influenced primarily by belt speed, type of material being ground and its hardness, pressure of the belt against the work, type of contact roll, type of lubricant (if a lubricant is required), and uniformity of the finish desired. In belt grinding of stainless steel, the recommended belt speed is approximately 20 m/s (4000 sfm).

With the exception of the precipitation-hardening stainless steels, the hardness of the steel has a greater effect on the life of a grinding belt than its composition. Hardness also affects surface finish, and a high-quality finish is easier to obtain on a harder stainless than on one that is softer. With precipitation-hardening alloys, best grinding results are obtained with a waterproof cloth abrasive belt and a water-soluble oil lubricant.

Pressure of the workpiece against the abrasive belt is probably the most important factor affecting belt life. Excessive pressure on a new belt causes glazing of the abrasive and greatly reduces cutting action. Therefore, new belts should be subjected to very light pressures during the break-in period and until the belt is capable of maintaining a uniform cutting action. A light belt pressure is preferred, and increased stock removal should be obtained by changing to a coarser belt.

The contact roll that backs up the abrasive belt is another important factor; a properly serrated contact roll may increase belt life by as much as 60%. The angle of the serration affects both belt life and finish. To obtain fine finishes, contact rolls serrated at an angle of 75° to the axis of the spindle should be used. Rough finishing requires a 30° angle. For general work, contact rolls may be made with a 45° serration, using a 9.5 mm ($\frac{3}{8}$ in.) groove and 9.5 mm ($\frac{3}{8}$ in.) land. Hardness of the contact roll should range between 50 to 65 on the Shore scleroscope A-scale.

When lubricants are used, they should maintain free-cutting (nonloading) edges, add color to the finished product, maintain a cool cutting surface, and be easy to apply. Lubricants may be in the form of grease sticks, waxes, or cutting oils. Cutting oils generally are more effective when they are diluted as much as 4 to 1 with kerosene.

Safety. Metal fines collected in a container near machines during the belt grinding of stainless steel should be removed regularly, because the fines, together with polishing compounds or oils that are collected with them, constitute a potential fire hazard. Fires in the duct system can be extremely serious because of the high air flow in the ducts. Fire-extinguishing equipment should be close to any machines using abrasive belts.

When wide abrasive belts are used, equipment with automatic tracking to center the belt in relation to the work is advantageous. All abrasive belt machinery should be equipped with motors that are totally enclosed.

Safety training for operators should begin with thorough instruction in the proper use of equipment, because most severe injuries result from improper use. Most common injuries are burns, cuts, and eye injuries. Serious accidents may arise

from the snagging of parts because of improper loading, improper use of lubricating devices, and careless placement of hands and arms while the machine is in operation.

Polishing

Polishing operations use abrasives that are mounted on prepared shaped wheels or on belts that provide a resilient backing. The stainless steel to be polished may be in either a smooth rolled or a previously ground condition. For the smooth rolled condition, the starting grit size should be selected in a range of 150 to 220. For the ground condition, the initial grit should be coarse enough to remove or smooth out any residual cutting lines or other surface imperfections left from grinding. In either instance, the treatment with the initial grit should be continued until a clean, uniform, blemish-free surface texture is obtained. The initial grit size to use on a preground surface may be set at about 20 numbers finer than the last grit used in grinding and may be changed, if necessary, after inspection. A tallow lubricant may be used to reduce the sharpness of cutting. With broad-belt grinding of stainless steel sheet, the use of a lubricant or coolant is mandatory.

After completion of the initial stage of polishing, wheels or belts are changed to provide finer grits. The step-up in fineness is usually by 30 to 40 numbers. Each succeeding treatment is continued until all residual marks of the preceding cut are removed. Grease in stick form is applied to wheels carrying abrasives of 150 mesh and finer. Aluminum oxide buffing compounds and powdered pumice are preferred for use with abrasives of 200 mesh and finer grit size.

Polishing speeds are generally somewhat higher than those used in grinding. A typical speed for a coated-wheel operation is 38 m/s (7500 sfm).

The same precautions that must be observed in the grinding of stainless steel are equally applicable to polishing:

- Avoidance of iron or other contamination
- Care of wheels and belts when not in use
- Restriction of the use of wheels and belts to stainless steel only
- Avoidance of excessive pressure while polishing
- Operation at proper speeds
- Avoidance of localized heat buildup because of dwelling at one spot
- Removal of loose cuttings and bits of abrasive from work surfaces before changing from one grit size to another

Buffing

Buffed finishes are produced on stainless steel surfaces by using equipment, materials, and techniques that are similar to those used on other materials (see the article "Finishing Methods Using Multipoint or Random Cutting Edges" in this Volume). However, the skill needed for producing the high lusters obtainable on stainless steel is gained only through actual experience. Buffed finishes are not recommended for the stabilized grades of stainless steel, such as types 321 and 347, because these materials contain fine, hard particles of titanium or niobium compound that show up as pits on bright finishes.

The first step in applying a buffed finish of desired luster and color is that of providing a smooth surface, free of scratches and any other defects. For this reason, buffing is generally performed in two stages: the first is known as hard buffing (or cutting down); the second, as color buffing.

Hard buffing follows polishing, which generally ends with the use of abrasives of 200- to 250-mesh grit size. The fine scratches left by polishing are cut down with a buff that carries no previously glued on abrasive. Instead, such abrasive as is needed is applied intermittently to the buffing wheel as it rotates, either by rubbing a cutting compound in bar or stick form against it or by spraying it with a liquid compound. These cutting compounds contain (1) very fine artificial abrasives, such as Al_2O_3, of about 300-mesh grit size; and (2) a stiff grease or other material that acts as a binder. They adhere to the wheel by impregnating the cloth disks. Hard buffing may be conducted at from 33 m/s (6500 sfm) up to a maximum of 51 m/s (10,000 sfm).

Color buffing is performed in the same manner as hard buffing, except that a coloring compound is substituted for the cutting compound and speeds are held below 36 m/s (7000 sfm). Various compounds (rouges and other extremely fine

abrasives) for use on stainless steel are available commercially, both in bar form for hand application and in liquid form for automatic application. The use of any material that may result in loss of corrosion resistance by stainless steel surfaces should be avoided.

Direct color buffing, without previous polishing or hard buffing, may be satisfactory for certain applications, such as:

- A color-buffing wheel may be applied directly on type 430 that has been given a finishing pass on a polished mill roll after final pickling.
- Small articles blanked from bright finished straight chromium steel strip and then tumbled for burr removal may have a satisfactory appearance if run under a color buff for brightening.
- Smooth, defect-free surfaces that have been electrolytically polished provide a good base for color buffing. By masking before buffing, contrasting surface effects can be obtained, as a result of the difference in reflectivity obtainable by electrolytic polishing and by color buffing.

Color buffing, however, does not remove scratches or other surface defects because cloth wheels without coarse abrasives, which are used for color buffing, do not remove surface imperfections. Therefore, the continued presence of such imperfections on finished products must be expected.

Effect of Polishing and Buffing on Corrosion Resistance. In addition to altering the appearance of stainless steels, polishing and buffing may have a considerable effect on the corrosion resistance of these materials. For example, a steel with a No. 2B finish as received from the mill has excellent corrosion resistance. This can be adversely affected by polishing with coarse abrasive, but it can be fully restored by polishing to a No. 4 finish or higher. Polishing to a No. 7 or 8 finish, by removing very fine pits and other surface defects, improves corrosion resistance over that afforded by the original No. 2B finish.

Tanks for storing raw milk provide a commercial example of the importance of a polished finish to sanitary and corrosion-resistance properties. According to the sanitary codes, these tanks must be made of 300-series stainless steel, and all surfaces that come in contact with the milk must be polished to a pit-free No. 4 finish or better. The high finish not only promotes sanitary properties, but also provides improved resistance to corrosion by the chlorine-bearing chemical used in scouring the tanks after each use.

Several polishing and buffing compounds contain iron and iron compounds, which can be highly deleterious to the corrosion resistance of stainless steel. The amount of iron in these compounds that can be tolerated is extremely small (for maximum protection, less than 0.01% Fe). If more than one polishing operation is involved, slightly more iron can be tolerated in the early stages of polishing, but the final stage should be virtually iron-free. Magnetic oxides of iron are as damaging as iron powder; the oxides generally occur in Turkish emery as well as in several synthetic abrasives. Their presence is most accurately determined by chemical analysis.

Cleaning and Passivation After Buffing. Cleaning is always required after a final buffing operation in which a surface finish of No. 4 or finer is achieved. The workpiece is vapor degreased or is cleaned with whiting (precipitated calcium carbonate), powdered chalk, or dehydrated lime, which is applied with a soft flannel cloth. This picks up the grease or lubricant from a color-buffing operation. The workpiece must then be protected from damage in handling.

Passivation is not required after buffing or fine polishing if the surface obtained is chemically clean and free of oil, grease, or adhesives used in the polishing media. A clean surface passivates itself naturally when it is exposed to air. However, if foreign metal, such as iron, has been picked up in the buffing operation, it must be removed by pickling or passivation.

Reference cited in this section

2. *Finishes for Stainless Steel,* Publ. 201-683-14M-EB, American Iron and Steel Institute, 1983

Matching Mill Finishes

In the fabrication of No. 4 polished sheet, it frequently is necessary to refinish weld zones to blend them with the original finish. Although it is virtually impossible to match a machine-polished surface except by duplicating the original polishing, a close blending may be obtained by skillful use of manual methods.

If the original machine-polished lines are parallel with the line of the weld, the bead can be dressed down by grinding with a hard or soft wheel and then finished by polishing with, progressively, No. 80 and No. 120 (and possibly No. 150) grit on a setup wheel driven by a portable machine. The traversing of this wheel should be kept in line with the run of the bead so that its cut lines are kept parallel with those of the original machine-polished surface.

To avoid residual ridges or grooves, the metal of the joint should be brought flush with that of the base metal. For a given starting grit size, the depth of the scratches produced depends on the amount of use it has received; thus, samples should be run before starting on finish work.

If the machine-polished lines are not parallel with the line of the weld, final manual polishing should be done in the direction of the machine polishing. If the original polish lines on the two sides of a joint are not parallel with each other (for example, if they are parallel with the bead on one side and perpendicular to the bead on the other) the best procedure is to run the polishing cut lines along (not across) the bead. The girth weld between a tank shell and head exemplifies this problem. The cut lines of the shell extend around the unit and lie parallel with the girth joint, whereas the cut lines on the head are perpendicular, parallel, and at an angle around the periphery. Swinging such an assembly on the faceplate of a large lathe would permit repolishing the head and dressing the weld joint on the same setup, thus rendering parallel all of the cut lines on the head, joint, and shell. For this application, abrasive paper (or pieces cut from a belt) may be backed up with a block of wood or some softer material and guided by hand along the line of the weld joint.

Electrocleaning and Electropolishing

Electrocleaning, an electropolishing technique, is a useful alternative to pickling treatments (Ref 5). Although electrocleaning is not covered under ASTM A 380, it is widely used to remove imperfections from the surface of stainless steel after fabrication. It removes embedded iron particles and similar film defects as does pickling. Unlike pickling, electrocleaning does not roughen the surface, but makes it smoother. A 12 V dc power source with variable current capability is connected to the stainless steel, making it the anode. A copper cathode and an electrolyte--usually phosphoric acid (H_3PO_4)--are then used to corrode away the protective film and several layers of the surface in a controlled manner by varying the current and dwell time.

Electrocleaning can be performed in most plating shops by immersion. Localized electrocleaning with field kits is widely practiced to remove heat tint and weld-related defects from the heat-affected zone (see Fig. 3).

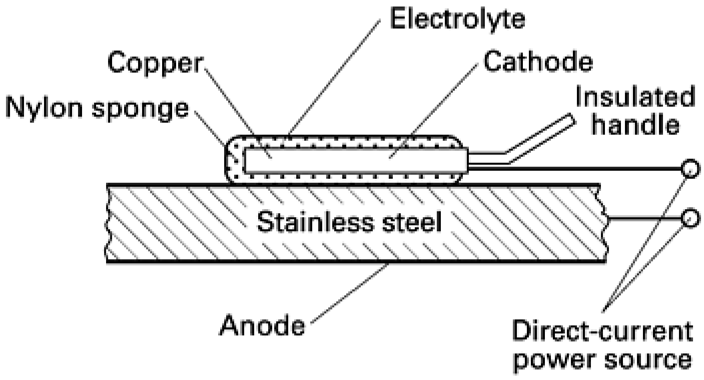


Fig. 3 Equipment for localized electrocleaning of heat tint from the surface of stainless steel. Source: Ref 5

Electropolishing is the same process as electrocleaning, but is generally performed for a longer time (Ref 5). Electropolishing is used primarily to produce a very smooth, bright, easily cleaned surface with maximum corrosion resistance. It removes the surface layer of a metal by anodic treatment in an acid bath. Conditions for electropolishing of stainless steels in acid electrolytes are given in Table 10.

Table 10 Conditions for electropolishing in acid electrolytes

Type of metal (and product)	Purpose of treatment	Bath volume		Installed power		Current density		Polishing cycle, min	Daily production			Oper-ators
									No. of parts	Area		
		L	gal	A	V	A/dm^2	A/ft^2			m^2	ft^2	
Sulfuric-phosphoric acid electrolytes												
302 and 430 stainless (job-shop work)	Bright finish	1150	300	1500	15	30	300	3-8	3500	25	250	2
302 and 202 stainless (plumbingware)	Bright finish	1150	300	1500	12	30	300	3-4	1000-2000	. . .	. . .	1
303 stainless (food-processing equipment)	Bright finish	2650	700	2500	18	20	200	4-10	400-500	190-370	2000-4000	2
Series 300 and 400 stainless (job-shop work)	Various	2250	600	3000	18	. . .	. . .	10(avg)	25-400	5-45	50-500	2
304 stainless	Brighten; deburr	1300	350	2000	12	30	300	4	3000	55-75	600-800	1
Stainless steel (aircraft components)	. . .	2650	700	3000	18	25-30	250-300	5	200	30	300	1
430 stainless	Bright finish	1500	400	1500	14	. . .	. . .	1-2	7000	75	800	1
430 stainless (trim items)	Brighten; deburr	1500	400	750	18	. . .	. . .	3	12,000	230	2500	1
430 stainless (automotive trim)	Bright finish	3800	1000	3000	18	30	300	4	250/h	. . .	. . .	1
430 stainless (automotive rain shields)	Bright finish	3800	1000	3000	18	25	250	5	450/h	. . .	. . .	1
Stainless and carbon steels (job-shop work)	Brighten; deburr	1500	400	1500	12	25-40	250-400	Varies	Varies	. . .	. . .	1
Sulfuric-phosphoric-chromic acid electrolytes												

302 stainless (surgical instruments)	Smooth; polish	3600	950	3000	18	30	300	5	5000	. . .	. . .	1

Electropolishing is applicable to all stainless steel grades, hot or cold finished, cast or wrought. The amount of metal removed is subject to close control, depending on the desired result. The resulting surfaces have a bright, passive finish. The process is most frequently applied to cold-finished surfaces, because they yield a smoother finish than can conventionally be obtained on hot-finished surfaces. As in electroplating, the results depend on the contour and shape of the part. The end-grain surfaces of the free-machining stainless grades, such as types 303 and 416, will appear frosty after electropolishing due to removal of the sulfide inclusions.

Electropolishing can be used as a preliminary brightening operation before final buffing, particularly on drawn parts with burrs, sharp radii, or recessed areas, and it serves to reduce the amount of buffing required. Electropolishing is applied to decorative automotive parts and accessories, conveyor systems for food-handling equipment, animal cages, and pharmacy equipment. It provides an economical finish on many parts that are difficult or impossible to finish by conventional polishing, such as items made from wire.

In contrast to mechanical finishing methods, electropolishing may make inclusions in the material more visible. Some types of inclusions are dissolved out, whereas others remain in relief. Electropolishing has been used as a surface inspection technique to reveal residual foreign material, such as embedded scale and particles of iron, carbide precipitation, and weld defects. The surface obtained by electropolishing is directly related to the original surface quality--the process cannot be used to remove digs, gouges, scratches, and the like.

Chemical polishing is another method for providing a smooth and bright surface on stainless steel. Unlike electropolishing, chemical polishing can be done without the use of electricity and without racking of individual parts. Thus, chemical polishing offers significant savings in capital investment and labor. In addition, chemical polishing offers a greater degree of freedom in polishing items with blind holes and other recessed areas. However, it does not produce the high specular reflectivity (brightness) obtained with electropolishing.

Proprietary products for chemical polishing are available on the market. Generally, they are based on combinations of H_3PO_4, HNO_3, H_2SO_4, hydrochloric acid (HCl), organic acids, and special surfactants and stabilizers to promote a high degree of brightness and long bath life. Unlike the HNO_3-HF mixtures that are used in chemical cleaning, the proprietary chemical bright dips do not cause severe attack on the grain boundaries or intergranular corrosion.

Reference cited in this section

5. A.H. Tuthill and R.E. Avery, Specifying Stainless Steel Surface Treatments, *Advanced Materials & Processes,* Vol 142 (No. 6), Dec 1992, p 34-38

Passivation Treatments

Exposure to air is the natural, primary passivation treatment for stainless steel. This exposure produces a thin, durable chromium oxide film that forms rapidly on the alloy surface and gives stainless steel its characteristic "stainless" quality. Exposure of the surface to water or other oxidizing environments also produces this passivating film. Additional passivation is called for in many specifications to remove light surface contamination from machined stainless steel parts, including shop dirt, iron particles from cutting tools, and machining lubricants. Passivation treatments of stainless steel with HNO_3 or mild organic acids are useful mild cleaning operations performed after machining to enhance the protective nature of the natural, air-formed film. Nitric acid treatment enhances the level of chromium in the protective film on stainless steels. DeBold (Ref 6) has published an excellent practical review of HNO_3 passivation of stainless steel machined parts.

ASTM A 380 (Ref 1) describes eight HNO_3-based cleaning/passivation treatments and four cleaning treatments using other chemicals (Table 11). None of these passivation treatments corrodes or etches the surface. Several are designed to clean bright or polished surfaces by removing loosely adherent foreign matter. The most common treatment is immersion in a 20 to 40% solution of HNO_3 at a temperature of 50 to 60 °C (120 to 140 °F).

Table 11 Acid cleaning and passivation of stainless steel

Alloy	Condition	Treatment				
		Code	Solution, vol%[a]	Temperature		Time, min
				°C	°F	
Part 1: Cleaning with HNO_3-HF						
Purpose: For use after descaling by mechanical or other chemical methods as a further treatment to remove residual particles of scale or products of chemical action (i.e., smut), and to produce a uniform "white pickled" finish						
200 and 300 series, 400 series containing 16% Cr or more, and precipitation-hardening alloys (except free-machining alloys)	Fully annealed only	D	6-25% HNO_3 plus $\frac{1}{2}$ to 8% HF[b][c]	20-60	70-140	As necessary
Free-machining alloys, maraging alloys, and 400 series containing less than 16% Cr	Fully annealed only	E	10% HNO_3 plus $\frac{1}{2}$ to 1 $\frac{1}{2}$% HF[b][c]	20 (up to 60 with caution)	70 (up to 140 with caution)	1-2
Part 2: Cleaning/passivation with HNO_3solution						
Purpose: For removal of soluble salts, corrosion products, and free ion and other metallic contamination resulting from handling, fabrication, or exposure to contaminated atmospheres						
200 and 300 series, 400 series, precipitation hardening and maraging alloys containing 16% Cr or more (except free-machining alloys)[d]	Annealed, cold rolled, or work hardened, with dull or nonreflective surfaces	F	20-50% HNO_3	50-70	120-160	10-30
				20-40	70-100	30-60[c]
	Annealed, cold rolled, or work hardened, with bright-machined or polished surfaces	G	20-40% HNO_3 plus 2-6 wt% $Na_2CrSO_7 \cdot 2H_2O$	50-70	120-155	10-30
				20-40	70-100	30-60[c]
400 series, maraging and precipitation-hardening alloys containing less than 16% Cr, and high-carbon/straight-chromium alloys (except free-machining alloys)[d]	Annealed or hardened, with dull or nonreflective surfaces	H	20-50% HNO_3	45-55	110-130	20-30
				20-40	70-100	60
	Annealed or hardeneith bright-machined or polished surfaces	I[f]	20-25% HNO_3 plus 2-6 wt% $Na_2Cr_2O_7 \cdot 2H_2O$	50-55	120-130	15-30
				20-40	70-100	30-60

200, 300, and 400-series free-machining alloys[d]	Annealed or hardened, with bright-machined or polished surfaces	J[f]	20-50% HNO_3 plus 2-6 wt% $Na_2Cr_2O_7 \cdot 2H_2O$[g]	20-50	70-120	25-40
		K[e]	1-2% HNO_3 plus 1-5 wt% $Na_2Cr_2O_7 \cdot 2H_2O$	50-60	120-140	10
		L[f]	12% HNO_3 plus 4 wt% $CuSO_4 \cdot 5H_2O$	50-60	120-140	10
Special free-machining 400-series alloys with more than 1.25% Mn or more than 0.40% S[d]	Annealed or hardened, with bright-machined or polished surfaces	M[f]	40-60% HNO_3 plus 2-6 wt% $Na_2Cr_2O_7 \cdot 2H_2O$	50-70	120-160	20-30
Part 3: Cleaning with other chemical solutions						
200, 300, and 400 series (except free-machining alloys), precipitation hardening and maraging alloys	Fully annealed only	N	1 wt% citric acid plus 1 wt% $NaNO_3$	20	70	60
		O	5-10 wt% ammonium citrate	50-70	120-160	10-60
Assemblies of stainless and carbon steel (for example, heat exchanger with stainless steel tubes and carbon steel shell)	Sensitized	P	Inhibited solution of 2 wt% hydroxyacetic acid and 1 wt% formic acid	95	200	6 h
		Q	Inhibited ammonia-neutralized solution of EDTA (ethylene-diamene-tetraacetic acid) followed by hot-water rinse and dip in solution of 10 ppm ammonium hydroxide plus 100 ppm hydrazine	Up to 120	Up to 250	6 h

Source: Ref 1

(a) Solution prepared from reagents of following weight percent: HNO_3, 67; HF, 70.

(b) For reasons of convenience and handling safety, commercial formulations containing fluoride salts may be found useful in place of HF for preparing HNO_3-HF solutions.

(c) After acid cleaning and water rinsing, a caustic permanganate solution containing 10 wt% NaOH and 4 wt% $KMnO_4$, 70 to 80 °C (160 to 180 °F) 5 to 60 min, may be used as a final dip for removal of smut, followed by thorough water rinsing and drying.

(d) The purchaser shall have the option of specifying in his purchase documents that all 400-series ferritic or martensitic parts receive additional treatment as follows: Within 1 h after the water rinse following the specified passivation treatment, all parts shall be immersed in an aqueous solution containing 4 to 6 wt% $Na_2Cr_2O_7 \cdot 2H_2O$, at 60 to 70 °C (140 to 160 °F) 30 min. This immersion shall be followed by thorough rinsing with clean water. The parts then shall be thoroughly dried.

(e) Shorter times may be acceptable where established by test and agreed upon by the purchaser.

(f) The high-carbon and free-machining alloys may be subject to etching or discoloration in nitric acid. This tendency can be minimized by the use of high acid concentrations with inhibitors such as $Na_2Cr_2O_7 \cdot 2H_2O$ and $CuSO_4 \cdot 5H_2O$. Oxidizing action increases with increasing concentration of nitric acid; additional oxidizing action is provided by $Na_2Cr_2O_7 \cdot 2H_2O$. Avoid acid cleaning when possible; use mechanical cleaning followed by scrubbing with hot water and detergent, final thorough water rinsing, and drying.

(g) If flash attack (clouding of stainless steel surface) occurs, a fresh (clean) passivating solution or a higher HNO_3 concentration will usually eliminate it.

The complete passivation treatment includes degreasing, immersion, and rinsing. Degreasing, preferably in a nonchlorinated solvent, removes organic contaminants from the surface.

Degreasing. Neither air nor HNO_3 can form or enhance the protective film when grease, oil, fingerprints, or other organic contamination is present on the surface. Parts must be thoroughly degreased prior to any passivation treatment. The water-break test, described in ASTM A 380 (Ref 1), is easy to apply and is effective in detecting residual organic matter that may not have been removed in the degreasing operation. A sheet of water directed over the surface will "break" around oil, grease, and other organic contaminants not completely removed from the surface. Specifications can simply call for no break in the film as it drains from the vertical surface.

Immersion. The part is immersed in a passivating solution selected from Table 11 (Part 2 or 3). In addition to the standard HNO_3 solution, there are a number of solution variations appropriate for all grades of 200, 300, and 400 series, maraging, precipitation hardening, and free-machining alloys in various heat treatment conditions and surface finishes.

Rinsing. Immediate and thorough rinsing in clean water of pH 6 to 8 is mandatory. In many instances neutralization prior to rinsing is helpful. Immersion, neutralization, and rinsing must follow one another without allowing the surface to dry between steps. When passivating stainless steel sheet material, each sheet must be completely dry before it is stacked to avoid marks.

In addition to the cleaning precautions given in ASTM A 380 (Ref 1), different grades of stainless steel should not be mixed in the same passivating bath, as this can initiate corrosion where surfaces come in contact.

Although HNO_3 does not normally corrode stainless steel, it will corrode surfaces that are significantly altered. Acid cleaning should not be used for carburized and nitrided stainless steel parts or for improperly heat-treated high-carbon/high-chromium martensitic grades that have not been fully hardened.

Passivating Free-Machining Steels. The procedure for passivating free-machining stainless steels is somewhat different from that used for non-free-machining grades; that is because sulfides of sulfur-containing free-machining grades, that are totally or partially removed during passivation, create microscopic discontinuities in the surface of the machined part. Even normally efficient water rinses can leave residual acid trapped in these discontinuities after passivation. This acid can then attack the surface of the part unless it is neutralized or removed. For this reason, a special passivation process is required for free-machining grades.

The alkaline-acid-alkaline (A-A-A) method described in Ref 6 neutralizes trapped acid and is accomplished in less than two hours. The A-A-A method consists of the following steps:

- After degreasing, the parts are soaked for 30 min in a 5% solution of sodium hydroxide at 70 to 80 °C (160 to 180 °F)
- Water rinse
- The parts are then immersed for 30 min in a 20% HNO_3 solution containing 22 g/L (3 oz/gal) of sodium dichromate at 50 to 60 °C (120 to 140 °F)
- Water rinse
- Immerse the part for another 30 min in the sodium hydroxide solution at 70 to 80 °C (160 to 180 °F)

- Water rinse and dry (passivation is now complete)

References cited in this section

1. "Standard Practice for Cleaning and Descaling Stainless Steel Parts, Equipment, and Systems," A 380, *Annual Book of ASTM Standards,* ASTM, 1988

6. T. DeBold, Passivation of Stainless Steel Parts, *TAPPI J.,* Jan 1988, p 196-198

Electroplating

Stainless steels may be plated with copper, brass, chromium, nickel, cadmium, and the precious metals for such purposes as:

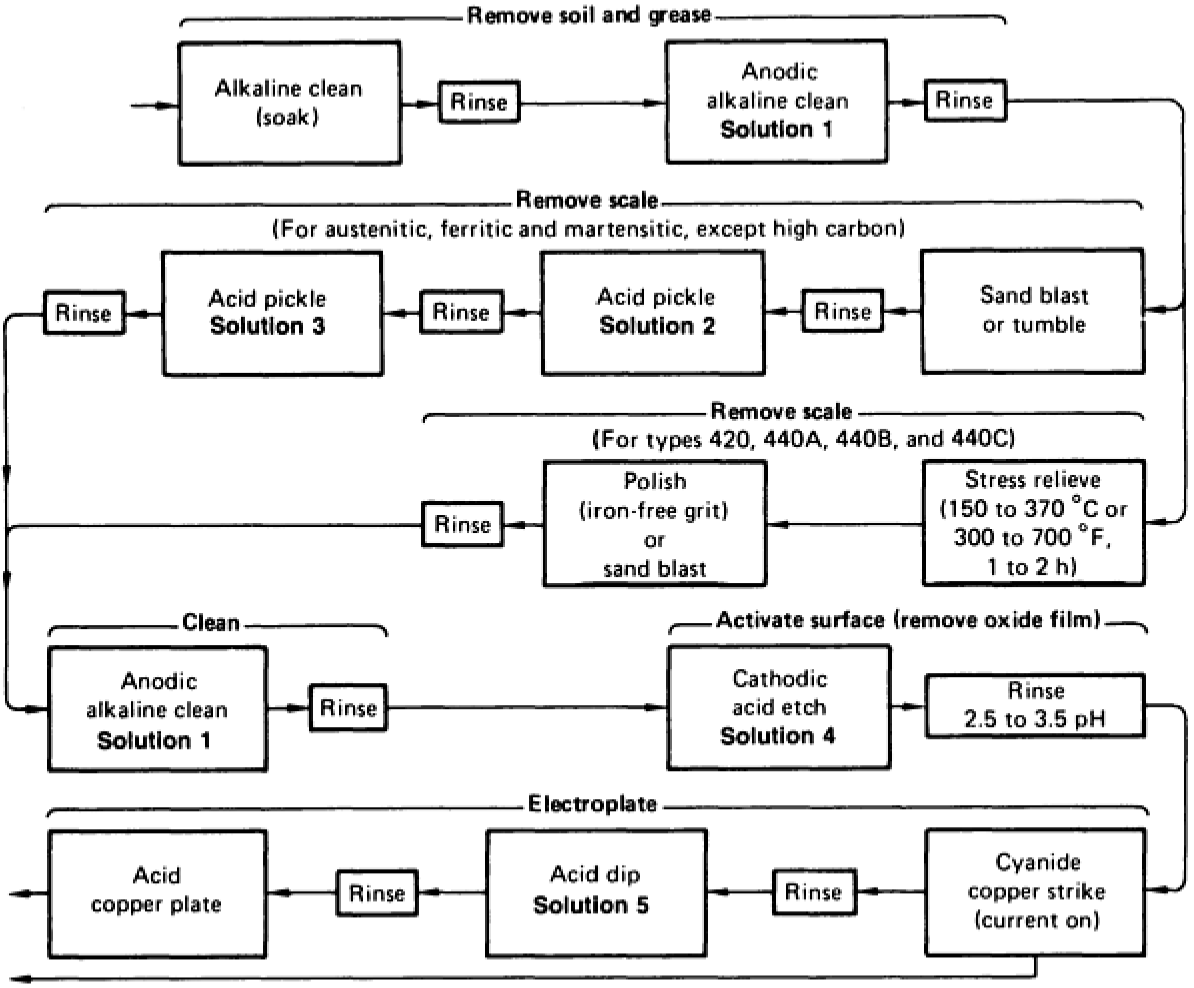
- Color matching
- Lubrication during cold heading, spring coiling, or wire drawing
- Reduction of scaling at high temperature
- Improvement of wettability or of conductance of heat or electricity
- Prevention of galling
- Decorative uses in such applications as jewelry
- Prevention of superficial rusting

Detailed information on plating bath compositions, control of bath composition, bath temperature, plating equipment, process limitations or advantages, and applications for electrodeposits can be found in the articles contained in the Section on "Plating and Electroplating" in this Volume.

Although a stainless steel surface may be clean and scale-free, an adherent electrodeposit cannot be obtained until the surface is activated for removal of its normally ever-present oxide film. Activation, which is performed immediately before plating, may be accomplished by cathodic treatments, immersion treatments, or simultaneous activation-plating treatments. These treatments, together with other procedures necessary for preparing stainless steel for electroplating, are fully described in ASTM B 254 (Ref 7).

Figure 4 summarizes some of the data from ASTM B 254. The same cleaning procedures would be appropriate before electrodeposition of other metals. When preparing stainless steel for electroplating, the following should be considered:

- *Electrocleaning:* When bright plating is desired, the alkalinity, current density, and temperature of the cleaning bath should be kept as low as possible, especially for the high-chromium alloys. To minimize the severity of electrocleaning when a bright finish is desired, a short electropolishing treatment may be used in lieu of electrocleaning, provided that the preliminary cleaning is adequate.
- *Acid pickling:* Freshly prepared pickling baths should be activated by dissolving some iron in them before using the bath; otherwise, the rate of pickling is slow until the bath has dissolved some iron from the steel being treated.
- *Activating:* The activation step is the most important in surface preparation of stainless steel for electroplating. If the simultaneous activation-plating treatment is used, where the anodes are nickel, the nickel content of the solution gradually increases because of the low cathode efficiency. This can be compensated for by removing a portion of the solution and replenishing with HCl. The activation-plating treatment is usually preferred for stainless steel parts that are to be copper plated.
- *Plating:* After activating and rinsing, the work should be entered directly into the electrolyte. When possible, the rinse water should be slightly acid (2.5 to 3.5 pH); the required acidity is usually provided by the dragout of acid from the activation treatment. Stainless steel has much lower electrical conductivity than most other metals, and thus adequate attention should be paid to racking when introducing work into copper electrolyte, to ensure an adequate number of contacts to obtain complete coverage in minimum time.



Solution no.	Type of solution	Composition of solution	Operating temperature		Cycle time, min
			°C	°F	
1	Anodic alkaline cleaner[(a)]	Alkali, as low as possible	[(b)]	[(b)]	[(b)]
2	Acid pickle	H_2SO_4, 8-11%	65-70	150-70	10-45
3	Acid pickle	HNO_3, 6-10 vol%; HF, 1.5 vol%	Room temperature	Room temperature	10-30
4	Cathodic acid etch[(c)]	H_2SO_4, 5-15 vol%	Room temperature	Room temperature	1-5[(d)]

(a) Current density, as low as possible.

(b) As low as possible.

(c) Current density, 54 A/m^2 (5 A/ft^2).

(d) After subsequent rinse, place parts into copper electrolyte while parts are still wet

Fig. 4 Electroplating copper on stainless steels

Reference cited in this section

7. "Standard Practice for Preparation of and Electroplating on Stainless Steel," B 254, *Annual Book of ASTM Standards,* ASTM, 1988

Other Coating Processes (Ref 2)

Painting. In the painting of stainless steel surfaces, the main requirement to be satisfied is that of providing a good permanent bond. Stainless steel surfaces are dense, hard, and smooth, particularly when in the cold-rolled or polished condition. For that reason, it is usually advisable to roughen them by means of strong pickling or sandblasting. The latter is advantageous because it can be readily confined to limited areas by masking.

In the transportation industry, acid etching is usually favored as a preliminary step in painting stainless steels. The etchants are solutions of either HCl or HF:

Solution 1

- 25 parts water by volume
- 75 parts HCl by volume
- 5 parts HNO_3 by volume
- 20 wt% $FeCl_3$

Solution 2

- 10 to 20 vol% HNO_3
- 3 to 5 vol% HF
- Remainder water

The stainless steel has either a No. 2D or 2B finish. Paint companies are best qualified to suggest paint types and procedures for prime and finish coats.

Cleanliness is a key element in painting stainless steels. The surface must be clean, and it is good practice to paint only in a clean, dust-free atmosphere. Use thin coats and allow plenty of time to dry between coats.

Sandblasting is best accomplished with clean, hard sand of relatively small grit size driven by an air blast that is entirely free of compressor oil. (Glass beads are sometimes used.) Thin-gage material should be backed up to avoid distortion. Surfaces should be dry and completely free of grease, oil, or any other foreign material before applying the ground coat. More detailed information on the selection and application of various paint types can be found in the article "Painting" in this Volume.

Surface Blackening. Stainless steel surfaces can be readily blackened by immersion in a molten salt bath of sodium dichromate. This practice, which is not complicated to set up and operate, is widely used by the automotive industry to blacken stainless steel parts, such as windshield wipers, and it is used by manufacturers of stainless steel solar collector panels.

The process applies a very thin, smooth black oxide film to the surface of all stainless steel types. The film is normally dull black in color, but it can be brightened by the application of oils or waxes. The film shows no tendency to age or lose color in service. It is ductile, will not chip or peel, and is resistant to heating to the normal scaling temperature of the stainless steel. A blackened stainless steel can be deformed moderately without harm, and the film exhibits good resistance to abrasion.

The salt bath operates at approximately 400 °C (750 °F), and dip time varies from 5 to 30 min, followed by a wash-water rinse. Solar panels achieve an ideal blackening in 5 min, while auto trim parts require about 30 min to obtain a deeper black color.

Coloring. A proprietary process used for coloring stainless steels involves immersing the material in a hot chromic-sulfuric acid solution, followed by a cathodic hardening treatment in another acidic solution. The reaction of the base material with the hot acid produces a transparent film which in itself is basically colorless, but which shows colors through the phenomenon of light interference. Colors produced, in normal time sequence, are bronze, blue, gold, red, purple, and green, and within this range a wide variety of shades are possible. A black finish is also available. Appearance is also dependent on the nature of the starting surface: matte and satin surfaces produce matte colors; polished surfaces exhibit a high degree of metallic luster. The process is being used throughout the world for architectural applications, furniture, bathtubs, consumer products, and automotive trim.

Different effects can be achieved, for example, by alternating bright polished and satin finished sheets, by selective polishing prior to coloring, and by using cold-embossed colored stainless steel. Masking, screen printing, and photo-resist techniques can be employed to achieve patterned effects and for the reproduction of photographic images. Colored stainless steel can be subjected to considerable deformation without detriment. It can, for example, be drawn, bent through quite sharp angles, and embossed without any deleterious effects or reduction of color intensity. Corrosion resistance of colored stainless is at least as good as that of the untreated material, and exposure tests extending over a number of years have shown no deterioration of color.

Terne coatings can be applied to stainless steels by hot dipping sheet in a lead-tin alloy that typically consists of 80% Pb and 20% Sn. Terne coatings were used as early as the 11th century on church roofs in western Europe. Terne-coated stainless steel, however, was introduced only in the 1960s. Since then it has grown in popularity, particularly for architectural (roofing) applications, because of its strength, long life, and attractive patina acquired with age.

The stainless steel that forms the core is usually S30400 or S31600. As well as providing corrosion resistance, the stainless steel offers superior strength and ductility compared to other roofing materials and, because of its high-temperature strength, provides enhanced structural integrity and safety in case of fire.

The terne-coated stainless steel sheet (minimum of 20 μm of coating per side) weathers in one to two years to a uniform gray, the precise shade depending on the sulfur content of the atmosphere. The result is a material with an aged appearance that can blend in with existing roofing or give a new building a distinctive appearance. Because terne coatings are anodic to stainless steel, corrosion resistance can be further improved.

Thermal Spraying. Wear-resistant coatings and thermal barrier coating systems have been applied to stainless steel substrates by plasma spraying and high-velocity oxyfuel (HVOF) thermal spray processes. Most of the work has centered around the use of stainless steels, such as S17400 (17-4 PH), in diesel engines. Plasma sprayed thermal barrier coatings on 17-4 PH piston rings include composite zirconia (ZrO_2)/NiCrAlY coatings (Ref 8). Wear resistant coatings include Cr_3C_2-20% NiCr cermets deposited by the HVOF process and plasma sprayed chromium oxide-based coatings (Ref 9).

References cited in this section

2. *Finishes for Stainless Steel,* Publ. 201-683-14M-EB, American Iron and Steel Institute, 1983

8. R.C. Brink, Material Property Evaluation of Thick Thermal Barrier Coating Systems, *Trans. ASME, Journal*

of Engineering for Gas Turbines and Power, Vol 111, July 1989, p 570-577
9. M.G.S. Naylor, "Development of Wear-Resistant Ceramic Coatings for Diesel Engine Components, Volume 1: Coating Development and Tribological Testing," ORNL/Sub/87-SA581/1, Oak Ridge National Laboratory, June 1992

Surface Modification

Surface modification is the alteration of surface composition or structure by the use of energy or particle beams. Elements may be added to influence the surface characteristics of the substrate by the formation of alloys, metastable alloys or phases, or amorphous layers. Surface-modified layers are distinguished from conversion or coating layers by their greater similarity to metallurgical alloying versus chemically reacted, adhered, or physically bonded layers.

Ion implantation is one of a number of surface modification processes that is emerging as an economical and viable process for improving the near-surface tribological properties of engineering components. In many engineering situations, material selection is often based on a compromise of bulk mechanical properties and near-surface tribological properties, with neither at their optimum values. As a result, there is considerable interest in fabrication processes, such as ion implantation, that make it possible to retain the bulk properties of a given compound yet still achieve desirable tribological properties in near-surface regions.

Ion implantation is a process by which virtually any element in the periodic chart can be injected into near-surface regions of any solid using a beam of high-velocity ions with energies typically ranging from 10 keV up to several MeV. As the ions slow down in the material, they are distributed at depths ranging from a few nanometers to several micrometers, depending on the particle energy, angle of incidence, and substrate composition. Depending on the ion type, mass, energy, dose, deposition temperature, and substrate composition, the chemical, electrical, thermal, microstructural, and crystallographic properties of near-surface regions can be significantly altered to improve the friction and wear performance of the component.

Examples of end-use applications of ion implanted stainless steels are bearing rings and ball bearings made from S44004 (type 440C) that are used in the Space Shuttle (Ref 10). The corrosive wear performance of the bearing rings was improved by implanting chromium plus nitrogen (CrN) ions. Significantly lower friction and wear rates were achieved in the ball bearings via ion implantation with titanium plus carbon (TiC) ions and titanium ions alone.

Laser surface processing includes laser transformation hardening, laser melting, laser alloying, laser cladding, and laser melt/particle injection. Of these five method, laser alloying and laser melt/particle injection have been carried out the most on stainless steels. A review of laser surface processing can be found in Ref 11.

Laser Alloying. A technique of localized alloy formation is laser surface melting with the simultaneous, controlled addition of alloying elements in powder form. These alloying elements diffuse rapidly into the melt pool, and the desired depth of alloying can be obtained in a short period of time. By this means, a desired alloy chemistry and microstructure can be generated on the sample surface; the degree of microstructural refinement will depend on the solidification rate.

Laser surface alloying was performed to incorporate molybdenum in type 304 stainless steel (Ref 12). The 304-3Mo material was similar in pitting resistance to type 316 stainless steel. The 304-9Mo material was superior to type 316 stainless steel and showed no pitting up to oxygen evolution potentials. Table 12 shows some of the results for the 304-Mo materials.

Table 12 Effect of laser surface alloying with molybdenum on pitting potentials of austenitic stainless steels in 0.1 *M* NaCl

Sample	Composition, %			Pitting potential (E_{pit}), (V vs SCE)
	Cr	Ni	Mo	
Type 304	18-20	8-10	0	0.300

Type 316	16-18	10-14	2-3	0.550
304-3Mo	18.9	9.1	3.7	0.500
304-9Mo	19.2	11.7	9.6	Did not pit

Laser melt/particle injection produces an *in situ*, metal-matrix/particulate composite surface layer by mixing, but not melting, the second phase with the substrate. The particulate material is injected with sufficient velocity as a spray into the melt pool formed by the laser beam. If the second phase is hard, such as a carbide, the injected layer can be made to resist wear. Reference 13 describes the processing and properties of a type 304 stainless steel workpiece that was injected with titanium carbide.

References cited in this section

10. G.R. Fenske, Ion Implantation, *Friction, Lubrication, and Wear Technology,* Vol 18, *ASM Handbook,* ASM International, 1992, p 850-860
11. K.P. Cooper, Laser Surface Processing, *Friction, Lubrication, and Wear Technology,* Vol 18, *ASM Handbook,* ASM International, 1992, p 861-872
12. E. McCafferty and P.G. Moore, *J. Electrochem. Soc.,* Vol 133 (No. 6), 1986, p 1090-1096
13. J.D. Ayers and D.S. Gnanamuthu, Hardening of Metal Surfaces by Laser Processing, *Welding, Brazing, and Soldering,* Vol 6, 9th ed., *Metals Handbook,* American Society for Metals, 1983, p 793-803

Surface Hardening

In certain applications, surface hardening is performed to improve the resistance of stainless steel alloys to galling and wear through the formation of hard dispersions. The more soft, tough interior of the alloy remains unaffected, and thus provides impact resistance. The process encompasses a variety of techniques, including nitriding, carburizing, boriding, and flame hardening.

Gas Nitriding

Gas nitriding is a case-hardening process whereby nitrogen is introduced into the surface of an alloy by holding the metal at a suitable temperature in contact with a nitrogenous gas, usually ammonia. Quenching is not required for the production of a hard case. The nitriding temperature for all steels is between 495 and 565 °C (925 and 1050 °F).

Because of the absence of a quenching requirement, with attendant volume changes, and the comparatively low temperatures employed in this process, nitriding produces less distortion and deformation than either carburizing or conventional hardening. Some growth occurs as a result of nitriding, but volumetric changes are relatively small. Although at suitable temperatures all steels are capable of forming iron nitrides in the presence of nascent nitrogen, nitriding results are more favorable in those steels that contain one or more of the major nitride-forming alloying elements. Aluminum is the strongest nitride former, but chromium can approximate the results obtainable with aluminum if the chromium content is high enough.

Because of their chromium content, all stainless steels can be nitrided to some degree. Although nitriding adversely affects corrosion resistance, it increases surface hardness and provides a lower coefficient of friction, thus improving abrasion resistance.

Austenitic and Ferritic Alloys. Austenitic stainless steels of the 300 series are the most difficult to nitride; nevertheless, types 301, 302, 303, 304, 308, 309, 316, 321, and 347 have been successfully nitrided. These nonmagnetic alloys cannot be hardened by heat treating; consequently, core material remains relatively soft, and the nitrided surface is limited as to the loads it can support. This is equally true of the nonhardenable ferritic stainless steels. Alloys in this group

that have been satisfactorily nitrided include types 430 and 446. With proper prior treatment, these alloys are somewhat easier to nitride than the 300-series alloys.

Hardenable Alloys. The hardenable martensitic alloys are capable of providing high core strength to support the nitrided case. Hardening, followed by tempering at a temperature that is at least 15 °C (25 °F) higher than the nitriding temperature, should precede the nitriding operation. Precipitation-hardening alloys, such as 17-4 PH, 17-7 PH, and A-286, also have been successfully nitrided.

Prior Condition. Before being gas nitrided, 300-series steels and nonhardenable ferritic steels should be annealed and relieved of machining stresses. The normal annealing treatments generally employed to obtain maximum corrosion resistance are usually adequate. Microstructure should be as nearly uniform as possible. Observance of these prior conditions will prevent flaking or blistering of the nitrided case. Martensitic steels should be in the quenched and tempered condition.

A special pretreatment for 410 stainless steel is hardening from a lower than normal temperature. This results in a very uniform nitrided case with reduced internal stresses. Cracking or spalling of the case is avoided; formation of brittle grain-boundary carbonitrides is suppressed. Austenitizing at 860 °C (1580 °F), followed by tempering at 595 °C (1100 °F), uniformly distributes carbides and provides low residual stress. Case growth is accommodated by a hardness of about 25 HRC.

Surface Preparation. The nitriding of stainless steels requires certain surface preparations that are not required for nitriding low-alloy steels. Primarily, the film of chromium oxide that protects stainless alloys from oxidation and corrosion must be removed. This can be accomplished by dry honing, wet blasting, pickling, chemical reduction in a reducing atmosphere, submersion in molten salts, or one of several proprietary processes. Surface treatment must precede placement of the parts in the nitriding furnace. If there is any doubt of the complete and uniform depassivation of the surface, further reduction of the oxide may be accomplished in the furnace by means of a reducing hydrogen atmosphere or halogen-based proprietary agents. Of course, hydrogen must be dry (free of water and oxygen).

Before being nitrided, all stainless parts must be perfectly clean and free of embedded foreign particles. After depassivation, care should be exercised to avoid contaminating stainless surfaces with fingerprints. Sharp corners should be replaced with radii of not less than 1.6 mm ($\frac{1}{16}$ in.).

Nitriding Cycles. In general, stainless steels are nitrided in single-stage cycles at temperatures from about 495 to 595 °C (925 to 1100 °F) for periods ranging from 20 to 48 h, depending on the depth of case required. Dissociation rates for the single-stage cycle range from 20 to 35%; a two-stage cycle using 15 to 30% in the first phase and 35 to 45% in the second phase is also used. Thus, except for the prior depassivation of the metal surface, the nitriding of stainless steels is similar to the single-stage nitriding of low-alloy steels.

Nitriding Results. Hardness gradients are given in Fig. 5 for types 302, 321, 430, and 446. These data are based on a 48-h nitriding cycle at 525 °C (975 °F), preceded by suitable annealing treatments. A general comparison of the nitriding characteristics of series 300 and 400 steels is presented in Fig. 6; the comparison reflects the superior results that are obtained with series 400 steels, as well as the effects of nitriding temperature on case depth. Data are plotted for single-stage nitriding at temperatures of 525 and 550 °C (975 and 1025 °F). For steels of both series, greater case depths were obtained at the higher nitriding temperature.

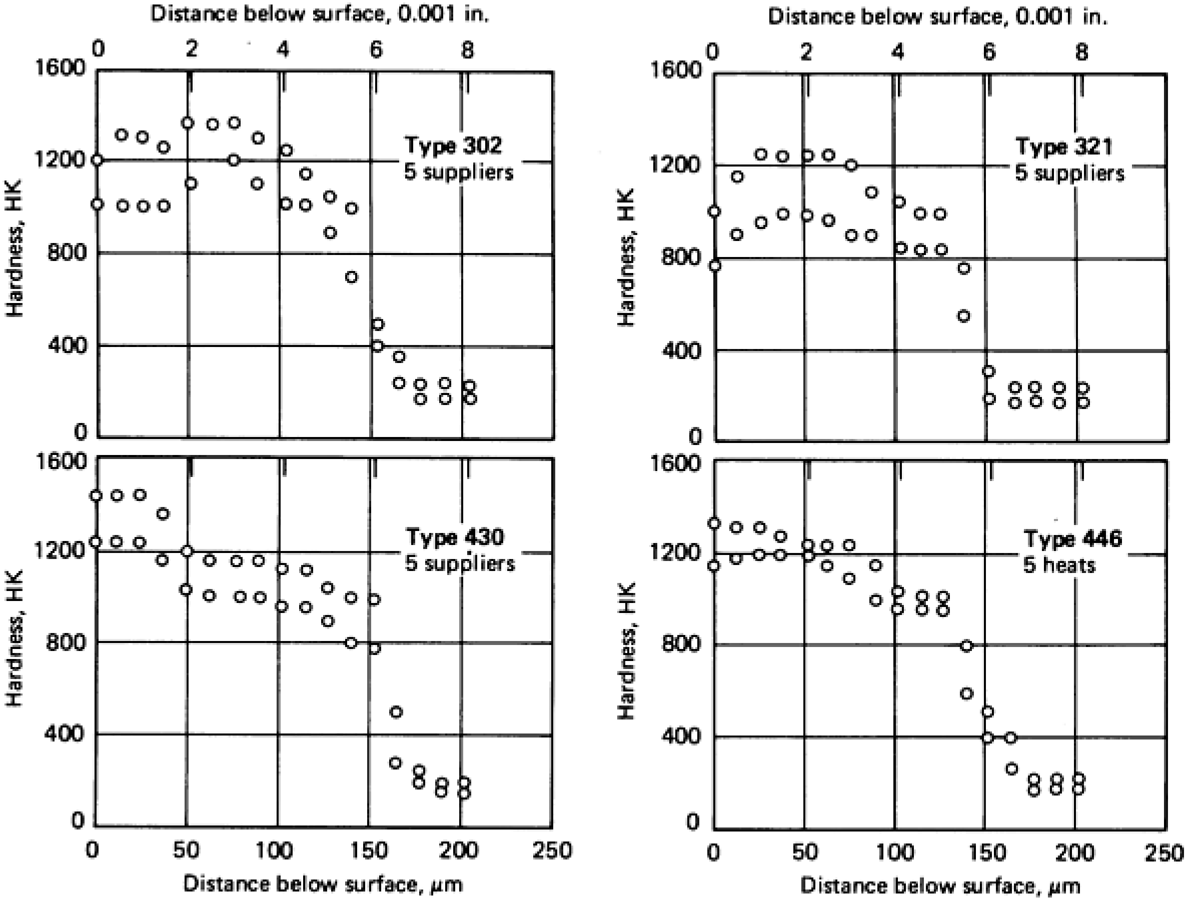


Fig. 5 Hardness range as a function of case depth for four stainless steels that were annealed prior to nitriding. Annealing temperature: types 302 and 321, 1065 °C (1950 °F); type 430, 980 °C (1800 °F); and type 446, 900 °C (1650 °F)

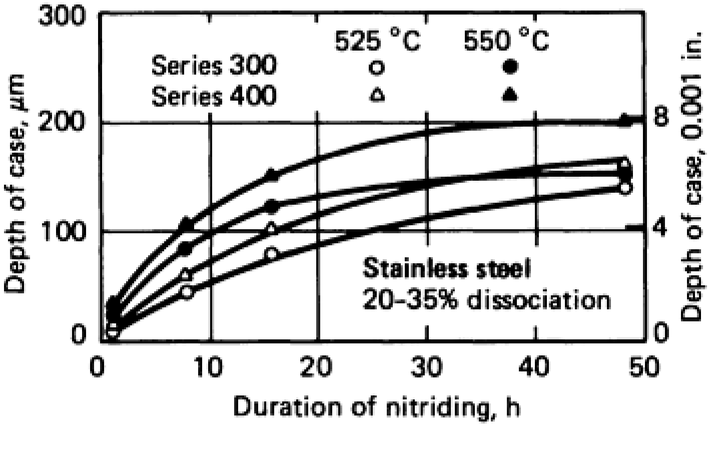


Fig. 6 Comparison of the nitriding characteristics of series 300 and 400 stainless steels, single-stage nitrided at 525 and 550 °C (975 and 1025 °F)

Applications. Although nitriding increases the surface hardness and wear resistance of stainless steels, it decreases general corrosion resistance by combining surface chromium with nitrogen to form chromium nitride. Consequently, nitriding is not recommended for applications in which the corrosion resistance of stainless steel is of major importance. For example, a hot-air valve made of cast type 347 and used in the cabin-heating system of a jet airplane was nitrided to

improve its resistance to wear by the abrading action of a sliding butterfly When the valve remained in the closed position for an extended period, the corrosive effects of salt air froze the valve into position so that it could not be opened.

In contrast, a manufacturer of steam-turbine power-generating equipment has successfully used nitriding to increase the wear resistance of types 422 and 410 stainless steel valve stems and bushings that operate in a high-temperature steam atmosphere. Large quantities of these parts have operated for 20 years of more without difficulty. In a few instances, a light-blue oxide film formed on the valve stem diameter, causing it to "grow" and thus reduce the clearance between stem and bushing; the growth condition, however, was not accompanied by corrosive attack.

Nitrided stainless steel is also being used in the food-processing industry. In one application, nitrided type 321 was used to replace type 302 for a motor shaft used in the aeration of orange juice. Because the unhardened 302 shaft wore at the rubber-sealed junction of the motor and the juice, leaks developed within 3 days. The nitrided 321 shaft ran for 27 days before wear at the seal resulted in leakage. In machinery used in the preparation of dog foods, nitrided type 420 gears have replaced gears made of an unhardened stainless alloy and have exhibited a considerable increase in life.

Modern synthetic fibers, several of which are highly abrasive, have increased the wear of textile machinery. Mechanical parts in textile machines are subjected to high humidity, absence of lubrication, high-speed movements with repeated cycling, and the abrasive action of fibers traveling at high speeds. A shear blade made of hardened (62 to 64 HRC) 1095 steel experienced a normal life of about one million cuts (4 weeks of service) in cutting synthetic fibers at the rate of 90 cuts per minute. In contrast, a nitrided type 410 blade with 0.04 mm (0.0015 in.) case depth showed less wear after completion of five million cuts.

With nitrided stainless steels, the case almost always has lower corrosion resistance than the base material; nevertheless, the corrosion resistance of the case can be adequate for certain applications. For example, nitrided types 302 and 410 stainless steel resist attack from warp conditioner and size in the textile industry but do not resist attack from the acetic acid used in dyeing liquors.

Nitrided stainless steel is not resistant to mineral acids and is subject to rapid corrosion when exposed to halogen compounds. However, a nitrided type 302 piston lasted for more than 5 years in a liquid-ammonia pump; it replaced a piston made of an unnitrided 300-series alloy that lasted approximately 6 months. Nitrided 17-4 PH impellers have performed satisfactorily and without corrosion in various types of hydraulic pumps.

Plasma (Ion) Nitriding and Liquid Nitriding

Plasma, or ion, nitriding is a method of surface hardening that uses glow discharge technology to introduce nascent (elemental) nitrogen to the surface of a metal part for subsequent diffusion into the material. In a vacuum, high-voltage electrical energy is used to form a plasma, through which nitrogen ions are accelerated to impinge on the workpiece. This ion bombardment heats the workpiece, cleans the surface, and provides active nitrogen. Ion nitriding provides better control of case chemistry and uniformity and has other advantages, such as lower part distortion than conventional gas nitriding.

The diffusion zone of a nitrided case can best be described as the original core microstructure with some solid solution and precipitation strengthening. In iron-base materials, the nitrogen exists as single atoms in solid solution at lattice sites or interstitial positions until the limit of nitrogen solubility (!0.4 wt% N) in iron is exceeded. This area of solid-solution strengthening is only slightly harder than the core. The depth of the diffusion zone depends on the nitrogen concentration gradient, time at a given temperature, and the chemistry of the workpiece.

As the nitrogen concentration increases toward the surface, very fine, coherent precipitates are formed when the solubility limit of nitrogen is exceeded. The precipitates can exist both in the grain boundaries and within the lattice structure of the grains themselves. These precipitates, in the form of nitrides, distort the lattice and pin crystal dislocations and thereby substantially increase the hardness of the material. Hardness profiles for various ion-nitrided materials, including stainless steels, are shown in Fig. 7.

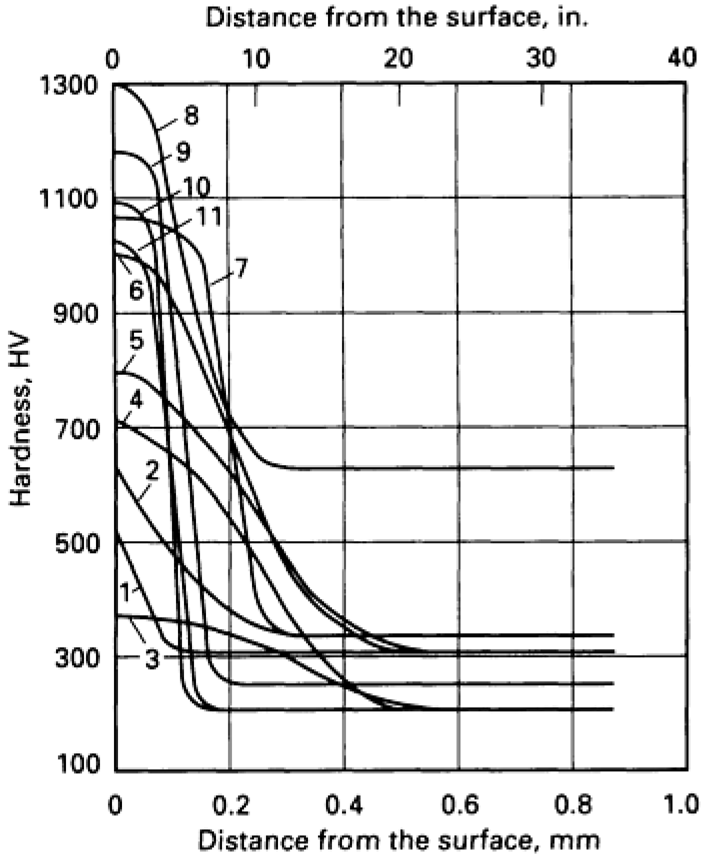


Fig. 7 Hardness profiles for various ion-nitrided materials. 1, gray cast iron; 2, ductile cast iron; 3, AISI 1040; 4, carburizing steel; 5, low-alloy steel; 6, nitriding steel; 7, 5% Cr hot-work steel; 8, cold-worked die steel; 9, ferritic stainless steel; 10, AISI 420 stainless steel; 11, 18-8 stainless steel

In most ferrous alloys, the diffusion zone formed by nitriding cannot be seen in a metallograph because the coherent precipitates generally are not large enough to resolve. In stainless steels, however, the chromium level is high enough for extensive nitride formation, which can be seen in etched cross section (Fig. 8).

Fig. 8 Observable diffusion zone on the unetched (white) portion of an ion-nitrided 416 stainless steel. Nital etched. 500×

Ion nitriding has a strong advantage over competing processes in the case of stainless steels, particularly austenitic or 300-series materials. The chromium oxide passive layer on the surface represents a barrier to nitriding and must be removed prior to processing. When gas nitriding stainless steels, this passive layer is removed by wet blasting, pickling, or chemical reduction. With ion nitriding, however, this layer can be removed by sputtering in hydrogen in the vessel itself just before introduction of the process gas. With most materials, even the sputtering that occurs naturally during the actual nitriding process is enough to yield good nitriding results.

Liquid nitriding is performed in a molten, nitrogen-bearing, fused-salt bath containing either cyanides or cyanates. Unlike liquid carburizing and cyaniding, which employ baths of similar composition, liquid nitriding is a subcritical (that is, below the critical transformation temperature) case-hardening process. Thus, processing of finished parts is possible because dimensional stability can be maintained. Also, liquid nitriding adds more nitrogen and less carbon to ferrous materials than that obtained through higher-temperature diffusion treatments.

Cyanide-free liquid nitriding salt compositions have also been introduced. However, in the active bath, a small amount of cyanide, generally up to 5%, is produced as part of the reaction. This is a relatively low concentration, and these compositions have gained widespread acceptance within the heat treating industry because they contribute substantially to the alleviation of a potential source of pollution.

The wear and gall resistance of stainless steels can be improved by aerated liquid nitriding, a proprietary process (U.S. Patent 3,022,204) in which measured amounts of air are pumped through the molten bath. Immersion in the molten salt at 570 °C (1060 °F) develops a physical compound zone in stainless steels that, depending on treatment time, varies between 0.005 and 0.025 mm (0.0002 and 0.001 in.). Although the hardness of this wear-resistant surface measures 70 to 72 HRC, the surface is tough and ductile (Ref 14).

Liquid nitriding treatments result in some loss in corrosion resistance, because the formation of nitrides and carbides depletes adjacent matrix areas. Corrosion data based on weight loss indicate that liquid-nitrided stainless steels lose approximately 50% of their corrosion resistance; however, these materials remain substantially superior to untreated carbon and low-alloy steels (Ref 14).

Liquid nitriding is one of the few heat treatments that can produce a wear-resistant hard surface, improve fatigue properties, and retain to a significant extent the good corrosion resistance of stainless steels in a single operation. In addition, subsequent quenching is not required, allowing flexibility in design and final machining (Ref 14).

Carburizing, Boriding, and Flame Hardening

Carburizing is a case-hardening process in which carbon is dissolved in the surface layers of a steel part at a temperature sufficient to render the material austenitic, followed by quenching and tempering to form a martensitic microstructure. The resulting gradient in carbon content below the surface of the part causes a gradient in hardness, producing a strong, wear-resistant surface layer. In gas carburizing, commercially the most important variant of carburizing, the source of carbon is a carbon-rich furnace atmosphere produced either from gaseous hydrocarbons (e.g., methane, propane, or butane) or from vaporized hydrocarbon liquids.

Stainless steels can be carburized to improve surface hardness and resistance to galling. The availability of substantial amounts of chromium promotes the rapid formation of chromium carbides at the surface, and surface hardness values of 700 to 750 HV have been measured. Precipitation-hardenable stainless steels can be gas carburized to improve resistance to galling. Treatment temperatures up to 1010 °C (1850 °F) may be required (Ref 14).

In austenitic grades, much of the chromium carbide formed migrates and is precipitated in the grain boundaries, promoting susceptibility to intergranular corrosion. Carbide distribution tends to be less segregated in the martensitic grades, but they are also subject to localized corrosion and particularly SCC (Ref 14).

Carburizing is not generally recommended for stainless steels because of the reduction in corrosion resistance brought on by chromium precipitation. Since the precipitated chromium tends to exist at the expense of adjacent areas, localized galvanic cells may develop. In the carburizing process, surface physical properties are obtained at the expense of surface chemical properties (Ref 14).

Because of these disadvantages, most of the carburizing of stainless steel is "accidental" and can be traced to surface contamination. Carbonaceous compounds such as charcoal, coke, oil, and grease can promote carburization under the

proper conditions. Molten salt baths that contain cyanide to prevent decarburization may also become carburizing in contact with stainless steels (Ref 14).

Boriding, or boronizing, is a thermochemical surface hardening process that involves heating well-cleaned material in the range of 700 to 1000 °C (1300 to 1830 °F), preferably for 1 to 12 h, in contact with a boronaceous solid powder (boronizing compound), paste, liquid, or gaseous medium.

The resultant diffusion zone is known for its low coefficient of friction and high surface hardness, which may reach values of 1800 HV. Case depths of 0.05 mm (0.002 in.) can be achieved with 1 to 5 h treating time (Ref 14). Figure 9 shows the influence of steel composition on abrasive wear resistance. Boriding can considerably enhance the corrosion-erosion resistance of ferrous materials in nonoxidizing dilute acids (Fig. 10) and alkali media, and is increasingly used to this advantage in many industrial applications (Ref 17).

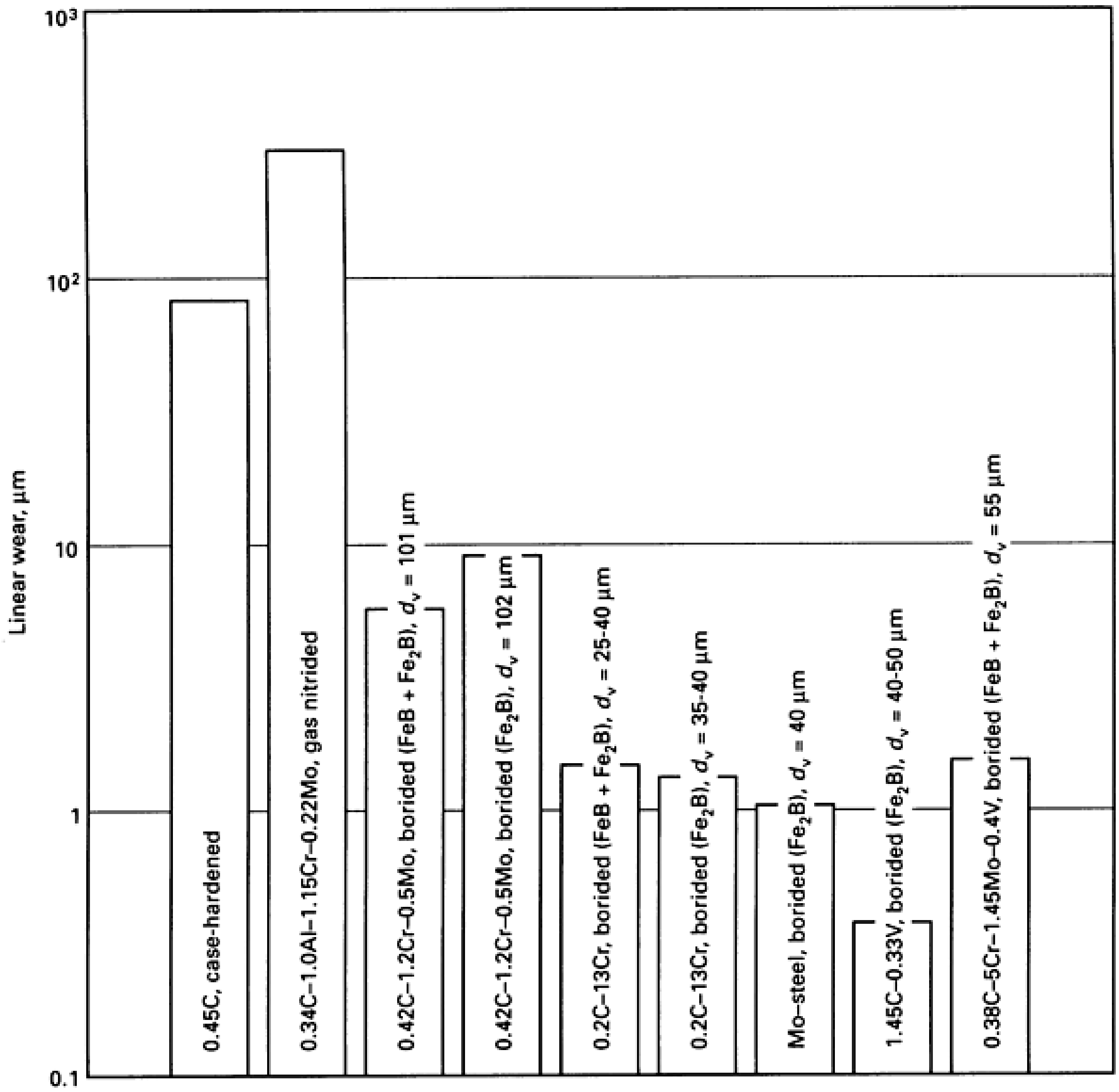
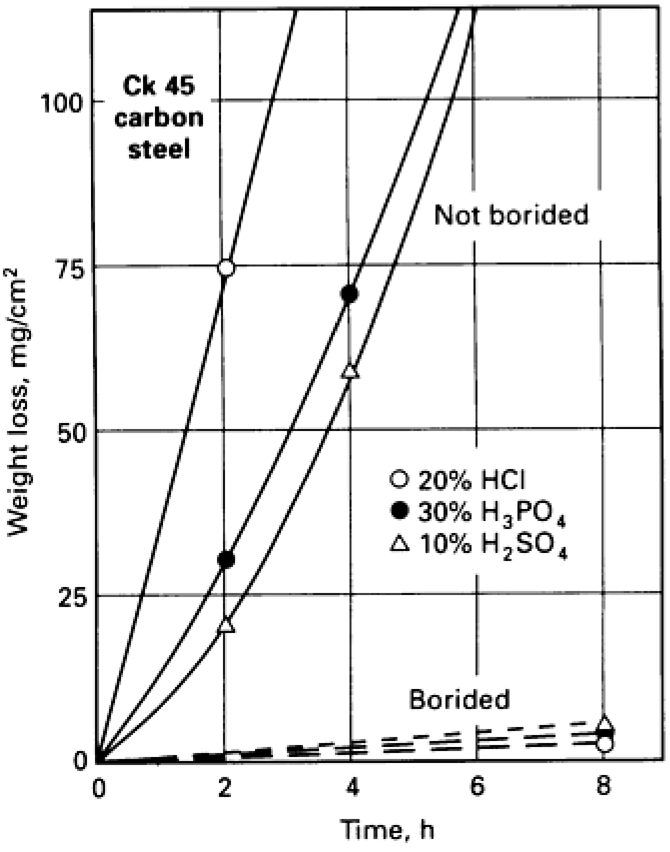
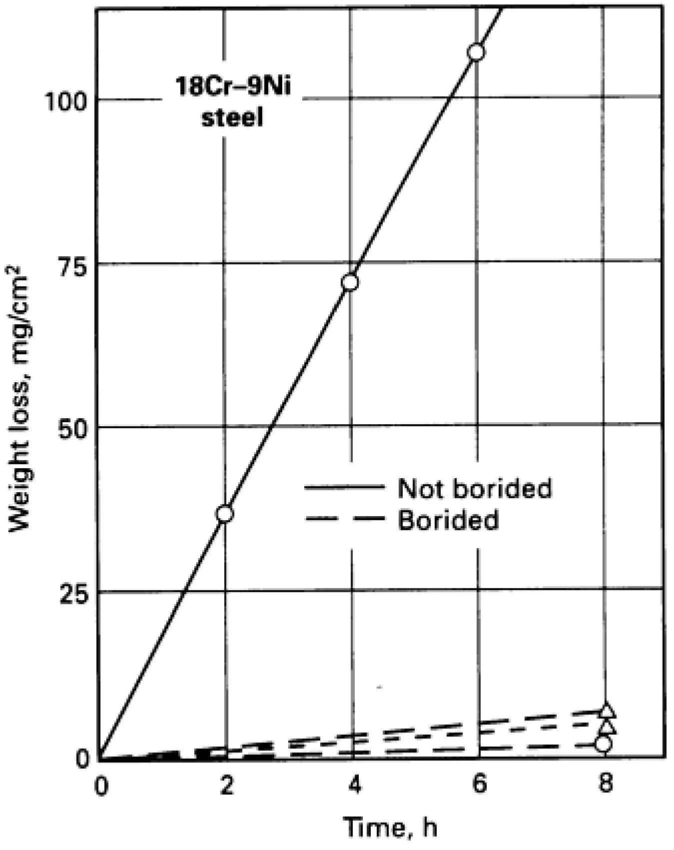


Fig. 9 Effect of steel composition (nominal values in wt%) on wear resistance under abrasive wear (d_v = thickness of the boride layer). Test conditions: DP-U grinding tester, SiC paper 220, testing time 6 min. Source: Ref 15, 16


Ck 45
carbon
steel
Not borided
Borided
○ 20% HCl
● 30% H3PO4
△ 10% H2SO4
Weight loss, mg/cm2
Time, h
0
25
50
75
100
0
2
4
6
8

(a)


18Cr–9Ni
steel
Not borided
Borided
Weight loss, mg/cm2
Time, h
0
25
50
75
100
0
2
4
6
8

(b)

Fig. 10 Corroding effect of mineral acids on boronized and nonboronized (a) 0.45% C (Ck 45) steel and (b) 18Cr-9Ni (X10CrNiTi189) steel at 56 °C (130 °F). Source: Ref 17, 18

Chromium considerably modifies the structure and properties of iron borides. As the chromium content in the base material increases, progressive improvements in the following effects are observed: formation of boron-rich reaction products, decrease in boride depth, and flattening or smoothening of the coating/substrate interface (Ref 19). A reduction of boride thickness has also been noticed in ternary Fe-12Cr-C steels with increasing carbon content (Ref 20).

Flame hardening is a heat treating process in which a thin surface shell of a steel part is heated rapidly to a temperature above the critical point of the steel. After the grain structure of the shell has become austenitic (austenitized), the part is quickly quenched, transforming the austenite directly to martensite while leaving the core of the part in its original state.

Flame hardening employs direct impingement of a high-temperature flame or high-velocity combustion product gases. The part is then cooled at a rate that will produce the desired levels of hardness and other properties. The high-temperature flame is obtained by combustion of a mixture of fuel gas with oxygen or air; flame heads are used for burning the mixture. Depths of hardening from about 0.8 to 6.4 mm ($\frac{1}{32}$ to $\frac{1}{4}$ in.) or more can be obtained, depending on the fuels used, the design of the flame head, the duration of heating, the hardenability of the work material, and the quenching medium and method of quenching used.

Hardening by flame differs from true case hardening because the hardenability necessary to attain high levels of hardness is already contained in the steel, and hardening is obtained by localized heating. Although flame hardening is mainly used to develop high levels of hardness for wear resistance, the process also improves bending and torsional strength and fatigue life.

Flame hardening can be applied to martensitic stainless steels. The nature of flame hardening, however--especially the relatively high temperature gradients and higher than normal surface temperatures-- may cause the retention of excessive amounts of austenite in many highly alloyed materials, with possible low hardness and transformation to untempered martensite in service, accompanied by brittleness. Typical hardnesses obtained for martensitic stainless steels by flame heating and quenching in air or oil are given in Table 13.

Table 13 Response of martensitic stainless steels to flame hardening

Material	Typical hardness, HRC, as affected by quenchant	
	Air[(a)]	Oil[(b)]
410, 416	41-44	41-44
414, 431	42-47	42-47
420	49-56	49-56

(a) To obtain the hardness results indicated, those areas not directly heated must be kept relatively cool during the heating process.

(b) Thin sections are susceptible to cracking when quenched with oil.

References cited in this section

14. W.G. Wood, "Surface Hardening of Stainless Steels," in *Handbook of Stainless Steels,* D. Peckner and I.M. Bernstein, Ed., McGraw-Hill, 1977
15. R. Chatterjee-Fischer, Chapter 8, in *Surface Modification Technologies,* T.S. Sudarshan, Ed., Marcel Dekker, 1989, p 567-609
16. K.H. Habig and R. Chatterjee-Fischer, *Tribol. Int.,* Vol 14 (No. 4), 1981, p 209-215
17. W.J.G. Fichtl, "Saving Energy and Money by Boronizing," presented at meeting of the Japan Heat Treating Association, Tokyo, 25 Nov 1988; "Boronizing and Its Practical Applications," presented at 33rd Harterei-Kolloquium, Wiesbaden, 5-7 Oct 1977; *Heat Treat. Met.,* 1983, p 79-80
18. W.J.G. Fichtl, *Härt.-Tech. Mitt.,* Vol 29 (No. 2), 1974, p 113-119
19. M. Carbucicchio and G. Sambogna, *Thin Solid Films,* Vol 126, 1985, p 299-305
20. P. Goeurist, R. Fillitt, F. Thevenol, J.H. Driver, and H. Bruyas, *Mater. Sci. Eng.,* Vol 55, 1982, p 9-19

Surface Engineering of Specialty Steels

J.R. Davis, Davis & Associates

Introduction

SPECIALTY STEELS encompass a broad range of ferrous alloys noted for their special processing characteristics (powder metallurgy alloys), corrosion resistance (stainless steels), wear resistance and toughness (tool steels), high strength (maraging steels), or magnetic properties (electrical steels). Each of these material groups--with the exception of stainless steels, which were discussed in the previous article in this Section--will be reviewed below. Additional information on these materials can be found in Volumes 1 and 2 of the *ASM Handbook*.

Ferrous Powder Metallurgy Alloys

Powder metallurgy (P/M) in its simplest form consists of compressing metal powders in a shaped die to produce green compacts. These are then sintered, or diffusion bonded, at elevated temperatures in a furnace with a protective atmosphere. During sintering, the constituents usually do not melt, and the compacts become substantially strengthened by the development of bonds between individual particles.

For a specific metal powder and sintering condition, increased compact density results in improved mechanical properties. The density of sintered compacts may be increased by re-pressing. When re-pressing is performed primarily to increase dimensional accuracy rather than density, it is termed sizing. When re-pressing is intended to change the contour of the surface in contact with the punches, it is termed coining. For example, a sintered blank could be coined so that the surface is indented with small slots or letters and numbers. The re-pressing may be followed by re-sintering, which relieves the stresses due to cold work and may further strengthen the compact. More detailed information on consolidation practices for ferrous P/M parts can be found in Ref 1 and 2.

By pressing and sintering only, parts are produced at 80 to 93% of theoretical density. By re-pressing, with or without sintering, the materials may be further densified to 85 to 96% of theoretical density. High-temperature sintering will also produce parts at these high densities. The density of pressed parts is limited by the size and shape of the compact. The most common P/M materials for structural parts are iron-copper-carbon, iron-nickel-carbon, and iron-carbon. Parts made from these materials respond to heat treatment with a defined hardenability band. Iron parts that are low in carbon and high in density can also be case hardened.

Designation of Ferrous P/M Materials

Ferrous P/M materials are customarily designated by the specifications or standards to which they are made, such as those listed in Table 1. Comparable standards are published by ASTM, SAE, and MPIF (Metal Powder Industries Federation).

Table 1 Compositions of ferrous P/M structural materials

Description	Designation[(a)]			MPIF composition limits and ranges, %[(b)]				
	MPIF	ASTM	SAE	C	Ni	Cu	Fe	Mo
P/M iron	F-0000	B 783	853, Cl 1	0.3 max	. . .	. . .	97.7-100	. . .
P/M steel	F-0005	B 783	853, Cl 2	0.3-0.6	. . .	. . .	97.4-99.7	. . .
P/M steel	F-0008	B 783	853, Cl 3	0.6-1.0	. . .	. . .	97.0-99.1	. . .
P/M copper iron	FC-0200	B 783	. . .	0.3 max	. . .	1.5-3.9	93.8-98.5	. . .
P/M copper steel	FC-0205	B 783	. . .	0.3-0.6	. . .	1.5-3.9	93.5-98.2	. . .
P/M copper steel	FC-0208	B 783	864, Gr 1, Cl 3	0.6-1.0	. . .	1.5-3.9	93.1-97.9	. . .
P/M copper steel	FC-0505	B 783	. . .	0.3-0.6	. . .	4.0-6.0	91.4-95.7	. . .
P/M copper steel	FC-0508	B 783	864, Gr 2, Cl 3	0.6-1.0	. . .	4.0-6.0	91.0-95.4	. . .
P/M copper steel	FC-0808	B 783	864, Gr 3, Cl 3	0.6-1.0	. . .	6.0-11.0	86.0-93.4	. . .
P/M copper steel	. . .	. . .	864, Gr 4, Cl 3	0.6-0.9	. . .	18.0-22.0	75.1 min	. . .
P/M iron-copper	FC-1000	B 783	862	0.3 max	. . .	9.5-10.5	87.2-90.5	. . .
P/M prealloyed steel	FL-4205	B 783	. . .	0.4-0.7	0.35-0.45	. . .	95.9-98.7	0.50-0.85
P/M prealloyed steel	FL-4605	B 783	. . .	0.4-0.7	1.70-2.00	. . .	94.5-97.5	0.40-0.80
P/M iron-nickel	FN-0200	B 783	. . .	0.3 max	1.0-3.0	2.5 max	92.2-99.0	. . .
P/M nickel steel	FN-0205	B 783	. . .	0.3-0.6	1.0-3.0	2.5 max	91.9-98.7	. . .
P/M nickel steel	FN-0208	B 783	. . .	0.6-0.9	1.0-3.0	2.5 max	91.6-98.4	. . .
P/M iron-nickel	FN-0400	B 783	. . .	0.3 max	3.0-5.5	2.0 max	90.2-97.0	. . .

P/M nickel steel	FN-0405	B 783	. . .	0.3-0.6	3.0-5.5	2.0 max	89.9-96.7	. . .
P/M nickel steel	FN-0408	B 783	. . .	0.6-0.9	3.0-5.5	2.0 max	89.6-96.4	. . .
P/M iron-nickel	FN-0700	. . .	. . .	0.3 max	6.0-8.0	2.0 max	87.7-94.0	. . .
P/M nickel steel	FN-0705	. . .	. . .	0.3-0.6	6.0-8.0	2.0 max	87.4-93.7	. . .
P/M nickel steel	FN-0708	. . .	. . .	0.6-0.9	6.0-8.0	2.0 max	87.1-93.4	. . .
P/M infiltrated steel	FX-1000	B 783	. . .	0-0.3	. . .	8.0-14.9	82.8-92.0	. . .
P/M infiltrated steel	FX-1005	B 783	. . .	0.3-0.6	. . .	8.0-14.9	80.5-91.7	. . .
P/M infiltrated steel	FX-1008	B 783	. . .	0.6-1.0	. . .	8.0-14.9	80.1-91.4	. . .
P/M infiltrated steel	FX-2000	B 783	870	0.3 max	. . .	15.0-25.0	70.7-85.0	. . .
P/M infiltrated steel	FX-2005	B 783	. . .	0.3-0.6	. . .	15.0-25.0	70.4-84.7	. . .
P/M infiltrated steel	FX-2008	B 783	872	0.6-1.0	. . .	15.0-25.0	70.0-84.4	. . .

(a) Designations listed are nearest comparable designations; ranges and limits may vary slightly between comparable designations.

(b) MPIF standards require that the total amount of all other elements be less than 2.0%, except in infiltrated steels, for which the total amount of other elements must be less than 4.0%.

The MPIF designations for ferrous P/M materials, described in detail in Ref 3, include a prefix of one or more letters (the first of which is F to indicate an iron-base material), four numerals, and a suffix. The second letter in the prefix identifies the principal alloying element (if one is specified); the percentage of the element is indicated by the first two digits. The third and fourth digits indicate the amount of carbon in the compacted and sintered part; the code designation 00 indicates less than 0.3%, 05 indicates 0.3 to 0.6%, and 08 indicates 0.6 to 0.9%. The suffix is used to indicate the minimum 0.2% yield strength of as-sintered parts and the minimum ultimate tensile strength of heat-treated materials in units of 1000 psi (6.894 MPa). The letters HT designate heat treated.

Commercially produced iron-base powders often contain controlled amounts of alloying elements other than those specified by any of the designations listed in Table 1. Manganese and molybdenum may be added to improve strength and the response to heat treatment. Sulfur may be added to enhance machinability. Additions of 0.45 to 0.80% P can improve the toughness of the part and reduce magnetic hysteresis losses. These powders are usually identified by the trade name of the producer even though the amounts of alloy additions are small enough that the designations listed in Table 1 could be applied to the powders. Commercially produced iron-base powders usually contain very little carbon because carbon lowers compressibility and the amount of carbon in the finished part is readily controlled by the amount of admixed graphite and the composition of the sintering atmosphere.

Deburring P/M Parts (Ref 4)

Although cleaning and deburring generally are considered different operations, they are often accomplished simultaneously. Therefore, much of the discussion on deburring is applicable to the subsequent section of this article on cleaning.

The inherent porosity in P/M parts demands special considerations in all secondary operations. This is also true for cleaning and deburring; the relatively small size and complex shape of the parts also require special procedures and/or precautions that are not required for wrought or cast parts. The P/M parts shown in Fig. 1 are typical of small, intricate parts that frequently present deburring problems.

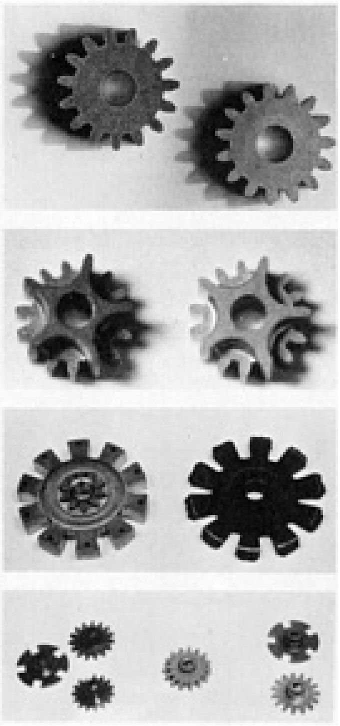


Fig. 1 Typical shapes of P/M parts that present deburring or cleaning difficulties

Deburring Methods. Due to the nature of the P/M process, burrs typically form on the edges and surfaces of P/M parts. In many simple shapes, deburring is almost automatic--that is, burrs are broken off during handling operations. If parts are surface hardened or steam treated, subsequent deburring may be unnecessary. However, for intricate parts such as those shown in Fig. 1, separate deburring operations generally are required.

The use of liquid deburring methods is not usually suitable, especially if such liquids are corrosive. Thus, acid pickling is not recommended, because acid may be entrapped in the pores, resulting in severe corrosion. Tumbling in a wet medium is used frequently as a deburring method, but removal of the liquid from the pores requires extra drying time. Preferred methods of deburring include:

- Rotary tumbling (self or with abrasive)
- Vibratory
- Abrasive blasting
- Centrifugal or high-energy methods

These methods, which are used for deburring and sometimes for cleaning, are described in the articles "Mechanical Cleaning Systems" and "Mass Finishing Methods" in this Volume. The discussions that follow are unique to P/M parts.

Rotary Tumbling. Self-tumbling, tumbling with dry abrasive, and tumbling with abrasive in a liquid medium are suitable for deburring of P/M parts. Wet tumbling is not suitable for deburring P/M parts because of the difficulty of removing the tumbling liquid from the pores of the parts.

During self-tumbling, the workpieces are tumbled in a revolving barrel. This method provides an economical and efficient means of deburring, but is effective only on relatively simple parts. For parts such as those shown in Fig. 1, the internal surfaces and recesses are not completely deburred by this method. For more complete deburring, an abrasive is added. Size of the abrasive is important. At least a portion of the added abrasive should have a mesh size that is smaller than the smallest hole or recess in the workpiece; otherwise, not all surfaces will be reached.

Over-tumbling of P/M parts must be avoided, because it peens the surfaces and may partially close pores (not necessarily desirable). Over-tumbling also may damage gear teeth or other protrusions by removing too much metal or by excessive peening. Tumbling cycles should be based on the minimum time that will provide acceptable deburring.

Vibratory processing is similar to rotary tumbling in principle. However, the shaking involved in the vibratory method is faster and provides more uniform results compared to rotary tumbling. As in rotary tumbling, care must be taken to prevent over-tumbling.

Abrasive blasting, in which various materials are propelled by air or centrifugal force, offers another method of deburring. For practical reasons, it is used less frequently than tumbling or vibrating. The abrasive must be selected carefully. Coarse shot or grit tends to peen the surfaces and close the pores. Also, abrasive blasting can "hammer" bits of abrasive into the workpiece, thus "charging" it.

Another disadvantage of conventional abrasive blasting is that, especially for large volumes of small workpieces, results are likely to be nonuniform. One type of blasting machine, which tumbles and blasts simultaneously, has been used successfully for deburring of P/M parts. Silica sand or a milder abrasive is suitable and is less likely to damage intricate workpieces. As with other deburring methods, overprocessing must be avoided.

Centrifugal or High-Energy Methods. Centrifugal finishing combines rotating action with high centrifugal force, which results in a more severe abrading action than can be obtained by conventional rotary tumbling. This action is obtained by revolving several rotating barrels around the periphery of a large carrier disk.

As a result, the action within one barrel consists of a combination of rotating motion and high centrifugal forces, which provides pressures up to 25 times the weight of the abrasive medium (if used) and the workpiece. As the disk rotates in one direction, the barrels rotate at a faster speed in the opposite direction. This counter movement within the entire mass accomplishes the desired results in a shorter time compared to other abrading processes. An advantage of this process is that it drives the abrasive into relatively inaccessible areas where burr removal may present problems.

Cleaning of P/M Parts (Ref 4)

Some of the deburring methods discussed above also may be considered as methods of cleaning. Frequently, however, methods such as tumbling and blasting are considered as preliminary cleaning operations to be followed by a more thorough cleaning, especially if the parts are to be coated.

Cleaning Methods. The inherent porosity in P/M parts imposes restrictions on selection of cleaning method. The use of a cleaning solution that is corrosive to the metal being cleaned is not recommended, because even the most thorough washing is not likely to remove all of the fluid, which presents a corrosion problem. Acid cleaning is therefore not recommended.

Because of porosity, thorough cleaning of P/M parts is more difficult than their wrought counterparts; P/M parts require more attention than is provided in many conventional cleaning systems. Preferred methods are hot caustic washing, ultrasonic degreasing, and electrolytic alkaline cleaning.

Ultrasonic Degreasing. Oils, greases, and other shop soil may be removed by vapor degreasing techniques such as vapor phase, vapor-spray-vapor, warm liquid-vapor, or boiling liquid-warm liquid-vapor techniques. For most P/M parts, especially if the degree of soiling is severe and/or part density is low, the boiling liquid-warm liquid-vapor process is preferred. This technique should be used in conjunction with an ultrasonic transducer, which literally shakes all entrapped contaminants out of the pores, resulting in a thorough and safe method of cleaning.

Electrolytic Alkaline Cleaning. Ferrous P/M parts can be cleaned, deoxidized, and stripped of nonmetallic coatings by subjecting them to electrolysis in a strongly alkaline aqueous solution. In this method the base metal is not attacked, and the possibility of rusting is minimal. Typical alkaline solutions are comprised of a:

- Source of caustic to aid cleaning
- Chelating agent to detach scale or rust
- Complexing agent to hold relatively large amounts of iron in solution

Electrolytic alkaline cleaning bath compositions and operating conditions are described in the article "Alkaline Cleaning" in this Volume. This cleaning process is well suited to cleaning of P/M parts, because the electrolytic action provides additional energy required to dislodge contaminants from pores or from relatively inaccessible areas.

Steam Treating of P/M Parts (Ref 5)

Ferrous P/M parts have traditionally been steam treated for improved wear resistance, corrosion resistance, and sealing capacity. Here, P/M parts are heated in a specific manner under a steam atmosphere at temperatures between 510 to 595 °C (950 to 1100 °F) to form a layer of black iron oxide (magnetite, or ferrous-ferric oxide, $FeO\text{-}Fe_2O_3$) in the surface porosity according to the chemical reaction:

$$3Fe + 4H_2O\ (\text{steam}) \rightarrow Fe_3O_4 + 4H_2(\text{gas}) \qquad \textbf{(Eq 1)}$$

Steam treating cannot be described as a heat treatment because no structural changes occur in the matrix. In this process, magnetite (Fe_3O_4) is formed at the interconnecting surface porosity, filling the porosity with a second phase. Magnetite has a microhardness equivalent to HRC 50.

The process itself is straightforward, the primary variables being temperature, time, and steam pressure. Caution must be used to prevent the formation of hydroxides and lower oxides such as ferrous oxide (FeO) and ferric oxide (Fe_2O_3), which is red rust.

The recommended procedure for steam treating is:

- Preclean parts to remove any oil or lubricants that may have been absorbed into the porosity from prior machining, sizing, or finishing operations
- Load clean sintered parts in loosely packed baskets and place fixture into a furnace preheated to 315 °C (600 °F)
- Heat parts in air until the center of the load has stabilized at the set temperature
- Introduce superheated steam at a line pressure of 35 to 105 kPa (5 to 15 psi) and allow furnace to purge for at least 15 min
- Increase furnace temperature to desired set point and hold for no longer than 4 h at heat
- Upon completion of cycle, reduce furnace temperature to 315 °C (600 °F). When parts reach this temperature, the steam can be shut off and the parts unloaded

Caution should be used when opening the furnace door after the steam cycle. As shown in Equation 1, hydrogen is produced during this process and can ignite. It is recommended that a nitrogen purge be applied prior to unloading. This process, when correctly applied, can impart improved surface properties, and, depending upon steel composition, increased compressive yield strength.

In all steam-treated P/M steels, the ductility is significantly reduced due to the internal stresses created by the formation of the iron oxide. Care must be taken when treating high-carbon P/M steels because these internal stresses can initiate microcracking and cause severe loss of ductility. Many cases have been reported in which parts were accidentally dropped on the floor after being steam treated, and the parts subsequently shattered like glass. The best recommendation for preventing such an incident is to specify a 0.5% C (max) content on materials that are to be steam treated.

Figure 2(a) shows that transverse rupture strength increases proportionately with sintered density. Upon steam treating, low-carbon P/M steels exhibit a uniform increase in strength, whereas the high-carbon P/M steels show only a small incremental increase in strength.

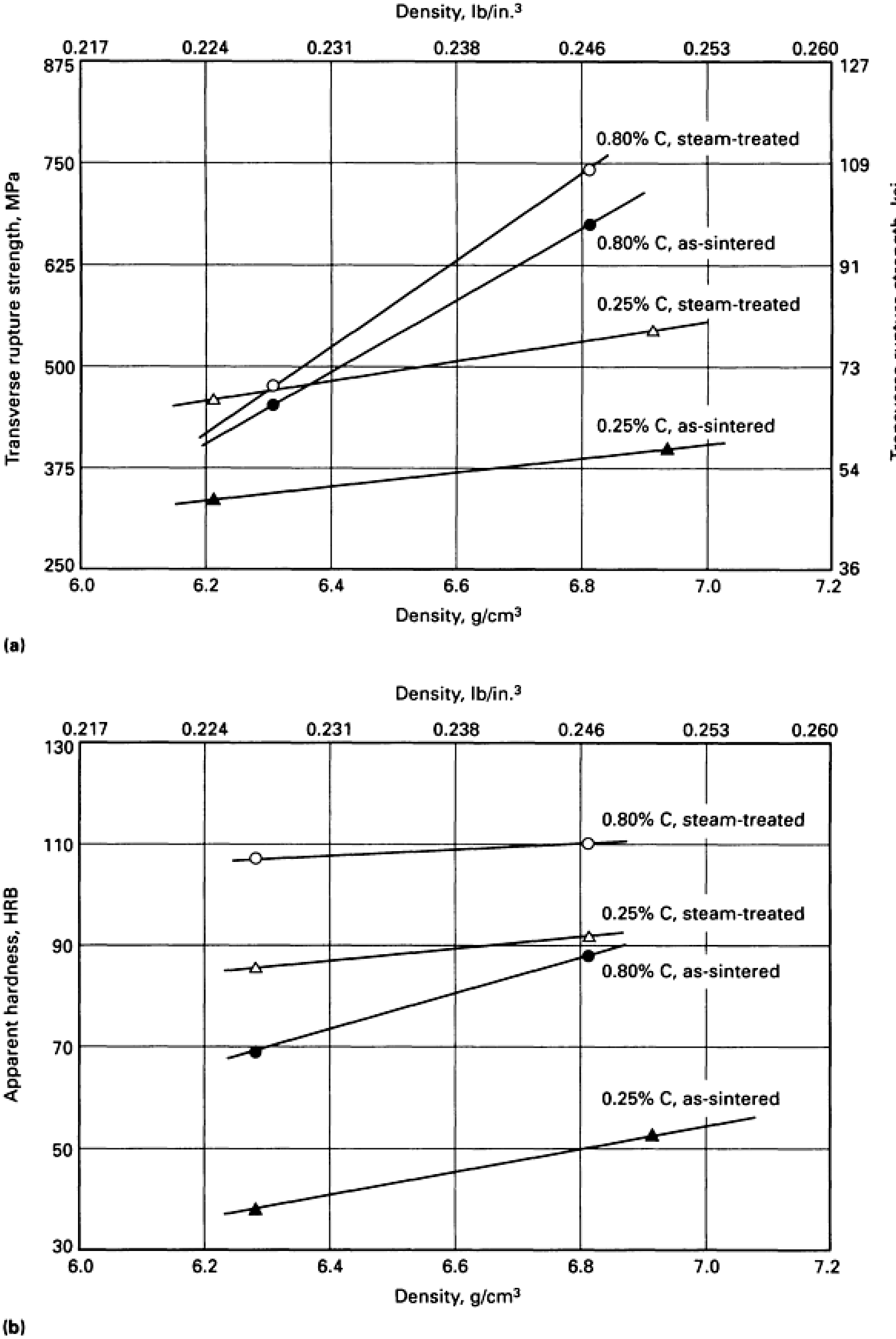


Fig. 2 Effect of steam treating on the mechanical properties of sintered carbon P/M steels as a function of density. (a) Transverse rupture strength. (b) Apparent hardness. Source: Ref 5

Apparent hardness also is improved as shown in Fig. 2(b). By filling the porosity with a hard second phase, the P/M steel can offer better support to an indentation hardness test. As with rupture strength, the incremental increase in hardness of high-carbon steels is less than that of low-carbon steels. Additional information on the properties of steam-treated P/M steels can be found in Ref 6.

Coating of P/M Parts (Ref 4)

In addition to the surfaces provided by steam treatment, P/M parts are frequently coated by mechanical means, painting, or electroplating. The blue-black oxide-covered surface produced by exposure to steam is often the final finish for a variety of hardware items. It may also be used as a preliminary coating for a final finishing process, such as painting.

Regardless of the method used for coating, major emphasis must be placed on initial cleaning. If liquid contaminants are allowed to remain in the pores of parts, bleeding occurs, and defective coatings result. Steam treatment provides an excellent paint base.

Mechanical coating uses kinetic energy to deposit metallic coatings on parts. This process is also known as mechanical plating, or peen plating, when the coating is less than 25 μm (1 mil) thick. Coating is accomplished by placing the workpiece, glass beads, water, and the metal plating powder in a tumbling barrel.

Zinc is most commonly used as a plating material, although a wide range of metals and mixtures of metals can be mechanically plated on ferrous metal parts. For example, a mixture of 75% Zn and 25% Sn is commonly used. Metal powders are added to the mixtures to be tumbled. Complete details on the mechanical coating process may be found in the article "Mechanical Plating" in this Volume.

Powder metallurgy parts with densities not less than 83% can be mechanically plated without special considerations for porosity. When density drops below 83%, tests should be conducted to determine whether moisture is entrapped, which is detrimental to the finished parts. Generally, when density is below 83%, parts must be impregnated with wax or resin.

Painting. Usually, P/M parts are ideal candidates for coating by painting; the porosity enhances paint adhesion. Furthermore, P/M parts can be painted by spraying, dipping, or the contact transfer method. Air-drying types are suitable only for indoor protective coatings. Baking produces finishes of higher quality that are well suited for outdoor exposure.

Spray painting has several advantages over dipping, including improved control of dimensions and coating quality, and the ability to coat localized areas. However, higher labor costs and more paint loss from overspray are associated with spraying.

For spraying, baking types of alkyds are reduced with solvents to a spraying viscosity of 35 s through a No. 4 Ford Cup. Parts are sprayed and then air dried for 10 min, after which they may be baked for 30 min at a temperature compatible with the type of paint being used. This practice results in a dry film coating 38 to 46 μm (1.5 to 1.8 mils) thick.

In paint dipping, the parts to be coated are placed in baskets or on racks, immersed in the paint, and then allowed to drain. Dipping saves labor and paint, compared to spraying, but general quality of dipped parts is lower, notably because of edge buildup.

Roll painting and lithographing (transfer coating) is a process in which paint is applied to external surfaces of cylindrical P/M parts, followed by the application of lithographing ink. Typically parts are roll coated and oven baked. The initial coating is usually a background color. Numbers of characters, as required, are then roll coated over the background coating, followed by baking dry.

Advantages of this painting procedure include:

- Precision painting can be achieved without applying paint to areas that do not require a coating

- With proper design of parts, areas can be painted with sharply defined edges
- Coating thickness can be closely controlled by varying the number of revolutions the part is permitted to make
- An unlimited number of character forms can be applied at relatively low cost

Principal limitations of the process are:

- Special handling is required
- Internal surfaces are not coated

Types of paint used in general procedures for painting of P/M parts are similar to those used for wrought counterparts, all of which are covered in detail in the article "Painting" in this Volume.

Electroplating. Powder metallurgy parts can be electroplated with various metals like their wrought counterparts. Methods used for plating of cast parts generally can be used for very dense parts (95% or more of theoretical). Plating of castings is described in the article "Surface Engineering of Cast Irons" in this Volume. For parts of lower densities, special preparation procedures are required.

During plating of P/M parts, the pores act as thermal pumps. Plating solutions are released from or absorbed by the pores, depending on the temperature differential between the workpiece and the solution. Interconnecting pores entrap solutions, which are then released slowly. Part density should be known before the sequence of cleaning and plating operations begins, and suitable precautions should be taken to prevent solution entrapment.

Entrapped solutions not only cause spotty plating and staining, which may develop within days, but also can cause contamination and depletion of all solutions used in the production process. It is therefore necessary that, if part density is below about 95%, pores must be closed before coating by electroplating.

Methods of closing pores that have proved successful include burnishing, buffing, rolling, heat treating, steam treating, and impregnation. All of these methods, except impregnation, provide varying degrees of closure. Mechanical methods are often excluded because of dimensional tolerances. Consequently, impregnation is the most suitable approach to closing pores.

Infiltration of iron compacts with metals such as copper is common practice and completely solves the porosity problem for subsequent electroplating. However, the cost of metal infiltration usually cannot be justified only to ensure satisfactory electroplating.

Impregnation with plastic seals P/M parts for further processing, such as electroplating. Pressure tightness and frequently an improvement in machining characteristics are added benefits derived from plastic impregnation. The process is not unlike the plastic impregnation process used to attain pressure tightness in porous castings. Optimum results are obtainable with various types of plastic sealants, although the most commonly used are polyester resins and anaerobic sealants.

A typical processing cycle consists of:

- Cleaning thoroughly
- Baking at 120 to 150 °C (250 to 300 °F) to drive off all moisture or solvent
- Applying sealant under vacuum, such as in an autoclave
- Removing excess sealant by means of an emulsion cleaner
- Curing at 120 to 150 °C (200 to 250 °F)
- Tumbling, polishing, or abrasive blasting to remove excess cured sealant

Parts are now ready for routine cleaning and plating cycles, as required by the plating method used. Plating procedures are the same as those used for wrought parts (see the articles contained in the Section "Plating and Electroplating" in this Volume).

Case Hardening of P/M Parts (Ref 5)

Powder metallurgy parts can be case hardened by several processes, although various available processes are not equally suited to every application. Generally the best results (a clear case/core relationship) are obtained with P/M parts with densities exceeding 7.2 g/cm^3 (90% of theoretical density). More detailed information on each of the processes described below can be found in *Heat Treating*, Volume 4 of the *ASM Handbook.*

Carburizing is normally specified in parts with a large cross-sectional thickness to attain maximum fatigue and impact properties. The material usually specified for carburizing contains hardenability agents such as nickel, molybdenum, and copper with relatively low carbon content. To develop optimum dynamic properties at porosity levels between. 10 to 15%, a combined carbon level of 0.30 to 0.35% is recommended. As porosity is reduced below 10%, combined carbon can be reduced to 0.15 to 0.25% C. Because improved dynamic properties are also associated with high densities, it is recommended that combined carbon be adjusted to a level best suited for re-pressing after sintering.

In wrought steel, carburizing is normally characterized by a surface hardness range and an effective case depth. Microhardness measurements can accurately show the hardness profile in wrought steel but can be erratic when used on P/M steels. With P/M steels, however, subsurface porosity can influence the microhardness readings, resulting in false hardness readings. It is recommended that at least three hardness readings be taken at each level below the surface and averaged to determine effective case depth.

Carburizing of P/M steels is usually done at temperatures between 900 to 930 °C (1650 to 1705 °F). Time cycles are normally short because of the rapid diffusion of carbon through the interconnected porosity. Therefore, atmosphere carbon potentials need to be somewhat higher than those required for wrought steels of similar composition.

Carbonitriding is probably the more common case-hardening treatment used on P/M parts. Here process temperatures are lower (800 to 850 °C, or 1470 to 1560 °F) and ammonia additions to approximately 10% are made. Ammonia dissociates on the parts, allowing nitrogen to diffuse into the surfaces. This retards the critical cooling rate upon quenching and provides a more consistent martensite transformation. It also produces a more consistent surface hardness, which improves wear resistance and toughness of the P/M steel. Because lower temperatures can be used, carbonitriding provides better control of distortion compared to carburizing. Care must be taken when adding ammonia, however, since excessive nitrogen diffusion into the internal pore surfaces can cause embrittlement.

Carbonitriding is a shallow case-hardening treatment. Case depths greater than 0.50 mm (0.020 in.) deep are seldom specified. For this reason, cycle times are relatively short, usually on the order of 30 to 60 min. As in neutral hardening, carbon control is a critical aspect of the treatment. Normally carbon potentials of 1.0 to 1.2% are specified to maintain the carbon profile in the part.

Tempering is usually required after case hardening when densities exceed 90%. In this case, significantly high stresses that could initiate cracking are developed upon quenching. As porosity increases, this stress level is reduced to a level at which a posttemper is not necessary. However, judgment should be used when deciding whether tempering is required. If a substantial amount of retained austenite is formed upon carbonitriding, a temper is advisable.

If the part has thin cross sections, sharp corners, or undercuts that would act as stress raiser, then tempering would also be advisable. Recommended tempering temperatures for P/M parts range from 105 to 200 °C (220 to 390 °F). Above this temperature, entrained quench oil can ignite, creating a hazardous condition in the furnace. Tempering above 200 °C (390 °F) will result in improved toughness and fatigue properties of the heat-treated P/M steel. However, furnaces will need special adaptations to handle the high volume of smoke created by the ignition of the quench oil.

Induction Hardening. Spur gears, bevel gears, splined hubs, and cams are ideal components to utilize P/M production techniques. These parts usually require hard wear-resistant surfaces in some areas, with the retention of the ductility of the sintered matrix in the remainder of the part. Induction hardening is commonly specified for these applications.

This process can be placed in an automated machining line that can reduce handling and be a cost-effective hardening treatment when high volumes of parts are being produced. Because the inductance of P/M materials is typically reduced

due to porosity, a higher power setting is normally required to reach a given depth of hardening compared to that used for a wrought material of similar composition. Furthermore, because the heat is rapidly dissipated, a rapid transfer to the quench is mandatory.

As with wrought steels, the response to hardening by induction is dependent upon combined carbon content, alloy content, and surface decarburization. This latter variable can be a major concern with P/M parts. With today's conventional belt-type sintering furnaces using an endogas atmosphere, decarburizing can occur as the parts leave the hot zone and cool slowly through the 1100 to 800 °C (2010 to 1470 °F) temperature range.

In most cases, P/M parts are quenched in a water-based solution containing some type of rust preventative to forestall internal corrosion. In those applications where induction hardening is considered, densities above 90% should be specified. With a decrease in density, the resistivity of the steel increases and permeability decreases. For this reason, integral quench coils using a high-velocity spray quench are generally used to attain maximum surface hardness in the P/M part.

Nitrocarburizing. This process is rapidly growing in popularity as a treatment for P/M parts. Here, nitrogen is diffused into the surfaces of the steel in sufficiently high concentration to form a thin layer of ε iron nitride on the surface of the part. This is done at temperatures ranging from 570 to 600 °C (1060 to 1110 °F). At these temperatures no austenite transformation occurs, thereby significantly reducing the dimensional changes and distortion.

The process uses conventional integral quench atmosphere furnaces. The atmosphere usually consists of a 50/50 mixture of endothermic gas and anhydrous ammonia. Control of the nitrided layer thickness, as with the other treatments, is dependent on density. If the nitrided layer is allowed to form on the internal pore surfaces to any significant extent, a volume expansion can occur. For this reason, density of the P/M part should be above 90% of theoretical. This nitrided layer, when properly applied, can reduce the coefficient of friction at the surface of the part and provide improved wear resistance compared to conventional hardening to martensite. This process is best applied to applications where sliding wear and fretting are involved.

Because the hard nitrided layer is relatively thin, this process should not be applied where high indentation or impact loading is involved. The ε nitride layer that is formed can attain a file hardness in excess of HRC 60, depending on the alloy content of the steel. Indentation hardness testing is not recommended when evaluating this process. Since no transformation occurs, the P/M parts can be air cooled without loss of surface hardness. Also, no oil absorption occurs, which leaves the porosity open for impregnation if desired.

Nitrocarburizing also provides improved strength and reduced notch sensitivity in P/M parts. Figure 3 shows the fatigue improvement of two low-carbon P/M steels after nitrocarburizing. A typical nitrocarburized microstructure of an iron-copper-carbon P/M steel is shown in Fig. 4.

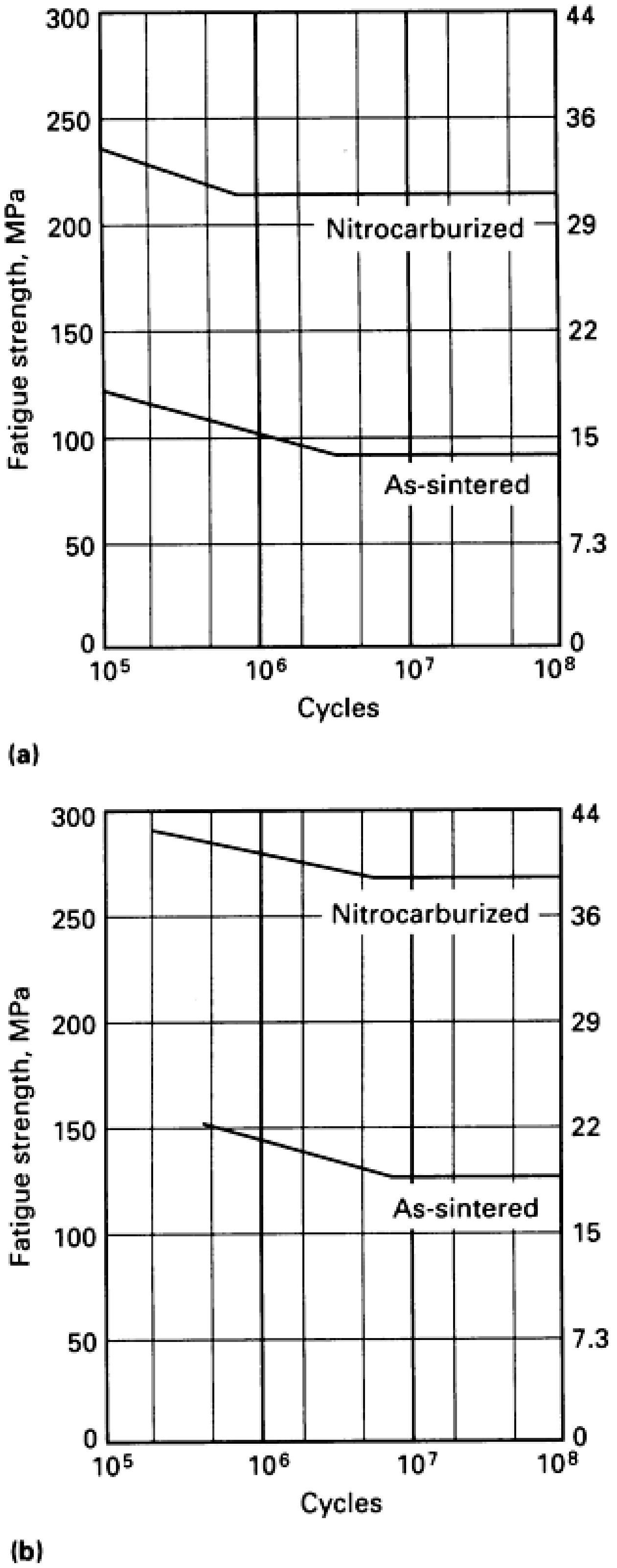


Fig. 3 Increase in the notched axial fatigue strength of sintered low-carbon P/M steels after nitrocarburizing for 2 h at 570 °C (1060 °F). (a) F-0000 carbon steel. (b) FC-0205 copper-carbon steel. Metal powder density was 7.1 g/cm^3 (0.256 lb/in.^{3}). Source: Ref 5

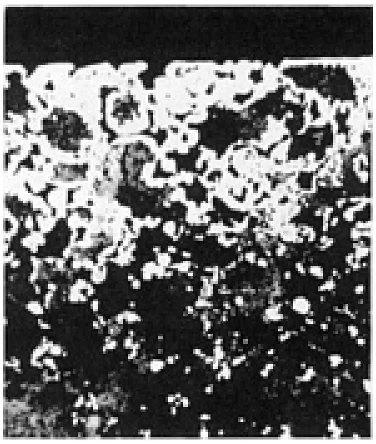


Fig. 4 Typical microstructure in a sintered ferritic nitrocarburized iron-copper-carbon P/M steel. 100×. Source: Ref 5

Plasma nitrocarburizing is in essence a variant of the now well-established glow-discharge plasma (ion) nitriding method (see the discussion that follows on ion nitriding). A technical argument against the use of plasma nitrocarburizing has been the effect of retained lubricant on the character and stability of the glow-discharge plasma, thus effecting the reliability of the plasma technology when applied to sintered parts. Lubricants are added to powdered products in order to achieve optimum pressing conditions. A method by which the lubricant can be satisfactorily removed prior to the P/M parts entering the vacuum chamber of the plasma unit is described in Ref 7. Using this method, it is now routinely possible to plasma nitrocarburize in one batch up to 4500 components, such as chain gear wheels, that have been manufactured by P/M. The microstructure of such a plasma nitrocarburized component is shown in Fig. 5. It is interesting to note that detailed examination shows that pores within the material, but close to the surface, also show the presence of the compound layer. The extent of the depth of such nitrocarburized pores is a function of the degree of interconnected porosity of the component, which is, in turn, a function of the pressing conditions.

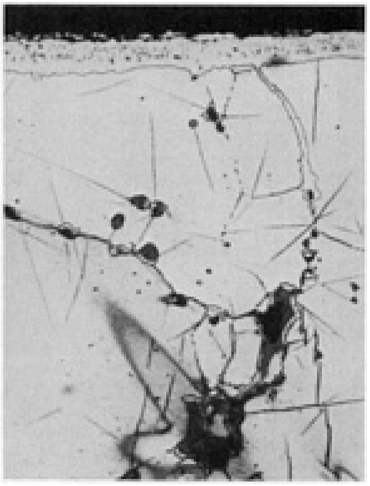


Fig. 5 Microstructure of a plasma nitrocarburized P/M steel with a compound surface layer thickness of 10 μm. Source: Ref 7

Ion Nitriding. The hardness, wear resistance, and fatigue strength can also be improved by plasma, or ion, nitriding. This is a method of surface hardening using glow discharge technology to introduce nascent (elemental) nitrogen to the surface of a metal part for subsequent diffusion into the material. In a vacuum, high-voltage electrical energy is used to form a plasma, through which nitrogen ions are accelerated to impinge on the workpiece. This ion bombardment heats the

workpiece, cleans the surface, and provides active nitrogen. Ion nitriding provides better control of case chemistry and uniformity and has other advantages, such as lower part distortion than conventional gas nitriding.

When ion nitriding of P/M steels, precleaning is more critical than with wrought alloys because of the porosity characteristic. A baking operation should precede the ion nitriding of P/M parts in order to break down or release agents and/or to evaporate any cleaning solvents.

References cited in this section

1. L.F. Pease III, Ferrous Powder Metallurgy Materials, *Properties and Selection: Irons, Steels, and High-Performance Alloys,* Vol 1, *ASM Handbook,* ASM International, 1990, p 801-821
2. W.B. James, M.J. McDermott, and R.A. Powell, Powder Forging, *Forming and Forging,* Vol 14, *ASM Handbook* (formerly 9th ed., *Metals Handbook*), ASM International, 1988, p 188-211
3. Materials Standards for P/M Structural Parts, MPIF Standard 35, Metal Powder Industries Federation, 1990
4. H.E. Boyer, Secondary Operations Performed on P/M Parts and Products, *Powder Metallurgy,* Vol 7, *ASM Handbook* (formerly 9th ed., *Metals Handbook*), ASM International, 1984, p 451-462
5. H.A. Ferguson, Heat Treating of Powder Metallurgy Steels, *Heat Treating,* Vol 4, *ASM Handbook,* 1991, p 229-236
6. L.F. Pease III, Mechanical Properties of Steam Blackened P/M Materials, in *Modern Developments in Powder Metallurgy: Proceedings of the International Powder Metallurgy Conference,* Metal Powder Industries Federation, 1988
7. W. Rembges, Ion Nitriding Applications Grow for Automotive Components, *Heat Treat.,* March 1990

Tool Steels

A tool steel is any steel used to make tools for cutting, forming, or otherwise shaping a material into a final part or component. These complex alloy steels, which contain relatively large amounts of tungsten, molybdenum, vanadium, manganese, and/or chromium, make it possible to meet increasingly severe service demands. In service, most tools are subjected to extremely high loads that are applied rapidly. The tools must withstand these loads a great number of times without breaking and without undergoing excessive wear or deformation. In many applications, tool steels must provide this capability under conditions that develop high temperatures in the tool. Most tool steels are wrought products, but precision castings can be used in some applications. The powder metallurgy process is also used in making tool steels. It provides, first, a more uniform carbide size and distribution in large sections and, second, special compositions that are difficult or impossible to produce in wrought or cast alloys.

Tool Steel Classifications

Tool steels are classified according to their composition, applications, or method of quenching. Each group is identified by a capital letter; individual tool steel types are assigned code numbers. Table 2 gives composition limits for the tool steels most commonly used. More detailed information on tool steels, including their processing, properties, and applications, can be found in Ref 8 and 9.

Table 2 Composition limits of principal types of tool steels

Designations			Composition[(a)], %								
AISI	**SAE**	**UNS**	**C**	**Mn**	**Si**	**Cr**	**Ni**	**Mo**	**W**	**V**	**Co**
Molybdenum high-speed steels											
M1	M1	T11301	0.78-0.88	0.15-0.40	0.20-0.50	3.50-4.00	0.30 max	8.20-9.20	1.40-2.10	1.00-1.35	. . .

Designations			Composition[a], %								
AISI	SAE	UNS	C	Mn	Si	Cr	Ni	Mo	W	V	Co
M2	M2	T11302	0.78-0.88; 0.95-1.05	0.15-0.40	0.20-0.45	3.75-4.50	0.30 max	4.50-5.50	5.50-6.75	1.75-2.20	. . .
M3, class 1	M3	T11313	1.00-1.10	0.15-0.40	0.20-0.45	3.75-4.50	0.30 max	4.75-6.50	5.00-6.75	2.25-2.75	. . .
M3, class 2	M3	T11323	1.15-1.25	0.15-0.40	0.20-0.45	3.75-4.50	0.30 max	4.75-6.50	5.00-6.75	2.75-3.75	. . .
M4	M4	T11304	1.25-1.40	0.15-0.40	0.20-0.45	3.75-4.75	0.30 max	4.25-5.50	5.25-6.50	3.75-4.50	. . .
M6	. . .	T11306	0.75-0.85	0.15-0.40	0.20-0.45	3.75-4.50	0.30 max	4.50-5.50	3.75-4.75	1.30-1.70	11.00-13.00
M7	. . .	T11307	0.97-1.05	0.15-0.40	0.20-0.55	3.50-4.00	0.30 max	8.20-9.20	1.40-2.10	1.75-2.25	. . .
M10	. . .	T11310	0.84-0.94; 0.95-1.05	0.10-0.40	0.20-0.45	3.75-4.50	0.30 max	7.75-8.50	. . .	1.80-2.20	. . .
M30	. . .	T11330	0.75-0.85	0.15-0.40	0.20-0.45	3.50-4.25	0.30 max	7.75-9.00	1.30-2.30	1.00-1.40	4.50-5.50
M33	. . .	T11333	0.85-0.92	0.15-0.40	0.15-0.50	3.50-4.00	0.30 max	9.00-10.00	1.30-2.10	1.00-1.35	7.75-8.75
M34	. . .	T11334	0.85-0.92	0.15-0.40	0.20-0.45	3.50-4.00	0.30 max	7.75-9.20	1.40-2.10	1.90-2.30	7.75-8.75
M36	. . .	T11336	0.80-0.90	0.15-0.40	0.20-0.45	3.75-4.50	0.30 max	4.50-5.50	5.50-6.50	1.75-2.25	7.75-8.75
M41	. . .	T11341	1.05-1.15	0.20-0.60	0.15-0.50	3.75-4.50	0.30 max	3.25-4.25	6.25-7.00	1.75-2.25	4.75-5.75
M42	. . .	T11342	1.05-1.15	0.15-0.40	0.15-0.65	3.50-4.25	0.30 max	9.00-10.00	1.15-1.85	0.95-1.35	7.75-8.75
M43	. . .	T11343	1.15-1.25	0.20-0.40	0.15-0.65	3.50-4.25	0.30 max	7.50-8.50	2.25-3.00	1.50-1.75	7.75-8.75

Designations			Composition[a], %								
AISI	**SAE**	**UNS**	**C**	**Mn**	**Si**	**Cr**	**Ni**	**Mo**	**W**	**V**	**Co**
M44	. . .	T11344	1.10-1.20	0.20-0.40	0.30-0.55	4.00-4.75	0.30 max	6.00-7.00	5.00-5.75	1.85-2.20	11.00-12.25
M46	. . .	T11346	1.22-1.30	0.20-0.40	0.40-0.65	3.70-4.20	0.30 max	8.00-8.50	1.90-2.20	3.00-3.30	7.80-8.80
M47	. . .	T11347	1.05-1.15	0.15-0.40	0.20-0.45	3.50-4.00	0.30 max	9.25-10.00	1.30-1.80	1.15-1.35	4.75-5.25
Tungsten high-speed steels											
T1	T1	T12001	0.65-0.80	0.10-0.40	0.20-0.40	3.75-4.00	0.30 max	. . .	17.25-18.75	0.90-1.30	. . .
T2	T2	T12002	0.8-0.90	0.20-0.40	0.20-0.40	3.75-4.50	0.30 max	1.00 max	17.50-19.00	1.80-2.40	. . .
T4	T4	T12004	0.70-0.80	0.10-0.40	0.20-0.40	3.75-4.50	0.30 max	0.40-1.00	17.50-19.00	0.80-1.20	4.25-5.75
T5	T5	T12005	0.75-0.85	0.20-0.40	0.20-0.40	3.75-5.00	0.30 max	0.50-1.25	17.50-19.00	1.80-2.40	7.00-9.50
T6	. . .	T12006	0.75-0.85	0.20-0.40	0.20-0.40	4.00-4.75	0.30 max	0.40-1.00	18.50-21.00	1.50-2.10	11.00-13.00
T8	T8	T12008	0.75-0.85	0.20-0.40	0.20-0.40	3.75-4.50	0.30 max	0.40-1.00	13.25-14.75	1.80-2.40	4.25-5.75
T15	. . .	T12015	1.50-1.60	0.15-0.40	0.15-0.40	3.75-5.00	0.30 max	1.00 max	11.75-13.00	4.50-5.25	4.75-5.25
Chromium hot-work steels											
H10	. . .	T20810	0.35-0.45	0.25-0.70	0.80-1.20	3.00-3.75	0.30 max	2.00-3.00	. . .	0.25-0.75	. . .
H11	H11	T20811	0.33-0.43	0.20-0.50	0.80-1.20	4.75-5.50	0.30 max	1.10-1.60	. . .	0.30-0.60	. . .
H12	H12	T20812	0.30-0.40	0.20-0.50	0.80-1.20	4.75-5.50	0.30 max	1.25-1.75	1.00-1.70	0.50 max	. . .

Designations			Composition[a], %								
AISI	**SAE**	**UNS**	**C**	**Mn**	**Si**	**Cr**	**Ni**	**Mo**	**W**	**V**	**Co**
H13	H13	T20813	0.32-0.45	0.20-0.50	0.80-1.20	4.75-5.50	0.30 max	1.10-1.75	. . .	0.80-1.20	. . .
H14	. . .	T20814	0.35-0.45	0.20-0.50	0.80-1.20	4.75-5.50	0.30 max	. . .	4.00-5.25	. . .	. . .
H19	. . .	T20819	0.32-0.45	0.20-0.50	0.20-0.50	4.00-4.75	0.30 max	0.30-0.55	3.75-4.50	1.75-2.20	4.00-4.50
Tungsten hot-work steels											
H21	H21	T20821	0.26-0.36	0.15-0.40	0.15-0.50	3.00-3.75	0.30 max	. . .	8.50-10.00	0.30-0.60	. . .
H22	. . .	T20822	0.30-0.40	0.15-0.40	0.15-0.40	1.75-3.75	0.30 max	. . .	10.00-11.75	0.25-0.50	. . .
H23	. . .	T20823	0.25-0.35	0.15-0.40	0.15-0.60	11.00-12.75	0.30 max	. . .	11.00-12.75	0.75-1.25	. . .
H24	. . .	T20824	0.42-0.53	0.15-0.40	0.15-0.40	2.50-3.50	0.30 max	. . .	14.00-16.00	0.40-0.60	. . .
H25	. . .	T20825	0.22-0.32	0.15-0.40	0.15-0.40	3.75-4.50	0.30 max	. . .	14.00-16.00	0.40-0.60	. . .
H26	. . .	T20826	0.45-0.55[b]	0.15-0.40	0.15-0.40	3.75-4.50	0.30 max	. . .	17.25-19.00	0.75-1.25	. . .
Molybdenum hot-work steels											
H42	. . .	T20842	0.55-0.70[b]	0.15-0.40	. . .	3.75-4.50	0.30 max	4.50-5.50	5.50-6.75	1.75-2.20	. . .
Air-hardening medium-alloy cold-work steels											
A2	A2	T30102	0.95-1.05	1.00 max	0.50 max	4.75-5.50	0.30 max	0.90-1.40	. . .	0.15-0.50	. . .
A3	. . .	T30103	1.20-1.30	0.40-0.60	0.50 max	4.75-5.50	0.30 max	0.90-1.40	. . .	0.80-1.40	. . .

Designations			Composition[(a)], %								
AISI	SAE	UNS	C	Mn	Si	Cr	Ni	Mo	W	V	Co
A4	. . .	T30104	0.95-1.05	1.80-2.20	0.50 max	0.90-2.20	0.30 max	0.90-1.40	. . .	. . .	. . .
A6	. . .	T30106	0.65-0.75	1.80-2.50	0.50 max	0.90-1.20	0.30 max	0.90-1.40	. . .	. . .	. . .
A7	. . .	T30107	2.00-2.85	0.80 max	0.50 max	5.00-5.75	0.30 max	0.90-1.40	0.50-1.50	3.90-5.15	. . .
A8	. . .	T30108	0.50-0.60	0.50 max	0.75-1.10	4.75-5.50	0.30 max	1.15-1.65	1.00-1.50	. . .	. . .
A9	. . .	T30109	0.45-0.55	0.50 max	0.95-1.15	4.75-5.50	1.25-1.75	1.30-1.80	. . .	0.80-1.40	. . .
A10	. . .	T30110	1.25-1.50[(c)]	1.60-2.10	1.00-1.50	. . .	1.55-2.05	1.25-1.75	. . .	. . .	. . .
High-carbon, high-chromium cold-work steels											
D2	D2	T30402	1.40-1.60	0.60 max	0.60 max	11.00-13.00	0.30 max	0.70-1.20	. . .	1.10 max	1.00 max
D3	D3	T30403	2.00-2.35	0.60 max	0.60 max	11.00-13.50	0.30 max	. . .	1.00 max	1.00 max	. . .
D4	. . .	T30404	2.05-2.40	0.60 max	0.60 max	11.00-13.00	0.30 max	0.70-1.20	. . .	1.00 max	. . .
D5	D5	T30405	1.40-1.60	0.60 max	0.60 max	11.00-13.00	0.30 max	0.70-1.20	. . .	1.00 max	2.50-3.50
D7	D7	T30407	2.15-2.50	0.60 max	0.60 max	11.50-13.50	0.30 max	0.70-1.20	. . .	3.80-4.40	. . .
Oil-hardening cold-work steels											
O1	O1	T31501	0.85-1.00	1.00-1.40	0.50 max	0.40-0.60	0.30 max	. . .	0.40-0.60	0.30 max	. . .
O2	O2	T31502	0.85-0.95	1.40-1.80	0.50 max	0.35 max	0.30 max	0.30 max	. . .	0.30 max	. . .

Designations			Composition[a], %								
AISI	SAE	UNS	C	Mn	Si	Cr	Ni	Mo	W	V	Co
O6	O6	T31506	1.25-1.55[c]	0.30-1.10	0.55-1.50	0.30 max	0.30 max	0.20-0.30	. . .	. . .	. . .
O7	. . .	T31507	1.10-1.30	1.00 max	0.60 max	0.35-0.85	0.30 max	0.30 max	1.00-2.00	0.40 max	. . .
Shock-resisting steels											
S1	S1	T41901	0.40-0.55	0.10-0.40	0.15-1.20	1.00-1.80	0.30 max	0.50 max	1.50-3.00	0.15-0.30	. . .
S2	S2	T41902	0.40-0.55	0.30-0.50	0.90-1.20	. . .	0.30 max	0.30-0.60	. . .	0.50 max	. . .
S5	S5	T41905	0.50-0.65	0.60-1.00	1.75-2.25	0.35 max	. . .	0.20-1.35	. . .	0.35 max	. . .
S6	. . .	T41906	0.40-0.50	1.20-1.50	2.00-2.50	1.20-1.50	. . .	0.30-0.50	. . .	0.20-0.40	. . .
S7	. . .	T41907	0.45-0.55	0.20-0.80	0.20-1.00	3.00-3.50	. . .	1.30-1.80	. . .	0.20-0.30[d]	. . .
Low-alloy special-purpose tools steels											
L2	. . .	T61202	0.45-1.00[b]	0.10-0.90	0.50 max	0.70-1.20	. . .	0.25 max	. . .	0.10-0.30	. . .
L6	L6	T61206	0.65-0.75	0.25-0.80	0.50 max	0.60-1.20	1.25-2.00	0.50 max	. . .	0.20-0.30[d]	. . .
Low-carbon mold steels											
P2	. . .	T51602	0.10 max	0.10-0.40	0.10-0.40	0.75-1.25	0.10-0.50	0.15-0.40	. . .	. . .	. . .
P3	. . .	T51603	0.10 max	0.20-0.60	0.40 max	0.40-0.75	1.00-1.50	. . .	. . .	. . .	. . .
P4	. . .	T51604	0.12 max	0.20-0.60	0.10-0.40	4.00-5.25	. . .	0.40-1.00	. . .	. . .	. . .

Designations			Composition[a], %								
AISI	**SAE**	**UNS**	**C**	**Mn**	**Si**	**Cr**	**Ni**	**Mo**	**W**	**V**	**Co**
P5	. . .	T51605	0.10 max	0.20-0.60	0.40 max	2.00-2.50	0.35 max	. . .	. . .	. . .	. . .
P6	. . .	T51606	0.05-0.15	0.35-0.70	0.10-0.40	1.25-1.75	3.25-3.75	. . .	. . .	. . .	. . .
P20	. . .	T51620	0.28-0.40	0.60-1.00	0.20-0.80	1.40-2.00	. . .	0.30-0.55	. . .	. . .	. . .
P21	. . .	T51621	0.18-0.22	0.20-0.40	0.20-0.40	0.20-0.30	3.90-4.25	. . .	. . .	0.15-0.25	1.05-1.25Al
Water-hardening tool steels											
W1	W108, W109, W110, W112	T72301	0.70-1.50[e]	0.10-0.40	0.10-0.40	0.15 max	0.20 max	0.10 max	0.15 max	0.10 max	. . .
W2	W209, W210	T72302	0.85-1.50[e]	0.10-0.40	0.10-0.40	0.15 max	0.20 max	0.10 max	0.15 max	0.15-0.35	. . .
W5	. . .	T72305	1.05-1.15	0.10-0.40	0.10-0.40	0.40-0.60	0.20 max	0.10 max	0.15 max	0.10 max	. . .

(a) All steels except group W contain 0.25 max Cu, 0.03 max P, and 0.03 max S; group W steels contain 0.20 max P, and 0.025 max S. Where specified, sulfur may be increased to 0.06 to 0.15% to improve machinability of group H, M, and T steels.

(b) Available in several carbon ranges.

(c) Contains free graphite in the microstructure.

(d) Optional.

(e) Specified carbon ranges are designated by suffix numbers.

High-speed steels are tool materials developed largely for use in high-speed metal cutting applications. There are two classifications of high-speed steels; molybdenum high-speed steels, or group M, which contain from 0.75 to 1.52% C and 4.50 to 11.0% Mo, and tungsten high-speed steels, or group T, which have similar carbon contents but high (11.75 to 21.00%) tungsten contents. Group M steels constitute more than 95% of all high-speed steel produced in the United States.

Hot-work steels (group H) have been developed to withstand the combinations of heat, pressure, and abrasion associated with punching, shearing, or forming of metals at high temperatures. Group H steels usually have medium carbon contents (0.35 to 0.45%) and combined chromium, tungsten, molybdenum, and vanadium contents of 6 to 25%. H steels are divided into chromium hot-work steels, tungsten hot-work steels, and molybdenum hot-work steels.

Cold-work steels are restricted in application to those uses that do not involve prolonged or repeated heating above 205 to 260 °C (400 to 500 °F). There are three categories of cold-work steels: air-hardening steels, or group A; high-carbon, high-chromium steels, or group D; and oil-hardening steels, or group O.

Shock-resisting, or group S, steels contain manganese, silicon, chromium, tungsten, and molybdenum, in various combinations; carbon content is about 1.50%. Group S steels are used primarily for chisels, rivet sets, punches, and other applications requiring high toughness and resistance to shock loading.

The low-alloy special purpose, or group L, tool steels contain small amounts of chromium, vanadium, nickel, and molybdenum. Group L steels are generally used for machine parts and other special applications requiring good strength and toughness.

Mold steels, or group P, contain chromium and nickel as principal alloying elements. Because of their low resistance to softening at elevated temperatures, group P steels are used almost exclusively in low-temperature die casting dies and in molds for injection or compression molding of plastics.

Water-hardening, or group W, tool steels contain carbon as the principal alloying element (0.70 to 1.50% C). Group W steels, which also have low resistance to softening at elevated temperatures, are suitable for cold heading, coining, and embossing tools, woodworking tools, metal-cutting tools, and wear-resistant machine tool components.

Surface Treatments for Tool Steels (Ref 10)

Most surface treatments are employed to increase surface hardness and/or wear resistance, minimize adhesion (reduce friction), or improve the corrosion resistance of the tool steel base. The processes discussed below are described in greater detail elsewhere in this Volume or in *Heat Treating*, Volume 4 of the *ASM Handbook*.

Carburizing. The processes of case hardening and carburizing are of limited use in tool steel applications, because of the relatively high carbon contents of the tool steels. Carburizing can be accomplished in many ways, and essentially consists of heating the final machined tool into the austenite region in the presence of carbonaceous solids, liquids, or gases.

Low-carbon plastic mold steels (P type) are often carburized after hubbing or machining of the cavity in the mold. In this application, the tool steel is intentionally lean in carbon content to improve hubbing or machining, and must be carburized in order to have sufficient surface hardness for the end use.

Nitriding is a frequently used surface treatment that increases surface hardness, adds to the corrosion resistance of the tool, and reduces friction. Basically, the process involves heating the finished tool in the presence of a nitrogen-containing liquid or gas and allowing nitrogen to diffuse into the tool. Gas nitriding is usually accomplished at a lower temperature (about 527 °C, or 980 °F) and longer time (10 to 90 h) than liquid nitriding, which occurs at temperatures ranging from 538 to 552 °C (1000 to 1025 °F) for 2 to 4 h. A nitrided depth that ranges from 13 to 76 μm (0.0005 to 0.003 in.) is desired.

Because of decreased wear and die pickup, cold-extrusion punches experience a two to three-fold improvement in life. Nitriding is often used whenever mold wash is a problem in the die casting of zinc or aluminum alloys. Galling of sheet metal working dies can be alleviated by nitriding these dies before use.

Steels that will be nitrided should contain one or more of the nitride-forming elements (chromium, vanadium, or aluminum) in order to prevent the easy spalling and chipping that results when iron nitride is formed. Commonly nitrided tool steels include H11, H12, H13, A2, O2, and the high-speed tool steels.

Ion or plasma nitriding has many of the same characteristics of liquid or gas nitriding. This process relies on a nitrogen gas being ionized by glow discharge conditions between the tool (carbide) and the furnace wall or shield (anode).

The primary advantages are the reductions in time and temperature, which save money and reduce the distortion and softening of prehardened tools. Usually, treatment times vary between 0.5 and 36 h.

Boriding. In this process, boron atoms from a solid, liquid, gas, or plasma atmosphere surrounding the finished part are diffused into the surface, creating a hard, water-resistant iron boride layer. Metal-to-metal wear testing demonstrated a three-fold improvement in wear resistance of borided O1 and O2 tool steels and over a two-fold increase in A2 tool steel (Ref 11). Borided A2 tool steel showed twice the life of uncoated O2 tool steel in a deep-drawing operation in which low-carbon steel cups were manufactured (Ref 11). An H13 roller designed to flange milk cans was borided and produced three times as many cans before it wore out (Ref 12).

Boriding takes place at temperatures as low as 600 °C (1100 °F), but usual practice involves a period from 1 to 6 h at temperatures from 800 to 900 °C (1470 to 1650 °F) (Ref 11, 12). The resultant layer is between 13 and 130 μm (0.0005 and 0.005 in.), and tends to be dull because of the microroughness of the surface. This high process temperature requires that the boron treatment act as the austenitization step, or else the process must be followed by reaustenitization. This necessarily limits the process to applications where tolerances of about 25 μm (0.001 in.) can be tolerated.

Carbide Coating by Toyota Diffusion Process. Good surface covering and strongly bonding carbide coatings, such as VC, NbC, and Cr_7C_3, can be formed on die steel surfaces by a coating method developed at Toyota Central Research and Development Laboratory, Inc. of Japan.

In the Toyota Diffusion (TD) process, metal dies to be treated are degreased, immersed in a carbide salt bath for a specific time period, quenched for core hardening, tempered, and washed in hot water for the removal of any residual salt. The borax salt bath contains compounds (usually ferroalloys) with carbide-forming elements such as vanadium, niobium, and chromium. The bath temperature is selected to conform to the hardening temperature of the die steel. For example, the borax bath temperature would be between 1000 and 1050 °C (1830 and 1920 °F) for H13 die steel.

The carbide layer is formed on the die surface through a chemical reaction between carbide-forming elements dissolved in the fused borax and carbon in the substrate. The carbide layer thickens due to reaction between the carbide-forming element atoms in the salt bath and the carbon atoms diffusing into the outside surface layer from the interior of the substrate.

The thickness of the carbide layer is varied by controlling the bath temperature and immersion time. An immersion time of 4 to 8 h is needed for H13 steel to produce carbide layers with satisfactory thickness (5 to 10 μm) for die-casting applications. Dies are then removed from the bath and cooled in oil and salt or air for core hardening followed by tempering.

Coated tool steels, such as H12 and H13 steels, exhibit high hardness and excellent resistance to wear, seizure, corrosion, and oxidation. In addition, resistance to cracking, flaking, and heat checking is claimed. Hardness of the coating depends on layer composition: 3500 HV for vanadium carbide, 2800 HV for niobium carbide, and 1700 HV for chromium carbide.

Oxidation is a well-established process used for high-speed steel cutting tools. Increases in tool life of up to 100% are mostly due to a decrease in friction, because of the hard oxide coating and the ability of the porous oxide to entrap lubricant and draw it to the tool-workpiece interface. Steam oxidation of a finished tool is accomplished either by exposure to steam at a temperature of about 566 °C (1050 °F) or by treating in liquid sodium hydroxide and sodium nitrate salts at approximately 140 °C (285 °F) for periods of time ranging from 5 to 20 min. These treatments result in a black oxidized layer that is less than 5 μm (0.0002 in.) thick and will not peel, chip, nor crack, even when the tool is bent or cut. Tool life improvements due to steam oxidation are listed in Tables 3 and 4.

Table 3 Machining tool life improvements due to steam oxidation

Tool	Application	Tool life	
		Before steam treating	After steam treating
M2 broachers	Cutting AISI 1010 latch	20 h per grind	70 h per grind

M2 drills	Drilling Bakelite plastic insulating blocks	10 holes	25 holes
	Phenolic terminal plates	1700 holes per grind	8500 holes per grind
	Drilling AISI 4030 steel 25 mm (1 in.) thick	17 holes	81 holes
M7 end mill tools	Cutting 8740 steel forgings	30 pieces	200 pieces
A6 hobs	Cutting teeth on AISI 3140 forged gear	. . .	62.2% increased life
M2 milling cutters	Two slots in 1020 steel	150 cuts per grind	306 cuts per grind
	Slotting 1020 steel bars	2000 per grind	7000 per grind
M2 saw blades	Cutting 75 mm (3 in.) rods, austenitic steel	100% endurance at 0.52 m/s (102 sfm)	120% endurance at 0.57 m/s (112 sfm)
M2 taps	Cutting SAE 52100 steel	1800 pieces	3000 pieces

Source: Ref 13

Table 4 Effect of steam oxidation on tool life in forming various carbon steel nuts and bolts

Tool	**Application**	**Tool life**	
		Before steam treating[(a)]	**After steam treating**[(b)]
M2 4th station punch	Castle nut 1030 material	21,000 nuts	42,000 nuts
M2 4th station punch	Slotted insert nut 1030 material	22,000 nuts	38,000 nuts
M2 4th station punch	Castle nut 1030 material	29,000 nuts	80,000 nuts
M2 3rd station punch	Castle nut 1110 material	20,000 nuts	35,000 nuts
M2 4th station punch	Castle nut 1110 material	15,000 nuts	35,000 nuts
M2 trim die	Bolt head 1335 material	7,000 bolts	16,000 bolts

(a) Hardened and triple tempered.

(b) Hardened, triple tempered and steam treated.

Bright Finish. Most high-speed cutting tools are finished with a ground or mechanically polished surface that would be categorized as a bright finish. Bright finished tools are often preferred to tools with an oxide finish for machining nonferrous work material. The smooth or bright finish tends to resist galling, a type of welding or buildup associated with many nonferrous alloys. However, work materials of ferrous alloys tend to adhere to similar, iron-base tools having a bright finish. This buildup on the cutting edges leads to increased frictional heat, poor surface finish, and increased load at the cutting edge.

Plating. Three different kinds of plating are used on tool steels. Cadmium plating is used for appearance purposes and to reduce corrosion of the tool. It also has some usefulness in preventing adhesion. Nickel plating is commonly used for appearance purposes and to prevent corrosion.

The most commonly practiced tool steel plating process is hard chromium plating. Plating thickness varies between 2 and 13 μm (0.0001 and 0.0005 in.) and, because it is very hard, it prolongs life by increasing abrasive wear resistance. More important than plating hardness is its very low friction coefficient, which effectively prevents adhesive wear.

However, hard chromium plating is not without problems. Tool steels may be hydrogen embrittled when plated, and the plating has a tendency to spall and flake. These wear debris can actually accelerate abrasive wear.

Chemical vapor deposition (CVD), a process conducted in a vacuum chamber, relies on a deposition from reacted gas onto the tool steel surface. Many different materials can be used as coatings. Chromium, Al_2O_3, TiC, CrC, Fe_4N, and TiN are commonly used, and other materials are being studied. This process utilizes high temperatures, usually above 800 °C (1472 °F), which means that tool steels must be tempered after the CVD coating is applied. The most popular wear-resistant coatings are TiC and TiN, which are used to coat high-speed, cold-work die and hot-work die tool steels. These coatings commonly range in thickness from 2 to 20 μm (0.0001 to 0.001 in.). Using CVD coating with TiC and TiN, the primary mechanism of wear reduction is the extremely high hardness, which leads to excellent abrasion resistance, although some decrease in friction coefficient can often be realized. The chlorine content of the coating must carefully be maintained at a level below 5% to avoid degradation of the wear resistance (Ref 14).

Tool steels that can be successfully CVD coated include the AISI A, S, D, H, M, and T steel types. The lower-alloyed S type and all of the W and O types are either very difficult or impossible to properly coat, because of their low austenitization temperatures.

Physical vapor deposition (PVD), which is also conducted in a vacuum chamber, can be accomplished in several different ways. The process relies on plasma-aided precipitation of either TiC or TiN onto tool steel at temperatures ranging from 200 to 550 °C (400 to 1025 °F) (Ref 14). This temperature range is much more suitable for the coating of high-speed tool steels than the temperatures required for CVD.

Tool steel wear is reduced in about the same proportions (2 to 6 times less wear), whether the TiC or TiN is applied by CVD or PVD. TiN coatings on H13 pins reduced the friction coefficient in pin-on-disk tests from 0.7 to less than 0.2 (Ref 15). Modified ASTM G65-10 abrasive wear testing of D3 steel showed that wear of the TiN-coated samples was between 4 and 23% of the uncoated samples, depending on their initial surface roughness (Ref 15). This result led Sundquist et al. to propose that increases in tool life that are due to TiN coating can only be expected when the surface roughness is less than the coating thickness (Ref 15). Specific examples of the use of PVD coatings for improving the life of high-speed steel tools are listed in Table 5.

Table 5 Increased tool life attained with PVD coated cutting tools

Cutting tool	Coating	Workpiece material	Workpieces machined before resharpening

Type	High-speed tool steel, AISI type			Uncoated	Coated
End mill	M7	TiN	1022 steel, 35 HRC	325	1200
End mill	M7	TiN	6061-T6 aluminum alloy	166	1500
End mill	M3	TiN	7075T aluminum alloy	9	53
Gear hob	M2	TiN	8620 steel	40	80
Broach insert	M3	TiN	Type 303 stainless steel	100,000	300,000
Broach	M2	TiN	48% nickel alloy	200	3400
Broach	M2	TiN	Type 410 stainless steel	10,000-12,000	31,000
Pipe tap	M2	TiN	Gray iron	3000	9000
Tap	M2	TiN	1050 steel, 30-33 HRC	60-70	750-800
Form tool	T15	TiC	1045 steel	5000	23,000
Form tool	T15	TiN	Type 303 stainless steel	1840	5890
Cutoff tool	M2	TiC-TiN	Low-carbon steel	150	1000
Drill	M7	TiN	Low-carbon steel	1000	4000
Drill	M7	TiN	Titanium alloy 662 layered with D6AC tool steel, 48-50 HRC	9	86

Source: Ref 16

Ion implantation is a process by which atoms of virtually any element can be injected into the near-surface region of any solid. The implantation process involves forming a beam of charged ions of the desired element and then accelerating them at high energies towards the surface of the solid, which is held under high vacuum. The atoms penetrate into the solid to a depth of 0.25 to 25 nm (2.5 to 250 Å). This process differs from coating processes in that it does not produce a discrete coating; rather, it alters the chemical composition near the surface of the solid. The most common element implanted in tool steels in order to improve tribological properties, specifically adhesive and sliding wear, is nitrogen.

Examples of ion implantation in metal forming and cutting applications are listed in Table 6. Ion implantation of titanium and carbon has also improved the service life of stamping and cutting tools.

Table 6 Examples of ion implantation in metalforming and cutting applications

Part	Part material	Process	Work material	Ion	Energy, keV	Benefit
Tool inserts	TiN-coated tool steel	Machining	4140	N	80	3× life
Taps	HSS	Tapping	4140	N	80	3× life
	HSS	Tapping	4130	N	80	5× life
	HSS	Tapping	4140	N	50	10× life
	M35	Tapping	. . .	N_2	200	4× life
	M7	Tapping	. . .	N	100	2× life
Cutting blade	M2	Cutting	1050	N	100	2× life
	M2	Cutting	SAE 950	N	100	4× life
Dies	D2	Forming	321 SS	N	80	2× life
	M2	Forming	Steel	N	100	2-12× life
	M2	Forming	1020	N	100	Negligible effect
	D6	Forming	TiO_2 and rubber	N	100	6× life
Molds	D2	Forming	Polymers	N	50	5× life
Rollers	H13	Rolling	Steel	N	100	5× life

Note: HSS, high-speed steel; SS, stainless steel.

Laser surface processing methods, such as laser melting, have also been applied to tool steels. Hsu and Molian (Ref 18) reported that the tool life of laser-melted M2 steel tool bits was from 200 to 500% higher than if they were conventionally hardened using catastrophic failure criterion (Fig. 6). For laser-melted M35 steel tool bits, the tool life was from 20 to 125% higher than if they were conventionally hardened using flank wear failure criterion (Fig. 6). High-alloy martensite, fine austenite grain size, and finely dispersed carbides all contributed to high hardness, good toughness, and low coefficient of friction.

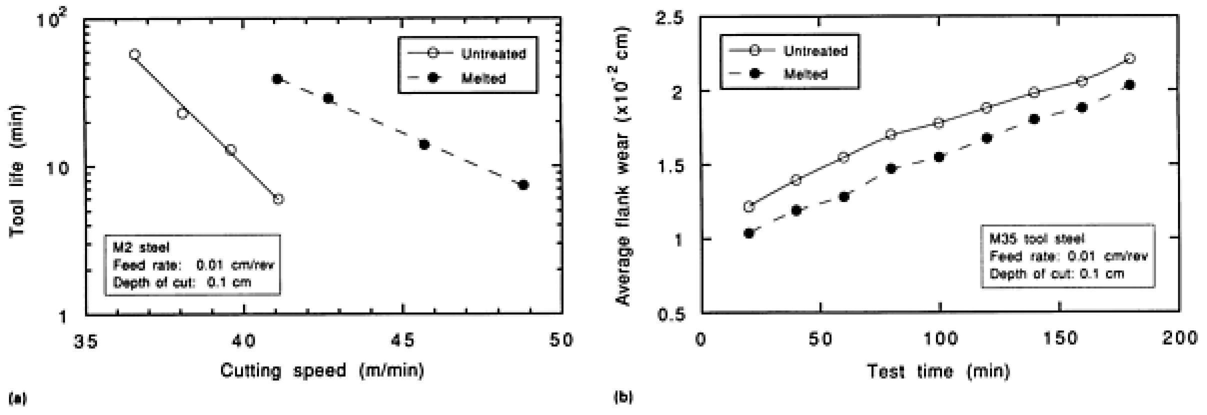


Fig. 6 Tool life of conventionally heat-treated and laser-melted tool bits. (a) M2 tool steel. (b) M35 tool steel. Source: Ref 18

References cited in this section

8. A.M. Bayer, Wrought Tool Steels, *Properties and Selection: Irons, Steels, and High-Performance Alloys,* Vol 1, *ASM Handbook* (formerly 10th ed., *Metals Handbook*), ASM International, 1990, p 757-779
9. K.E. Pinnow and W. Stasko, P/M Tool Steels, *Properties and Selection: Irons, Steels, and High-Performance Alloys,* Vol 1, *ASM Handbook* (formerly 10th ed., *Metals Handbook*), ASM International, 1990, p 780-792
10. J.L. Maloney III, Friction and Wear of Tool Steels, *Friction, Lubrication, and Wear Technology,* Vol 18, *ASM Handbook,* ASM International, 1992, p 734-740
11. H.C. Fiedler and R.J. Sieraski, Boriding Steels for Wear Resistance, *Met. Prog.,* Feb 1971, p 102-103
12. O.N. Guy, Boronizing--A Surface Heat Treatment for Critical Wear Surfaces, *New Developments in Tool Materials and Applications,* Illinois Institute of Technology, 1977
13. T.D. Deming, Steam Treating Emerges as Important Cog in Metal Surface Engineering, *Industrial Heating,* Jan 1990, p 28-30
14. F. Wendl, Current Trends in Surface Treatment of Tools Used for Plastics Processing, *Thyssen Edelstahl Tech. Ber.,* special issue, May 1990, p 82-99
15. H.A. Sundquist, E.H. Sirvio, and M.T. Kurkinen, Wear of Metalworking Tools Ion Plated With Titanium Nitride, *Met. Tech.,* Vol 10, 1983, p 130-134
16. C. Wick, HSS Cutting Tools Gain a Productivity Edge, *Manufacturing Engineering,* May 1987, p 38
17. G.R. Fenske, Ion Implantation, *Friction, Lubrication, and Wear Technology,* Vol 18, *ASM Handbook,* ASM International, 1992, p 850-860
18. M. Hsu and P.A. Molian, *Wear,* Vol 127, 1988, p 253

Maraging Steels (Ref 19)

Maraging steels comprise a special class of high-strength steels that differ from conventional steels in that they are hardened by a metallurgical reaction that does not involve carbon. Instead, these steels are strengthened by the precipitation of intermetallic compounds at temperatures of about 480 °C (900 °F). The term maraging is derived from martensite age hardening and denotes the age hardening of low-carbon, iron-nickel lath martensite matrix. The physical metallurgy and properties of maraging steels are described in Ref 19.

Commercial maraging steels are designed to provide specific levels of yield strength from 1030 to 2420 MPa (150 to 350 ksi). Some experimental maraging steels have yield strengths as high as 3450 MPa (500 ksi). These steels typically have very high nickel, cobalt, and molybdenum contents and very low carbon contents. Carbon, in fact, is an impurity in these steels and is kept as low as commercially feasible in order to minimize the formation of titanium carbide (TiC), which can adversely affect strength, ductility, and toughness.

Table 7 lists the chemical compositions of the more common grades of maraging steel. The nomenclature that has become established for these steels is nominal yield strength (ksi units) in parentheses. Thus, for example, 18Ni (200) steel is normally age hardened to a yield strength of 1380 MPa (200 ksi). The first three steels in Table 7--18Ni (200), 18Ni (250), and 18Ni (300)--are the most widely used and most commonly available grades. The 18Ni (350) grade is an ultrahigh-strength variety made in limited quantities for special applications. Two 18Ni (350) compositions have been produced (see the footnote in Table 7). The 18Ni (Cast) grade was developed specifically as a cast composition.

Table 7 Nominal compositions of commercial maraging steels

Grade	Composition, %[(a)]					
	Ni	**Mo**	**Co**	**Ti**	**Al**	**Nb**
Standard grades						
18Ni(200)	18	3.3	8.5	0.2	0.1	. . .
18Ni(250)	18	5.0	8.5	0.4	0.1	. . .
18Ni(300)	18	5.0	9.0	0.7	0.1	. . .
18Ni(350)	18	4.2[(b)]	12.5	1.6	0.1	. . .
18Ni(Cast)	17	4.6	10.0	0.3	0.1	. . .
12-5-3(180)[(c)]	12	3	. . .	0.2	0.3	. . .
Cobalt-free and low-cobalt bearing grades						
Cobalt-free 18Ni(200)	18.5	3.0	. . .	0.7	0.1	. . .
Cobalt-free 18Ni(250)	18.5	3.0	. . .	1.4	0.1	. . .
Low-cobalt 18Ni(250)	18.5	2.6	2.0	1.2	0.1	0.1

(a) All grades contain no more than 0.03% C.

(b) Some producers use a combination of 4.8% Mo and 1.4% Ti, nominal.

(c) Contains 5% Cr

A number of cobalt-free maraging steels and a low-cobalt bearing maraging steel have recently been developed. The driving force for the development of these particular alloys was the cobalt shortage and resultant price escalation of cobalt during the late 1970s and early 1980s. The nominal compositions for these alloys are also listed in Table 7.

Surface Treatments for Maraging Steels (Ref 19)

Cleaning. Grit blasting is the most efficient technique for removing oxide films formed by heat treatment. Maraging steels can be chemically cleaned by pickling in sulfuric acid or by duplex pickling in hydrochloric acid and then in nitric acid plus hydrofluoric acid (see Tables 7 and 11 in the article "Surface Engineering of Stainless Steels" in this Volume). As with conventional steels, care must be taken to avoid overpickling. The sodium hydride cleaning of maraging steels should be avoided to minimize problems with crack formation. Grease and oils can be removed by cleaning in trichloroethane-type solutions.

Nickel Plating. Maraging steels can be nickel plated in chloride baths provided that proper surface-activation steps are followed. Heavy chromium deposits can be plated on top of nickel electrodeposits. Maraging steels are less susceptible to hydrogen embrittlement during plating than conventional quenched and tempered steels of comparable hardness. They are not immune to hydrogen, however, and baking after plating is recommended. Baking should be done at temperatures of about 150 to 205 °C (300 to 400 °F) for periods of 3 to 10 h, depending on size and baking temperature. Baking cannot be combined with age hardening, because considerable hydrogen remains in the steel after heat treating at the higher temperatures.

Nitriding. Considerable surface hardening can be achieved by nitriding maraging steels in dissociated ammonia. Hardness levels equivalent to 65 to 70 HRC can be achieved at depths of up to 0.15 mm (0.006 in.) after nitriding for 24 to 48 h at 455 °C (850 °F). Nitriding at this temperature allows age hardening to occur during nitriding; therefore, the two processes can be accomplished simultaneously. Salt bath nitriding for 90 min at 540 °C (1000 °F) has been done successfully. Such treatment must be very carefully controlled to avoid excessive overaging. Both the fatigue strength and the wear resistance (Fig. 7) of maraging steels are improved by nitriding.

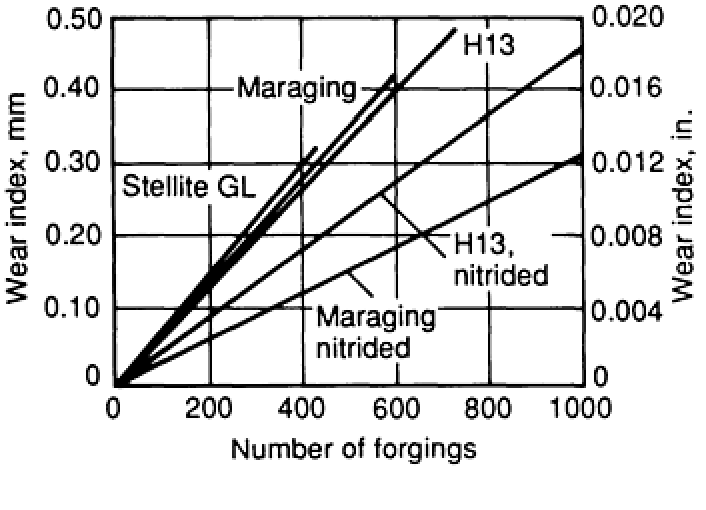


Fig. 7 Relative wear rates of nitrided and non-nitrided tool steels and maraging steels used in extrusion forging

Maraging steels can also be surface hardened by ion nitriding. Ozbaysal and Inal (Ref 20) have demonstrated that the surface hardening of maraging steels without a reduction in core hardness is possible using the ion nitriding process. Their studies on 18Ni(250), 18Ni(300), and 18Ni(350) showed that the highest surface hardness and the highest core hardness for all three grades were achieved by nitriding at approximately 440 °C (825 °F). Figure 8 shows the surface and core hardness as functions of ion nitriding time and temperature for 300-grade maraging alloy.

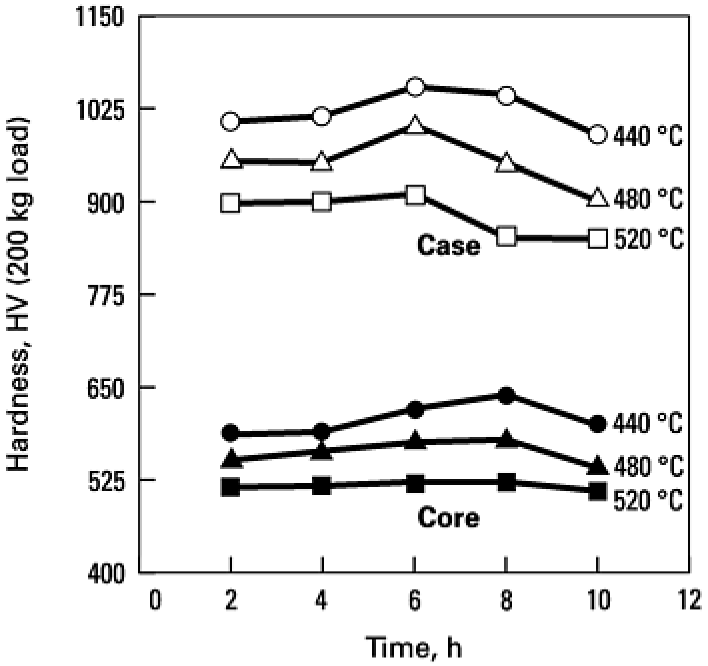


Fig. 8 Surface (case) and core hardness as functions of ion nitriding time and temperature for 18Ni (300) maraging steel. Source: Ref 20

References cited in this section

19. K. Rohrbach and M. Schmidt, Maraging Steels, *Properties and Selection: Irons, Steels, and High-Performance Alloys,* Vol 1, *ASM Handbook* (formerly 10th ed., *Metals Handbook*), ASM International, 1990, p 793-800
20. K. Ozbaysal and O.T. Inal, Surface Hardening of Marage Steels by Ion Nitriding without Reduction in Core Hardness, in *Ion Nitriding,* ASM International, 1986, p 97-115

Electrical Steels (Ref 21)

Electrical steels are flat-rolled silicon-containing alloys used for soft magnetic applications such as components (magnetic cores) for motors, generators, and transformers. The beneficial effects of silicon additions to iron include:

- Increase of electrical resistivity
- Suppression of the γ loop enabling desirable grain growth
- Development of preferred orientation grain structure

The addition of silicon also reduces magnetocrystalline anisotropy energy, and at ~6.5% Si content reduces the magnetostriction constants to nearly zero. High-permeability and low hysteresis losses can therefore be attained at the 6.5Si-Fe composition. On the negative side, the addition of silicon to iron lowers magnetic saturation, lowers Curie temperature, and seriously decreases mechanical ductility. At silicon levels above ~4%, the alloy becomes brittle and difficult to process by cold-rolling methods; thus, few commercial steels contain more than ~3.5% Si.

The commercial grades of silicon steel in common use are made mostly in electric or basic oxygen furnaces. Continuous casting and/or vacuum degassing (V-D) may be employed. Flat-rolled silicon-iron sheet and strip has low sulfur content, typically below 0.25%, with better grades below 0.01%. Carbon contents are frequently less than 0.04%. Manganese may be present up to approximately 0.70%. Residual elements such as chromium, molybdenum, nickel, copper, and phosphorus may also be present. The major alloying addition is silicon plus up to 0.6% Al (optional). These alloys are not generally sold on the basis of their composition, but rather are sold based upon controlled magnetic properties, particularly ac core losses.

Electrical sheet grades are divided into two general classifications, (1) oriented steels and (2) nonoriented steels. The oriented steels are given mill treatments designed to yield exceptionally good magnetic properties in the rolling, or lengthwise, direction of the steel. Nonoriented grades are made with a mill treatment that yields a grain structure, or texture, of a random nature and, therefore, the magnetic properties in the rolling direction of the steel are not significantly better than those in the transverse direction. Subdivisions of these steels include semiprocessed grades and the fully processed grades. The former must be given a heat treatment by the purchaser. Fully processed grades are process annealed by the manufacturer.

Table 8 gives examples of properties specified by ASTM and American Iron and Steel Institute (AISI) for standard grades of nonoriented and oriented electrical steel. The AISI designations were adopted in 1946 to eliminate the wide variety in nomenclature formerly used. When originally adopted, the AISI designation number approximated ten times the maximum core loss,* in watts per pound, exhibited by 29 gage (0.36 mm, or 0.014 in.) samples when tested at a flux density of 1.5 T (15 kG) and a magnetic circuit frequency of 60 Hz. Note that fully processed M-36 tested as 0.36 mm (0.14 in.) strip now has a maximum allowable core loss of 4.2 W/kg (1.9 W/lb), not an approximate level of 7.9 W/kg (3.6 W/lb). Low core loss is obtained with higher silicon contents, larger grain size optimization, lower impurity levels, thinner gages, and insulating coatings.

Table 8 Properties of selected electrical steels

AISI type (approximate equivalent)	Nominal (Si + Al) content, %	Thickness		ASTM designation	Maximum core loss at 60 Hz and B = 1.5 T (15 kG)	
		mm	in.		W/kg	W/lb
Nonoriented						
Semiprocessed (ASTM A 683)[(a)]						
M-47	1.10	0.64	0.025	64S350	7.71	3.50
	1.10	0.47	0.019	47S300	6.61	3.00
M-45	1.70	0.64	0.025	64S280	6.17	2.80
	1.70	0.47	0.019	47S250	5.51	2.50
M-43	2.00	0.64	0.025	64S260	5.73	2.60
	2.00	0.47	0.019	47S230	5.07	2.30
M-36	2.40	0.64	0.025	64S230	5.07	2.30
	2.40	0.47	0.019	47S200	4.41	2.00

M-27	2.70	0.64	0.025	64S213	4.69	2.13
	2.70	0.47	0.019	47S188	4.14	1.88
. . .	3.00	0.64	0.025	64S194	4.28	1.94
. . .	3.00	0.47	0.019	47S178	3.92	1.78
Fully processed (ASTM A 677)[b]						
. . .	0.50	0.64	0.025	64F600	13.22	6.00
. . .	0.80	0.47	0.019	47F450	9.92	4.50
M-47	1.05	0.64	0.025	64F470	10.36	4.70
	1.05	0.47	0.019	47F380	8.38	3.80
M-45	1.85	0.64	0.025	64F340	7.49	3.40
	1.85	0.47	0.019	47F290	6.39	2.90
M-43	2.35	0.64	0.025	64F270	5.95	2.70
	2.35	0.47	0.019	47F230	5.07	2.30
M-36	2.65	0.64	0.025	64F240	5.29	2.40
	2.65	0.47	0.019	47F205	4.52	2.05
	2.65	0.36	0.014	36F190	4.19	1.90
M-27	2.8	0.64	0.025	64F225	4.96	2.25
	2.8	0.47	0.019	47F190	4.19	1.90
	2.8	0.36	0.014	36F180	3.97	1.80
M-22	3.2	0.64	0.025	64F218	4.80	2.18
	3.2	0.47	0.019	47F185	4.08	1.85

	3.2	0.36	0.014	36F168	3.70	1.68
M-19	3.3	0.64	0.025	64F208	4.58	2.08
	3.3	0.47	0.019	47F174	3.83	1.74
	3.3	0.36	0.014	36F158	3.48	1.58
M-15	3.5	0.47	0.019	47F168	3.70	1.68
	3.5	0.36	0.014	36F145	3.20	1.45
Oriented						
Fully processed (ASTM A 876)[c]						
M-6	3.15	0.35	0.014	35G066	1.45	0.66
	3.15	0.35	0.014	35H094	2.07[d]	0.94
M-5	3.15	0.30	0.012	30G058	1.28	0.58
	3.15	0.30	0.012	30H083	1.83[d]	0.83
M-4	3.15	0.27	0.011	27G051	1.12	0.51
	3.15	0.27	0.011	27H074	1.63[d]	0.74
. . .	3.15	0.23	0.009	23G046	1.01	0.46
. . .	3.15	0.23	0.009	23H071	1.56[d]	0.71
. . .	3.15	0.27	0.011	27P066	1.45[d]	0.66
. . .	3.15	0.30	0.012	30P070	1.54[d]	0.70

(a) Refer to ASTM A 683-84 and companion specification A 683M-84 (metric) for detailed information.

(b) Refer to ASTM A 677-84 and companion specification A 677M-83 (metric) for detailed information.

(c) Refer to ASTM A 876-87 and companion specification A 876M-87 for detailed information.

(d) *B* (magnetic induction) = 1.7 T (17 kG).

The AISI designations are still in common use, but the newer ASTM designations provide more specific information regarding the grade identified. A typical ASTM designation is 47S200. The first two digits of the ASTM designation indicate the thickness in mm (×100). Following these digits is a letter (C, D, F, S, G, H, or P) that indicates the material type and the respective magnetic test conditions. The last three digits provide an indication of the maximum allowable core loss in units of either (watts/kg) × 100, or (watts/lb) × 100. If the core-loss value is expressed in watts/kg, the grade designation takes the suffix M, indicating an ASTM metric standard. Several ASTM flat-rolled products specifications are written in English and metric versions, such as A 677-84 and its companion metric specification A 677M-83.

Surface Treatments for Electrical Steels

The purpose of the core metal in a motor, generator, or transformer is to offer the best path for the magnetic lines of flux, and its success in this respect is measured by its permeability. Cores are usually composed of a larger number of thin metal laminations that are fabricated by punching from thin sheets of metal, and which are subsequently assembled to form a core.

Interlaminar insulation is necessary for high electrical efficiency in the magnetic core, whether the application is static or rotating. For small cores used in fractional-horsepower motors, an oxide surface on the laminations may insulate the core adequately. Insulations of AISI types C-1, C-2, C-3, C-4, and C-5 are used for more rigorous requirements. Table 9 describes the characteristics of these various core coatings.

Table 9 Types of core plate coatings used for lowering core losses in electrical steels

Core plate, designation	**Description**
C-1	An organic enamel or varnish coating sometimes used for cores not immersed in oil. It enhances punchability and is resistant to ordinary operating temperatures. It will not withstand stress-relief annealing.
C-2	An inorganic insulation consisting of a glass-like film formed during the high-temperature annealing of electrical steel, particularly grain-oriented electrical steel, as the result of the reaction of an applied coating of MgO and silicates in the surface of the steel. This insulation is intended for air-cooled or oil-immersed cores. It will withstand stress-relief annealing and has sufficient interlamination resistance for wound cores of narrow-width strip such as in distribution transformers. It is not intended for stamped lamination because it is abrasive to dies.
C-3	An enamel or varnish coating intended for air-cooled or oil-immersed cores. C-3 enhances punchability and is resistant to normal operating temperatures. It will not withstand stress-relief annealing.
C-4	Consists of a chemically treated or phosphated surface useful for air-cooled or oil-immersed cores. It will withstand stress-relief annealing in relatively neutral atmospheres.
C-5	An inorganic insulation similar to C-4 but with ceramic fillers (such as colloidal silica) added to increase the electrical insulation properties. C-5 can be used in air-cooled or oil-immersed cores and will endure stress-relief annealing.

Source: ASTM A 345

Organic-Type Insulation. Types C-1 and C-3 are organic and cannot be successfully applied to laminations before annealing. They are unsuitable for electrical equipment operated at high temperatures or for power transformers with certain types of coolants. However, they improve the punchability of the sheet steel.

Inorganic-Type Insulation. Inorganic types C-4 and C-5 are used when insulation requirements are severe and when annealing temperatures up to 790 °C (1450 °F) must be withstood. Typical values of interlaminar resistance for these two types are between 3 and 100 Ω· cm/lamination under a pressure of 2070 kPa (300 psi). These coatings also can be made to impart residual tensile stresses in the steel substrate, which can improve magnetic properties.

Core insulation must be sufficiently thin and uniform so as to have no more than 2.0% effect on the lamination factor (solidity of the core). To calculate the required insulation for most operations at power frequency, the square of the resistivity, in ohm-centimeters per lamination, should at least equal the square of the width of the magnetic path, in inches. This usually ensures a negligible interlaminar loss that is less than 1.0% of the core loss.

Ceramic Films. Japanese electrical steel producers have reported significant improvement in core loss as a result of ion plating of TiN and CrN ceramic coatings (Ref 22). Application of these ceramic films on chemically polished grain-oriented electrical steel sheet increased the magnetic flux density by 0.004 to 0.015 T (0.04 to 0.15 kG) and lowered the core loss by 0.12 to 0.20 W/kg (0.05 to 0.09 W/lb). By laser domain refining (see discussion below), it was possible to further improve the core loss by 0.04 to 0.09 W/kg (0.02 to 0.04 W/lb). Using this dual ceramic film/laser treatment, electrical steels with original core losses of 0.88 W/kg (0.4 W/lb) were improved to an ultralow core loss of 0.55 W/kg (0.25 W/lb), which corresponds to an improvement of about 40% (Ref 22).

Laser Magnetic Domain Refinement. Core loss improvements of 2 to 14% can be achieved by rapid scanning (typically 100 m/s, or 325 ft/s) a high-powered focused laser beam across the surface (transverse to the rolling direction) of grain-oriented glass-coated (Si-Mg-P-Al glass) 3% silicon-irons (Ref 23). There is no flame, spark, or smoke generated during this process, which is also referred to as laser scribing, and the material/coating shows no visible surface change. The improvement in core loss is due to a thermal shock imparted to the microstructure which causes slip plane dislocations to form, thereby producing new magnetic domain wall boundaries (Ref 23). By adjusting the spacing of the scanned laser lines, the energy lost due to moving domain walls back and forth under the action of the applied ac field in the transformer is minimized. The laser lines restrict the length of the domains and also act to control the width of the domains. Thus by adjusting the spacing of the laser lines, the domain sizes can be controlled, i.e., refined. Figure 9 illustrates the improvement in core loss as a function of applied field strength for a 0.26 mm (0.0104 in.) thick silicon steel sheet.

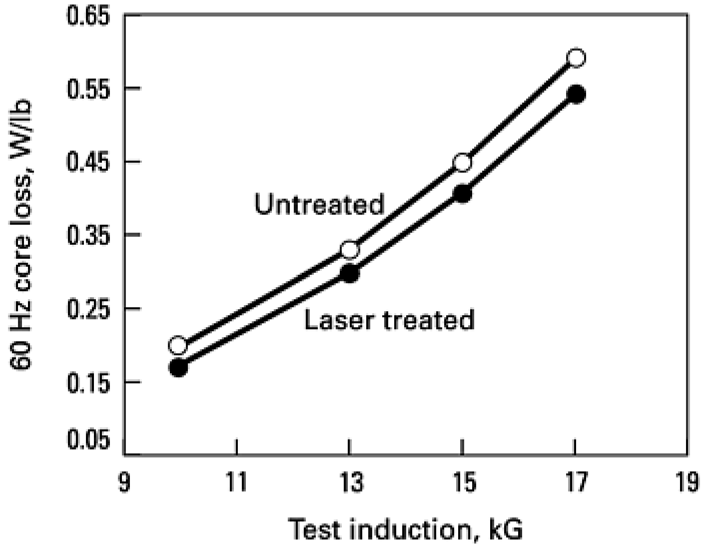


Fig. 9 Effect of laser scribing on the core loss of a high-permeability grain-oriented electrical steel. Source: Ref 23

References cited in this section

21. D.W. Dietrich, Magnetically Soft Materials, *Properties and Selection: Nonferrous Alloys and Special-Purpose Materials,* Vol 2, *ASM Handbook* (formerly 10th ed., *Metals Handbook*), ASM International, 1990, p 761-781
22. Y. Inokuti, K. Suzuki, and Y. Kobayashi, Grain Oriented Silicon Steel Sheet With New Ceramic Films Characterized by Ultra-Low Iron Loss, *Materials Transactions, J/M,* Vol 33 (No. 10), 1992, p 946-952
23. G.L. Neiheisel, Laser Magnetic Domain Refinement, LIA Vol 44, *Proc. Conf. ICALEO 1984, p 102-111*

Note cited in this section

* The term *core loss,* as applied to electrical steel, is a quantitative measure of the rate at which electrical energy is converted to thermal energy during 50 or 60 cycle ac magnetization. Core loss is separated into two components: hysteresis loss and eddy current loss.

Surface Engineering of Heat-Resistant Alloys

Revised by F.S. Pettit, University of Pittsburgh

Introduction

HEAT-RESISTANT ALLOYS (solid-solution-strengthened or precipitation-hardened nickel-, iron-, or cobalt-base alloys) are often referred to as superalloys, because of their strength, oxidation resistance, and corrosion resistance at elevated service temperatures (650 to 1205 °C, or 1200 to 2200 °F). The surfaces of parts made from these alloys must be cleaned of contaminants, of which there are several types.

Shop soils, such as oil, grease, and cutting fluids, must be removed by solvents or soaps. The article "Solvent Cold Cleaning and Vapor Degreasing" in the Section "Surface Cleaning" of this Volume describes those contaminants and the procedures that must be used to remove them. The Section "Environmental Protection Issues" contains articles that provide guidelines for selecting appropriate solvents or suitable alternatives.

The removal of metallic contaminants, tarnish, and scale resulting from hot-working or heat-treating operations on nickel-, cobalt-, and iron-base heat-resistant alloys is described in this article; a brief description of applicable finishing and coating processes is also provided. For additional information on heat-resistant alloys, see Volume 1 of the *ASM Handbook.*

Metallic Contaminant Removal

Parts made from heat-resistant alloys can accumulate traces of other metals on their surfaces after contacting cutting tools, forming dies, and heat-treating fixtures. Although metal contamination is not always harmful, its presence can be highly deleterious in certain cases. For example, Inconel X-750 may be unaffected by traces of zinc from drawing dies, but even the smallest particle of aluminum will readily alloy with the Inconel at elevated temperatures and degrade the corrosion resistance and mechanical integrity of the affected areas. Copper is another example of a metal that may affect some nickel-base alloys when they are subsequently exposed to high temperatures. Therefore, all surface contaminants should be removed from heat-resistant alloys before they are heat treated or subjected to service at elevated temperatures.

In operations such as cutting and forming, the use of lubricants can either prevent or sharply reduce metal contamination. This is the preferred practice, because lubricants can be removed easily and cheaply, if they have not been baked or fired.

When contamination is unavoidable, testing is recommended to determine the seriousness of the contamination. After heat-treating operations, metallographic examination can be conducted to detect alloy diffusion, and bend or hardness tests can be conducted to detect embrittlement. For example, lead can be detected by the yellow precipitate that forms when a test solution of chromic acid (10 wt%), sodium chlorate (1.5 wt%), and water (88.5 wt%) is applied to the suspected surface at temperatures ranging from 21 to 60 °C (70 to 140 °F).

Mechanical removal methods used for metallic contaminants include dry or wet abrasive blasting with metal-free abrasives, polishing with ceramic materials, and wet tumbling. The shape of a part, the required surface finish, the allowable loss of gage, and residual stress considerations will determine the suitability of these mechanical methods.

Chemical removal methods, however, are used more often than mechanical methods to remove metallic contaminants. A typical procedure for chemically removing iron, zinc, and thin films of lead is to first perform vapor degreasing or alkaline cleaning, and then immerse the parts in a 1:1 solution (by volume) of nitric acid (1.41 sp gr) and water for 15 to 30 min at approximately 35 °C (95 °F). Water rinsing, followed by drying, completes the process.

Another procedure that has been successful in removing brass, lead, zinc, bismuth, and tin from nickel-base and cobalt-base alloys involves vapor degreasing or alkaline cleaning, followed by soaking at room temperature in a solution of nitric acid (54 g/L, or 7.22 oz/gal), acetic acid (150 to 375 g/L, or 20 to 50 oz/gal), and hydrogen peroxide (19 to 64 g/L, or 2.5 to 8.5 oz/gal). Depending on the severity of the contamination, the soaking time can vary from 20 min to 4 h, as determined by visual observation of the reaction. After this treatment, parts must be rinsed thoroughly in water and dried. When possible, a test specimen should be immersed for the maximum time anticipated and then examined for chemical attack before the first load of parts is processed.

Nickel-base alloys should be acid etched to prepare for subsequent nondestructive inspection. The etching process removes smeared metal that may be present as a thin surface layer after machining and/or blast cleaning. The parts can be etched by immersing them in a bath containing hydrochloric acid (80%), hydrofluoric acid (13%), and nitric acid (7%) to remove the disturbed or smeared layer. This bath may leave smut that must be removed by a second bath containing iron chloride (22%), hydrochloric acid (75%), nitric acid (2%), and water. After being rinsed and dried, the parts can undergo visual and penetrant inspections. The extent of etching depends on the depth or thickness of the smeared layer. All of this layer should be removed. However, overetched parts will retain excessive amounts of penetrant.

Tarnish Removal

Tarnish, which is a thin oxide film, does not always have a harmful effect on the end use of parts made from heat-resistant alloys. In fact, it can even be useful, such as when it functions as a bond for paint, a barrier to prevent diffusion from another alloy, or a retardant to further oxidation. However, other functional requirements can necessitate the removal of tarnish from parts. Tarnish should always be removed before welding or brazing.

Abrasive cleaning methods, such as those used to remove metallic contaminants, are also used to remove tarnish. The applicability of these methods is determined by part shape, required surface finish, and allowable loss of gage or dimension.

However, abrasive cleaning can remove some metal and degrade surface finishes. Therefore, flash pickling is used more often than abrasive cleaning to remove tarnish. A typical flash-pickling formula uses nitric acid (1.41 sp gr; 23 vol%), hydrofluoric acid (1.26 sp gr; 4 vol%), and water (73 vol%). Parts are immersed in this solution for 1 to 5 min at approximately 52 °C (125 °F). Warming the parts in hot water before flash pickling speeds tarnish removal. Water rinsing and drying must follow pickling.

Oxide and Scale Removal

The most widely used methods for removing oxides or scale from heat-resistant alloys, in order of decreasing preference based on economic considerations, are acid pickling, abrasive cleaning by tumbling or blasting, and descaling in molten salt. Alkaline scale conditioning is helpful in modifying the scale to facilitate its removal by these methods. When extremely heavy oxide layers must be removed, grinding is an appropriate preliminary operation. Combinations of two or more methods are often used. Before these removal methods are discussed, the characteristics of the various products that need to be removed are described.

Oxide films will form on parts that are heated in reducing atmospheres, out of contact with air. Sometimes, these oxides can be removed by immersing the parts for 5 to 15 min in a tarnish-removing, flash-pickling bath, such as that with the formulation given above. However, most heat-resistant alloys form a tenacious coating in the presence of carbon monoxide or water because of their high content of oxide-forming metals, such as nickel, cobalt, and chromium. The resulting oxides vary widely with alloy composition and furnace atmosphere. Usually, pickling is required for their removal. Scale conditioners are useful.

Scale develops on hot-forged, hot-formed, or heat-treated parts that are processed in air. Usually, scale is tenacious and occurs in all gradations, including thick layers that result from heating in an oxidizing furnace using high-sulfur fuels. The scale that forms under such conditions has a dull, spongy appearance. Fine cracks may be present, and patches of scale

may break from the surface. The underlying metal is rough and cannot be corrected by pickling. In these extreme conditions, grinding or abrasive blasting to sound metal, followed by flash pickling, is recommended.

Scale conditioning is used to soften, modify, or reduce scale to promote easier and more uniform acid pickling, but is seldom required to remove discolorations or thin interference coatings. A scale-conditioning bath consists of a highly alkaline aqueous solution, sometimes containing complexing and chelating compounds. The main purpose of these agents is to solubilize the scale as much as possible. The performance of a particular chelating agent depends on the affinity of the compound for the metal ions present, the pH of the scale-conditioning solution, and the physical and chemical composition of the scale. Typical multicycle descaling operations, including scale conditioning, are defined in Tables 1 and 2.

Table 1 Procedure for removing scale from heat-resistant alloys

Operation	Time, min	Temperature		Solution	Concentration
		°C	°F		
Precleaning cycle					
Vapor degreasing	5-10	87-88	185-190	Stabilized trichloroethylene	. . .
Emulsion cleaning	10-20	54-66	130-150	Emulsion cleaner	20 vol%
Scale-conditioning cycle					
Alkaline chelating	15-30	125-135	260-275	Caustic solution containing alkanol amines and aliphatic hydroxy acids	. . .
Alkaline oxidizing	60-120	95-105	205-220	Potassium permanganate	5 wt%
				Sodium hydroxide	20 wt%
				Water	Remainder
Pickling cycle					
Acid pickling	5-30	49-60	120-	Hydrofluoric acid	4 wt%

Table 2 Procedure for removing scale from Inconel alloys

Operation	Time	Temperature		Solution[a]	Concentration[a]
		°C	°F		

Alkaline conditioning	1-2 h	96-105	205-220	Sodium hydroxide	20 wt%
				Potassium permanganate	5 wt%
Rinse	15-30 s	Not heated	Not heated	Water quench and water spray	. . .
Acid pickling	5-10 min	60-71	140-160	Sulfuric acid (1.83 sp gr)	7.5 vol%
				Hydrochloric acid (1.16 sp gr)	12 vol%
Rinse	15-30 s	Not heated	Not heated	Water	. . .
Acid pickling	10-20 min	60-71	140-160	Nitric acid (1.41 sp gr)	20 vol%
Rinse	15-30 s	Not heated	Not heated	Water	. . .
Acid pickling	5-60 min[b]	49-54	120-130	Hydrofluoric acid (1.26 sp gr)	3.7 vol%
				Nitric acid (1.41 sp gr)	22 vol%
Rinse	15-30 s	Not heated	Not heated	Water	. . .

(a) Undefined remainder is water.

(b) Type of oxide will determine immersion time required; until immersion time is established, inspect frequently to avoid overpickling.

Minimal scale removal occurs during treatment in the alkaline scale-conditioning bath. Further treatment in highly alkaline solutions containing a strong oxidizing material, such as potassium permanganate, is often necessary. The scale on heat-resistant alloys sometimes contains carbon and incompletely burned and polymerized residues, as well as metallic oxides. These organic components react with the oxygen that is released by the alkaline oxidizing bath.

Acid Pickling. After the scale is conditioned, it is subjected to acid pickling, during which most of the high-temperature scale either breaks away from or becomes so loosely attached to the parts that pressure rinsing with water completes the descaling. The acid pickle is usually a dilute nitric acid or a hydrofluoric-nitric acid solution. In addition to removing scale, pickling solutions that contain nitric acid will remove many surface contaminants through oxidation. However, because the acid solution attacks the base metal, it is necessary to limit the pickling time to prevent excessive metal loss or metal surface roughening.

Parts made from alloys that are high in aluminum and titanium, such as M252 and René 41, must undergo a special procedure before welding or brazing. When parts are in the solution-treated condition and descaling is required, they are treated in a scale-conditioning solution, as previously described, after which they are immersed in a solution of nitric acid (30 wt%) and hydrofluoric acid (3 wt%) for 5 to 10 min. Alloys in the aged condition are descaled anodically in an acid solution. A solution made for this procedure should contain sulfuric acid (75 wt%) and hydrofluoric acid (3 wt%). It should be operated using a current density of 215 to 430 A/mm^2 (20 to 40 A/ft^2) and graphite cathodes. The material should be immersed in the electrolytic cleaning bath for 3 to 12 min, and the operation will be complete when the amperage drops to nearly zero. Sodium sulfite (1.6 wt%) is used to reactivate the solution after a period of operation.

Alloys that contain less than approximately 12% Cr, unstabilized austenitic stainless steels, and martensitic and ferritic stainless steels can experience high metal loss or intergranular attack by acids during pickling. When the susceptibility of a material to these problems is unknown, it is safer to perform mechanical descaling than acid pickling. In one specific instance, acid descaling was proven to cause intergranular attack and a subsequent loss of ductility in aged René 41.

Weld areas typically differ, in terms of composition and structure, from the base metal and react differently to conditioning and pickling cycles. Weld areas or heat-affected zones are often susceptible to selective attack during pickling. Although inhibitors can eliminate or reduce this selective attack, it is preferable to use abrasive or other mechanical descaling methods, rather than acid pickling, to remove scale from welded parts, unless a safe pickling procedure has been found for a given application.

Hydrogen embrittlement does not occur in nickel-, cobalt-, or austenitic iron-base alloys as a result of aqueous descaling.

Abrasive blasting with dry aluminum oxide can be used to remove oxide and scale from all types of wrought and cast heat-resistant alloys. Silicon carbide is more expensive than aluminum oxide and is seldom used. Silica (silicon dioxide, or sand) has a limited application because of its lack of cutting ability. It is sometimes used to clean refractory metal forgings prior to pickling. Grit sizes as coarse as No. 30 (0.59 mm, or 0.023 in.) are recommended for cleaning forgings and castings. Finer grits, such as Nos. 90 and 100 (0.17 and 0.15 mm, or 0.0065 and 0.0059 in., respectively), are used for general blasting.

Metallic shot and grit should not be used to descale heat-resistant alloys unless their use is followed by pickling to remove metal contamination. For parts that must be welded or brazed, or that have highly tenacious scales produced by furnace atmospheres, pickling after dry abrasive cleaning is recommended, regardless of the abrasive used.

Wet abrasive blasting, also referred to as vapor honing, is also used to clean heat-resistant alloys. This process uses Nos. 200 to 1250 silica abrasive particles (0.074 to 0.010 mm, or 0.0029 to 0.0004 in.) mixed with water to produce a slurry that removes loose scale, discoloration, and soils. Metal loss is not excessive when normal pressures and exposure times are used.

When spherical beads made of high-quality optical crown glass are used as the abrasive, stock loss is minimized. Bead sizes of 0.038 to 0.074 mm (0.0015 to 0.0029 in.) are generally used, and blasting pressures are kept below 410 kPa (60 psi) to prevent the beads from fracturing.

Surfaces that have been wet blasted are usually suitable for welding, brazing, electroplating, and final inspection processes. Further cleaning is seldom necessary. Exceptions are alloys with a high titanium and aluminum content, which require the special procedure discussed in the section "Acid Pickling" in this article.

Most of the general advantages and limitations associated with the abrasive cleaning of steel will also apply to heat-resistant alloys. However, there is a risk of contamination from either metallic abrasives or abrasives that have been used to clean parts made from metals of widely different compositions. For example, heat-resistant alloys should not be blasted with abrasive material that has been used to clean low-alloy steel, aluminum, copper, or magnesium. However, abrasives used to clean titanium and corrosion-resistant steels have been used to clean heat-resistant alloys without serious contamination. The flash pickling of these alloys after abrasive cleaning provides additional assurance that no harmful surface contamination remains. Detailed information on equipment and procedures for dry and wet blasting is provided in the Section "Finishing Methods" in this Volume.

Wet tumbling by the barrel or vibratory method can be used to descale heat-resistant alloys if the shape and size of the parts are suitable. The removal of burrs and sharp edges is accomplished in the same operation. Shop soils are also removed, thus eliminating the need for preliminary degreasing.

Parts are tumbled or vibrated in a mixture of acid descaling compound and metal-free abrasives and then subjected to a neutralizing cycle. Precautions regarding metal contamination are similar to those noted above for abrasive blasting.

Pickling is required after tumbling and before resistance welding to remove residual smut, which can cause poor-quality weldments. There is less need for pickling prior to fusion welding, unless an inspection of the weldments reveals porosity or inclusions that are a result of pickup from the tumbling process.

Wire brushing is sometimes used to remove very light scale or surface discoloration. All brushes used on heat-resistant alloys must have stainless steel bristles.

Salt-bath descaling is an effective first step in removing scale from heat-resistant alloys. The process is generally more expensive than acid pickling, particularly if production is intermittent, because of the cost of maintaining the bath during idle time. The electrolytic salt bath used to descale heat-resistant alloys contains fused caustic soda, rather than sodium hydride. The parts and the tank are alternately negative and positive poles of a direct current circuit.

This fused caustic soda bath, which contains oxidizing salts such as sodium nitrate, is operated at 425 to 540 °C (800 to 1000 °F). It is slightly more effective than the sodium hydride bath on high-chromium alloys, such as type 310 stainless steel, and cobalt-chromium-nickel-base alloys, such as L-605. Processing steps are similar. Parts are immersed in the oxidizing bath for 5 to 15 min, quenched in water, soaked in a solution of 5 to 10% sulfuric acid at 70 °C (160 °F) for 1 to 5 min, and then dipped in a solution of 15 to 20% nitric acid and 2 to 4% hydrofluoric acid at 54 to 60 °C (130 to 140 °F) for 2 to 15 min.

A typical sequence for sodium hydride descaling and pickling is given in Table 3. Equipment details and other information on salt-bath descaling are provided in the Section "Surface Cleaning" in this Volume.

Table 3 Procedure for sodium hydride descaling and acid pickling of heat-resistant alloys

Operation	Time	Temperature		Solution[a]	Concentration, vol %[a]
		°C	°F		
Sodium hydride descale	1-2 h	370-390	700-730	Sodium hydroxide	. . .
Quench	15-30 s	Not heated	Not heated	Water	. . .
Neutralizing rinse	1-3 min	RT to 60	RT to 140	Sulfuric acid	2-10
Brightening pickle	5-15 min	54-60	130-140	Hydrofluoric acid Nitric acid	2-4 15-20
Rinse	15-30 s	Not heated	Not heated	Water	. . .
High-pressure spray wash	[b]	Not heated	Not heated	Water[c]	. . .

(a) Governed by shape of part.

(b) 1 min on parts with accessible surfaces.

(c) Water pressure of 690 kPa (100 psi)

Applicable Finishing and Coating Processes

Many finishing operations that are commonly used for steel and other metals are not required for the heat-resistant alloys for several reasons. First, these alloys are inherently resistant to corrosion in a wide range of environments. Second, the applications of parts made from these alloys do not typically require a polished finish.

The oxide coating that is obtained during processing is frequently of value to heat-resistant alloys that are subjected to elevated temperatures in service. Consequently, the dense, tenacious oxide that develops on formed or machined finished parts during final heat treatment is allowed to remain as protection against further oxidation.

Polishing of heat-resistant alloys is sometimes used to obtain a desired surface finish, as well as to remove light scale or oxide from parts that are to be welded or brazed. Silicon carbide in various grit sizes is commonly used to prepare surfaces for brazing.

Surfaces are usually prepared for welding by polishing with No. 90 grit aluminum oxide, set up with sodium silicate on a cloth wheel. Discoloration can be removed by polishing with No. 120 grit aluminum oxide, used with a greaseless compound and a cloth wheel. Buffing is seldom required for the finishing of heat-resistant alloys.

Electroplating. Chromium, copper, nickel, and silver are sometimes electroplated on heat-resistant alloys in order to:

- Prepare for brazing
- Deposit brazing metal
- Provide antigalling characteristics
- Repair expensive parts or correct dimensional discrepancies

Conventional nickel plating processes are often used to assist in brazing. Deposits can vary in thickness from 2.5 to 25 μm (0.1 to 1 mil). Alloys that contain titanium or aluminum will require the thicker deposits.

Silver and copper are the metals most often deposited as actual brazing materials. Some brazing alloys are deposited as separate layers of their various constituent metals on a weight-percentage basis. Plate thickness depends on the amount of metal needed for brazing.

Electrodeposited silver or nickel is used in special applications for antigalling purposes. Either nickel or chromium can be used to repair worn parts or build up dimensions. Procedures and electrolytes for plating these metals are described in the Section "Plating and Electroplating" in this Volume.

Ceramic coatings are frequently applied to heat-resistant alloys to increase the oxidation resistance of parts exposed to extremely high temperatures, such as gas turbine and missile components. Several types of ceramics are currently used, and some serve as thermal barriers, as well. The article "Ceramic Coatings and Linings" in this Volume describes the relevant procedures.

Diffusion coatings of aluminum, chromium, silicon, or combinations thereof, also are used to protect heat-resistant alloy parts from high-temperature corrosion and to prolong part life. The coating of engine exhaust valves with aluminum is a common example. Procedures for diffusion coating are described in the Section "Vacuum and Controlled-Atmosphere Coating and Surface Modification" in this Volume.

Shot peening is currently used to improve the mechanical properties of compressor blades, turbine-blade dovetails, and latter-stage turbine-blade airfoils by introducing favorable patterns of residual stress. Although all turbine-blade dovetails are peened with steel shot, glass beads are sometimes favored over metallic shot in other shot-peening applications. The advantages of glass beads are that they:

- Pose no risk of metal contamination
- Remove virtually no metal
- Are available in smaller sizes than metallic shot and can therefore be used to peen areas that are difficult to reach when using metallic shot

However, glass beads are not equivalent to metal shot for improving mechanical properties. Details on peening are given in the Section "Finishing Methods" in this Volume.

Cleaning and Finishing Problems and Solutions

The complex oxides and scale that form on heat-resistant alloys often create production problems and require the use of special procedures to obtain the desired surfaces. The examples described below, all of which are drawn from actual production experience, identify cleaning and finishing problems and the procedures used to solve them.

Example 1. After heat treatment, turbine combustion chambers made from Hastelloy X sheet exhibited irregular scale adherence, variations in surface finish, and loss of formability. An investigation disclosed that residual shop soils, such as lubricants, marking inks, and handprints, remained on the parts despite the solvent cleaning and vapor degreasing to which the parts were subjected before being heat treated. These soils were decomposing during heat treatment and causing carbon diffusion.

The substitution of electrolytic alkaline cleaning for the methods previously used eliminated the difficulty. In this procedure, parts were immersed for 5 min in a bath compounded to Federal Specification P-C-535 and operated at 82 to 93 °C (180 to 200 °F) using 6 to 8 V. Parts were anodic in the electrical circuit. The scale was easily removed by subjecting the heat-treated parts to a 5 min immersion in a room-temperature acid pickling bath composed of 70% nitric acid (20 to 30 vol%), 60% hydrofluoric acid (10 to 15 vol%), and water (55 to 70 vol%).

Example 2. The descaling of alloys A-286 and S-816 was inadequate when this procedure was used:

- Descale in an oxidizing salt bath at 480 to 495 °C (900 to 925 °F) for 25 min, and then quench in cold water
- Immerse in a solution of sulfuric acid (23 vol%) for 10 to 15 min, and then rinse with cold water
- Immerse in a solution of 25% nitric acid and 3% hydrofluoric acid for 2 min, and then rinse in cold water
- Immerse in 30% nitric acid for 5 min, rinse in cold water, rinse in hot water, and then dry

However, changing the procedure to the following proved to be successful:

- Descale in an oxidizing salt bath at 480 to 495 °C (900 to 925 °F) for 10 min, and then quench in cold water
- Immerse in 23% sulfuric acid for 5 min, and then rinse in cold water
- Immerse for 1 min in a solution of 25% nitric acid and 3% hydrofluoric acid, rinse in cold water, rinse in hot water, and then dry
- Reimmerse in oxidizing salt bath at 480 to 495 °C (900 to 925 °F) for 10 min, and then quench in cold water
- Immerse for 30 s in solution of 25% nitric acid and 3% hydrofluoric acid, and then rinse in cold water
- Immerse for 5 min in 30% nitric acid, rinse in cold water, rinse in hot water, and then dry

Example 3. Excessive zinc contamination of formed parts made from 19-9 DL alloy was traced to the contamination of drawing lubricants that had been stored too closely to zinc dies that were being finished by sanding. The zinc was removed from the parts by chemicals (see the section "Chemical Removal Methods" in this article). A recurrence of this problem was prevented by improved housekeeping and by direct instructions to personnel.

Example 4. It was not feasible to broach turbine disks made from D-979 alloy in the solution-treated and aged condition. The disks were first broached in the solution-treated condition, and then the surfaces were protected by a flash of nickel (Wood's plating) and a subsequent overlay of copper, so that they could undergo aging at temperatures higher than 730 °C (1350 °F) in a reducing gas atmosphere. After aging, the plated copper and nickel were removed from the disks by the procedures given in Tables 4 and 5.

Table 4 Procedure for stripping copper plate

Composition of bath	
Chromic oxide, g/L (oz/gal)	360 (48)
Sulfuric acid (concentrated), mL/L	39-55 (5-7)
Water	Remainder
Temperature	Room temperature
Time	Varies with thickness of plate

Table 5 Procedure for stripping nickel plate

Composition of bath	
Sodium cyanide, g/L (oz/gal)	90 (12)
Nitroaromatics, g/L (oz/gal)	60 (8)
Water	Remainder
Temperature, °C (°F)	49-66 (120-150)
Time	Varies with thickness of plate

Stripping the chemicals and using a light vapor blast to remove smut resulted in clean, dimensionally unaltered parts and had no detrimental effect on mechanical properties. The procedures defined in Tables 4 and 5 were based on the available facilities. A cheaper and faster method would be to strip the copper and nickel in a nitric acid solution (50 vol%) at room temperature.

Example 5. Conventional salt-bath descaling and pickling failed to remove all annealing scale from stampings made from 19-9 DL, Hastelloy X, Inconel 600, and Inconel X-750. The sequence of operations performed on these stampings was either to form, degrease, remove metal contamination, anneal, and descale, or to immerse in molten salt and then pickle. The difficulty was traced to the open-hearth, gas-fired annealing furnaces. It was found that the atmosphere was reducing while the burners were on, and that a thin, tight scale was produced.

A satisfactory remedy was to adjust the burners to bring the oxygen content to 3%. The resulting scale was loose and easily removed by the usual descaling and pickling procedures.

Example 6. Jet-engine combustion liners made from Hastelloy X require three in-process anneals. Forming without first removing scale required expensive carbide dies, and the resulting liners were unacceptable. The problem was solved by installing a salt-bath descaling line. The following cycle was satisfactory for descaling:

- Immerse in an oxidizing salt bath at 480 °C (900 °F) for 10 to 20 min, and then rinse, first in cold water and then in water at 82 °C (180 °F)

- Immerse in a solution of 24% hydrochloric acid for 2 to 10 min, and then rinse in cold running water
- Immerse in nitric-hydrofluoric acid for 2 to 10 min, rinse in cold running water, hose off, and then dry

Example 7. Small cracks appeared in welded 19-9 DL tubing (1.3 mm, or 0.050 in. wall) after annealing. The processing sequence was to form tubing from flat stock, degrease, perform an automatic seam weld, anneal, and descale. The tubing was formed on dies of zinc alloy, but was not dezinced before being welded. Small amounts of zinc on the surface near the weld melted during welding. This initiated zinc diffusion, and the residual stresses around the weld were sufficient to crack the embrittled material. The problem was solved by pickling the tubing in 20% nitric acid to remove the zinc before welding.

Surface Engineering of Aluminum and Aluminum Alloys

Introduction

ALUMINUM OR ALUMINUM ALLOY products often have various types of finishes applied to their surfaces to enhance appearance or improve functional properties. This article discusses the methods employed in the cleaning, finishing, and coating of aluminum.

Acknowledgements

The information in this article is largely taken from:

- Cleaning and Finishing of Aluminum and Aluminum Alloys, *Metals Handbook,* 9th ed., Vol 5, American Society for Metals, 1982, p 571-610
- Porcelain Enameling, *Metals Handbook,* 9th ed., Vol 5, American Society for Metals, 1982, p 509-525
- Shot Peening, *Metals Handbook,* 9th ed., Vol 5, American Society for Metals, 1982, p 138, 140-145

Abrasive Blast Cleaning

One of the simplest and most effective methods for cleaning aluminum surfaces is by blasting with dry nonmetallic or metallic abrasives. Although this method is normally associated with the cleaning of aluminum castings, it is also used to prepare surfaces of other product forms for subsequent finishes, such as organic coatings. In addition to cleaning, blasting is used to produce a matte texture for decorative purposes.

Abrasive blasting is an efficient means of removing scale, sand, and mold residues from castings. Because castings typically are thick, they generally suffer no distortion from the process. Blast cleaning of parts with relatively thin sections is not recommended, because such parts are readily warped by the compressive stresses that blasting sets up in the surface; coarse abrasives can wear through thin aluminum sections. Typical conditions for dry blasting with silica abrasive are given in Table 1.

Table 1 Conditions for abrasive blast cleaning of aluminum products with silica

Grit size	Mesh	Nozzle diameter		Nozzle to work[(a)]		Air pressure	
		mm	in.	mm	in.	kPa	psi
20-60	Coarse	10-13	$\frac{3}{8}$ - $\frac{1}{2}$	300-500	12-20	205-620	30-90
40-80	Medium	10-13	$\frac{3}{8}$ - $\frac{1}{2}$	200-350	8-14	205-620	30-90

100-200	Fine	6-13	$\frac{1}{4}$ - $\frac{1}{2}$	200-350	8-14	205-515	30-75
Over 200	Very fine	13	$\frac{1}{2}$	200-300	8-12	310	45

(a) Nozzle approximately 90° to work

Washed silica sand and aluminum oxide are most commonly used for abrasive blast cleaning of aluminum alloys. Steel grit is sometimes used and, because of the fragmenting characteristics of silica, is often preferred. It also has a longer life, which lowers cleaning costs. However, when an aluminum surface is blasted with grit, steel particles become embedded, and unless they are removed by a subsequent chemical treatment, they will rust and stain the surface. It is good practice to remove particle contamination with a nitric acid pickle to prevent degradation of corrosion resistance. A 20-min soak in 50% nitric acid solution at ambient temperature will dissolve embedded or smeared iron particles, but it will not remove silica or aluminum oxide. When aluminum is blasted with No. 40 or 50 steel grit, a 9.5 mm ($\frac{3}{8}$ in.) diameter nozzle and air pressure at about 276 kPa (40 psi) are commonly used. Organic materials such as plastic pellets and crushed walnut shells also are used to blast clean aluminum, often for the removal of carbonaceous matter.

Stainless steel shot is sometimes used for cleaning aluminum surfaces. Shot blasting is used as a preliminary operation for developing a surface with a hammered texture. An attractive finish is produced when this textured surface is bright dipped and anodized. In addition, the varying degrees of matte texture that can be produced by blasting offer many decorative possibilities. Blasting is often used to produce the maximum diffuseness of the reflectivity of a surface. For example, aluminum army canteens are blasted as a final finish to reduce glare. Glass bead blasting offers another approach to cleaning and producing diffuse surfaces.

Sandblasting with a fine abrasive produces a fine-grain matte finish on wrought or cast aluminum products. For plaques, spandrels, and related decorative architectural applications, sandblasting the background and polishing or buffing the raised portions of the surface produces an effect known as highlighting.

The matte finish produced by abrasive blasting is highly susceptible to scratching and to staining from fingerprints. Therefore, matte-finish surfaces usually are protected by an anodic coating or clear lacquer. Anodizing is the more popular protective treatment, because it does not alter the original texture of a surface. Clear lacquers smooth out roughened surfaces and produce various degrees of gloss, which may be undesirable. Anodizing of a blasted aluminum surface results in a gray color because of embedded abrasive particles in the surface. This color frequently is nonuniform because of variations in blasting conditions, such as nozzle-to-work distance, direction or movement of the nozzle, and air pressure.

Blasting conditions can be closely controlled by the use of specially designed equipment. Uniform movement of the work on conveyors, established nozzle movement, constant velocity of the abrasive, and controlled size of grit contribute to better color uniformity of subsequently anodized surfaces.

The nonuniform appearance that results from blasting can be corrected by bleaching prior to anodizing. Bleaching is done by deep etching in a solution of 5% sodium hydroxide at 40 to 65 °C (100 to 150 °F) to remove metal that contains embedded abrasive. Some trial and error may be necessary to determine etching time for specific conditions. If the surface is not etched enough, a mottled appearance may result. Embedded abrasive can also be removed with a solution of nitric acid and fluoride used at room temperature.

Care should be exercised when selecting the aluminum or aluminum alloy to be sandblasted. For example, alloy 1100, which contains 99% Al, provides a transparent anodic finish; alloys rich in manganese, silicon, and copper, on the other hand, are colored when anodized. Alloy segregation can occur in high-magnesium alloys, and pitting will result unless special pretreatments are used. Table 2 lists several typical applications for abrasive blast cleaning of aluminum products, indicating the type and size of abrasive used and typical production rates.

Table 2 Applications for abrasive blast cleaning of aluminum products

Automatic rotary equipment with five nozzles was used for blasting of all parts except the cake pan, for which a hand-operated single-nozzle setup was used.

Product	Size		Abrasive		Pieces, h
	mm	in.	Type	Mesh size	
Blasting to prepare for organic coating					
Cake pan	280 by 380 by 51	11 by 15 by 2	Alumina	100	60
Frying pan	250 mm diam	10 in. diam	Alumina	100	260
Griddle	6775 mm^2	10.5 $in.^2$	Alumina	100	225
Sauté pan	200 mm diam	8 in. diam	Alumina	100	250
Blasting for appearance produced					
Army canteen[(a)]	. . .	. . .	Steel	80	420
Cocktail-shaker body[(b)]	100 mm diam by 180	4 in. diam by 7	Steel	80	375

(a) 1 qt army canteen blasted for reduction of light reflectivity.

(b) Blasted for decorative effect

Wet blasting mixes a fine abrasive with water to form a slurry that is forced through nozzles directed at the part. Abrasive grits from 100 to 5000 mesh may be used. Wet blasting is generally employed when a fine-grain matte finish is desired for decorative purposes.

An attractive two-tone finish on appliance trim can be obtained by contrasting a buffed finish with a wet-blasted finish. Aluminum firearm components and eyeglass parts such as frames and temples often are wet-blasted to produce fine matte finishes. In these applications, anodic coatings, either plain or colored, are used to protect without distorting the intended surface texture.

Typical wet blasting procedures are listed in Table 3. Wet blasting is also used to prepare surfaces for organic or electroplated coatings. Ultrafine glass bead blasting is an alternative to wet blasting.

Table 3 Conditions for wet blasting of aluminum-base materials

At a nozzle-to-work distance of 75 to 100 mm (3 to 4 in.) and an operating pressure of 550 kPa (80 psi)

Operation	Abrasive	
	Type	Mesh size
Deburr and clean	Alumina	220
Blend and grind	Silica flour	325
Lap and hone	Glass	1000
	Diatomite	625-5000

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Barrel Finishing

Barrel finishing is a low-cost method of smoothing sharp edges, imparting a matte finish, and preparing surfaces for anodizing, painting, or plating. Many small aluminum stampings, castings, and machined parts are cleaned, deburred, and burnished by barrel finishing. In most instances, the main objective is deburring and/or burnishing, with cleaning being an accidental benefit of the treatment. Deburring sometimes is the final barrel operation, but more often it is followed by burnishing to obtain a smoother finish or one that is better suited to anodizing or plating. Parts that have only been deburred are often painted. Burnished parts are frequently anodized for protection.

Small aluminum parts are sometimes tumbled dry in media such as pumice and hardwood pegs, hardwood sawdust, or crushed walnut shells to remove burrs and improve the finish. However, this method is relatively inefficient compared to the more widely used wet process.

All aluminum alloys can be safely finished by wet barrel methods. Limitations imposed by workpiece size and shape are essentially the same as for steel and other metals. There are two general areas in which wet barrel finishing of aluminum parts is more critical than in processing similar parts made of steel. First, there is danger of surface contamination by ferrous metals, caused by the use of either a steel barrel or a steel medium. Second, the pH of the compounds is more critical when processing aluminum, because the metal is susceptible to etching by both acids and alkalis, and because gas generated during chemical attack can build up pressure in the barrel and cause serious accidents. Barrels must be vented when processing aluminum. Compounds that are nearly neutral (pH of about 8) are recommended, although some alloys can be safely processed in compounds having a pH as high as 9.

Barrels used for aluminum are basically the same as those used for processing steel. However, barrels made of steel or cast iron should be lined with rubber or similar material to prevent contamination. A preferred practice is to use specific barrels exclusively for processing aluminum.

Deburring is done by tumbling the work in a nonlubricating compound that contains abrasives. In most instances, media also are used to cushion the workpieces and increase the abrasive action. Synthetic detergents mixed with granite fines or limestone chips are usually preferred as the compound for deburring aluminum; aluminum oxide and silicon carbide are not desirable because they leave a smudge that is difficult to remove. High water levels, completely covering the mass, are used during deburring to assist in maintaining fluidity of the mass and to help prevent the medium from becoming glazed and losing cutting action. Deburring can also be accomplished by using vibratory units with synthetic abrasives.

Barrel burnishing is used to produce a smooth, mirrorlike finish on aluminum parts. Bright dipping immediately prior to burnishing aids in producing desired results. Other preliminary treatments also are helpful in specific instances, particularly for cast aluminum parts. One of these pretreatments entails etching the castings for 20 s in an alkaline solution at 80 °C (180 °F) and then dipping them for 2 to 3 s in a solution consisting of 3 parts by volume nitric acid (36° Bé) and 1 part hydrofluoric acid at 20 to 25 °C (70 to 75 °F).

The principle of barrel burnishing is to cause surface metal to flow, rather than to remove metal from the surface. Burnishing compounds must have lubricating qualities; soaps made especially for burnishing are usually used and are readily obtainable. Many of them have a pH of about 8, although more acidic materials can be used.

When burnishing aluminum, the pH of the burnishing compound must be closely controlled. This is accomplished by frequent titration of the compound, followed by the addition of small amounts of borax or boric acid as needed. Steel balls and shapes are the most commonly used burnishing media. Several examples of conditions used in barrel finishing applications are detailed in Table 4. Note that deburring and burnishing are sometimes accomplished in a single operation.

Table 4 Conditions for wet barrel finishing of aluminum products

Product	**No. of pieces per**		**No. of pieces per load**	**Cycle time, min**	**Barrel speed, rev/min**
	kg	**lb**			
Clean, deburr and brighten[(a)]					
Percolator spout	60	130	630	20	33
Measuring spoon	20	50	750	20	33
Flame guard	40	90	1500	15	33
Leg	35	80	2700	30	33
Toy spoon	80	180	5000	17	33
Handle	105	225	5800	25	33
Deburr and brighten[(b)]					
Die cast handles	11	25	600	120	15
Burnish to high gloss[(c)]					

(a) Rubber-lined steel, single-compartment drum, 560 mm (22 in.) diam, 760 mm (30 in.) long. Processing cycle: load drum with medium (20 kg or 50 lb of 3-mm or $\frac{1}{8}$-in. steel balls per load), parts, and compound (154 g or 5.5 oz of burnishing soap per load); cover load with water (66 °C or 150 °F); rotate drum for specified time; unload, rinse, separate parts from medium; tumble-dry parts in sawdust for 4 min.

(b) Rubber-lined steel, double-compartment drum; each component 740 mm (29 in.) long, 915 mm (36 in.) in diameter. Processing cycle: load deburring compartment with parts, compound (2 kg or 5 lb of burnishing soap), and medium (365 kg or 800 lb of No. 4 granite chips), using hoist; cover load with cold tap water; rotate drum for 1 h; unload, and rinse with cold water; separate parts and medium, and transfer parts to burnishing compartment; add burnishing compound (0.9 kg or 2 lb of burnishing soap) and medium (680 kg or 1500 lb of 3-mm or $\frac{1}{8}$-in. steel

balls); cover load with water (71 °C or 160 °F) and rotate drum for 1 h; separate parts and medium, and rinse parts in hot water and then in cold water; spin dry in a centrifugal hot-air dryer.

(c) Single-compartment drum, 1.5 m (5 ft) long, 1.2 m (4 ft) in diameter. Processing cycle: load drum with parts (parts are fixtured, to prevent scratching), medium (2040 to 2270 kg or 4500 to 5000 lb of steel balls 3, 6, and 8 mm or $\frac{1}{8}$, $\frac{1}{4}$, and $\frac{5}{16}$ in. in diameter, and 2 and 3 mm or $\frac{1}{16}$ and $\frac{1}{8}$ in. steel diagonals), and compound (5 kg or 12 lb of alkaline burnishing soap. pH 10); cover load with cold tap water; rotate drum for 22 $\frac{1}{2}$ min in one direction, then 22 $\frac{1}{2}$ min in reverse direction; rinse and unload; dip-rinse parts, and hand wipe

Self-tumbling is an effective means of cleaning, deburring, or burnishing small aluminum parts. Procedures for self-tumbling are basically the same as those for other methods of barrel finishing, except that the parts themselves serve as the medium. Compounds for self-tumbling of aluminum should be of nearly neutral pH, and oxides should be removed from the aluminum parts before tumbling. The size and shape of the parts usually determine whether self-tumbling is suitable. Interior surfaces receive little or no action during self-tumbling.

Vibratory finishing is a newer method used for deburring and burnishing metal parts. When applied to aluminum parts, compounds and media are subject to the same restrictions as discussed previously for conventional barrel finishing.

Polishing and Buffing

Because aluminum is more easily worked than many other metals, few aluminum parts require polishing prior to buffing for final finish. In some instances, polishing may be required for the removal of burrs, flash, or surface imperfections. Usually, buffing with a sisal wheel prior to final buffing is sufficient.

Polishing. Most polishing operations can be performed using either belts or setup wheels. Setup wheels may be superior to belts for rough polishing when canvas wheels in a relatively crude setup can be used. For fine polishing work, a specially contoured wheel may be more satisfactory than a belt. Setup wheels have two main disadvantages in comparison with belts: wheels may be costly; and time, skill, and equipment are necessary for setting up wheels. (The actual time required may be as short as 10 min, but this time is spread over several hours because of intermediate drying steps.) Inventory thus becomes an important factor when several wheels with different types of abrasives or grit sizes are needed. Considerable operator skill is required for wheel polishing, whereas unskilled labor can be used for belt polishing. Flap wheels have been used to replace setup wheels for many applications. The use of flap wheels tends to overcome the above-mentioned disadvantages. Typical conditions for polishing aluminum parts are discussed in the following examples.

The conditions for wheel polishing die cast aluminum soleplates for steam irons are as follows:

Type of polishing wheel	Felt
Setup time	10 min
Wheel speed	180-2000 rev/min
Lubricant	Tallow grease stick

The medium-hard felt polishing wheel is 350 to 400 mm (14 to 16 in.) in diameter, with a 125 mm (5 in.) face. The surface of the wheel is double coated with 240-mesh alumina abrasive bonded with hide glue. Setup time, spread out over several hours of operation, totals 10 min. The polishing wheel can cover 34 to 43 m/s (6600 to 8400 sfm).

The soleplates are made of alloy 380.0 and the sides are polished to remove holes or other surface defects. Buffing follows to produce the required mirror finish. The polishing conditions given in the list above are based on a production rate of 115 pieces/h per wheel. Each wheel has a service life of 5000 to 6000 pieces.

Table 5 gives the conditions and sequence of operations for belt polishing of die-cast steam-iron soleplates made of aluminum alloy 380.0. Ten polishing heads are used to produce a bright finish on the soleplate sides and bottom.

Table 5 Conditions of belt polishing for bright finishing aluminum die-cast soleplates

Operation	Area polished	Polishing head, No.	Type	Contact wheel			Belt[(a)]			
				Size		Hardness, durometer	Size		Abrasive mesh size	Life, pieces
				mm	in.		mm	in.		
1	Side	1, 2	Plain face	50 by 380	2 by 15	60	50 by 3050	2 by 120	280[(b)]	600
2	Side	3, 4	Plain face	50 by 380	2 by 15	60	50 by 3050	2 by 120	320[(b)]	600
3	Bottom	5	Serrated[(c)]	150 by 380	6 by 15	45	150 by 3050	6 by 120	120[(b)]	1200
4	Bottom	6	Serrated[(c)]	150 by 380	6 by 15	45	150 by 3050	6 by 120	150[(b)]	2000
5	Bottom	7	Serrated[(c)]	150 by 380	6 by 15	45	150 by 3050	6 by 120	220[(b)]	2000
6	Bottom	8	Serrated[(c)]	150 by 380	6 by 15	45	150 by 3050	6 by 120	280[(b)]	2000
7	Bottom	9	Plain face	150 by 380	6 by 15	60	150 by 3050	6 by 120	320[(b)]	2000

(a) Belt speed for all operations was 35 m/s (6900 sfm). All belts were cloth; bond, resin over glue.

(b) Aluminum oxide abrasive.

(c) 45° serration, 13 mm ($\frac{1}{2}$ in.) land, 10 mm ($\frac{3}{8}$ in.) groove.

(d) Silicon carbide abrasive

Buffing. Selection of a buffing procedure depends mainly on cost, because it is usually possible to obtain the desired results by any one of several different methods. For example, depending on the application, hand buffing might call for the use of equipment ranging from simple, light-duty machines to heavy-duty, variable-speed, double-control units. These machines represent a wide range in capital investment.

Automatic buffing requires custom-made machinery or special fixtures on standard machinery. The size and complexity of the machinery are determined by the required production rates and by the size or shape of the workpieces. High production requires more stations, heavier equipment, and more power. The configuration of the part may be so simple that one buff covers the total area to be finished, or it may be so complex as to require the use of many buffs set at angles and advanced toward the workpiece by cam action.

For cut and color work, buffs are bias types with a thread count of 86/93. For severe cut-down, treated cloth is used with the same thread count. The final color work is accomplished using a buff with very little pucker and a low thread count of 64/64 (see Table 6). A number of procedures that have proved successful for high-luster buffing of specific aluminum parts are summarized in Table 6; others are described in the following examples.

Table 6 Equipment and operating conditions for high-luster buffing of aluminum products

Product	Size		Type of buffing machine	Type	Buffing wheel										Production, pieces per hour
					Diameter						Thread count	Wheel speed		Type of compound	
					Overall		Center		Ply						
	mm	in.			mm	in.	mm	in.	mm	in.		m/s	sfm		
Biscuit pan	340 by 240	$13\frac{1}{4}$ by 9	Semiautomatic	Bias	360	14	125	5	410	16	86/93	40	8250	Bar	205
Burner ring	75 diam by 20	3 diam by $\frac{3}{4}$	Continuous rotary[a]	Radial, vented	[b]	[b]	30	$1\frac{1}{8}$	510	20	64/64	[c]	[c]	Liquid	297
Cake-carrier base	270 diam by 20	$11\frac{1}{4}$ diam by $1\frac{3}{16}$	Continuous rotary[a]	Bias	Two 360	Two 14	125	5	460	16	86/93	50	9550	Liquid	278
				Bias	Two 330	Two 13	75	3	50	2	64/68	45	8850	Liquid	. . .
Cake pan	350 by 241 by 65	14 by $9\frac{1}{2}$ by $2\frac{1}{2}$	Hand buffing (handles)	Bias	330	13	75	3	50	2	64/68	40	7650	Bar	438
			Semiautomatic (sides)	Bias	360	14	125	5	410	16	86/93	40	8250	Bar	200
Cake pan	200 by 203 by 50	8 by 8 by 2	Semiautomatic	Bias	360	14	125	5	410	16	86/93	40	8250	Bar	127

Cup	60 diam by 65	$2\frac{3}{8}$ diam by $2\frac{1}{2}$	Semiautomatic	Bias	360	14	125	5	410	16	86/93	40	8250	Bar	450
Pan bottom	280 by 280	$11\frac{1}{8}$ square	Semiautomatic	Bias	360	14	125	5	410	16	86/93	40	8250	Bar	106
Pan cover	285 by 285	$11\frac{1}{4}$ square	Semiautomatic[(d)]	Bias (sides)	360	14	125	5	410	16	86/93	40	8250	Bar	95
				Loose, vented (top)	[(e)]	[(e)]	50	2	510	20	64/64	[(f)]	[(f)]	Bar	95
Toy pitcher	65 diam by 90	$2\frac{1}{2}$ diam by $3\frac{1}{2}$	Continuous rotary[(g)]	Bias	360	14	125	5	410	16	64/68	50	9550	Liquid	817
Toy tumbler	50 diam by 65	$1\frac{7}{8}$ diam by $2\frac{1}{2}$	Continuous rotary[(g)]	Bias	360	14	125	5	410	16	64/68	50	9550	Liquid	864

(a) Five-spindle machine; four buffing heads, one load-unload station.

(b) Each of the four wheels used had one 330 mm (13 in.) and three 360 mm (14 in.) sections.

(c) For 330 mm (13 in.) section, 45 m/s (8850 sfm); for 360 mm (14 in.), 49 m/s (9550 sfm).

(d) Two machines, run by one operator.

(e) Buff made up of 360 mm (14 in.), 381 mm (15 in.), and 410 mm (16 in.) sections.

(f) 42 m/s (8250 sfm) for 360 mm (14 in.) sections, 45 m/s (8800 sfm) for 380 mm (15 in.) sections, and 48 m/s (9400 sfm) for 410 mm (16 in.) sections.

(g) Eight-spindle machine

Table 7 gives the conditions and sequence of operations for automatic buffing of wrought aluminum frying-pan covers. A specular finish was required. In another case, the sides of die-cast aluminum frying pans made from alloy 360 were buffed to a bright finish by an automatic machine with four buffing heads. The buffing wheel of each head consisted of a 14-ply, 16-spoke sewed bias buff with a 430 mm (17 in.) outside diameter, a 230 mm (9 in.) inside diameter, and a 44 mm ($13\frac{3}{4}$ in.) diameter arbor hole. Wheel speed was 1745 rev/min, equal to 39 m/s (7700 sfm). Each buff was made up of four sections. A liquid buffing compound was applied by one gun per wheel at the rate of 3 g per shot (0.1 oz per shot) for the first wheel, 2.5 g per shot (0.09 oz per shot) for the second and third wheels, and 1 g per shot (0.04 oz per shot) for the fourth wheel. The gun was on for 0.1 s and off for 5 s. The service life of each buffing wheel was 1600 to 2100 pieces.

Table 7 Sequence and conditions of automatic buffing operations for obtaining specular finish on aluminum frying-pan covers

Operation	Area buffed	Buffing head No.	Buffing wheel														Application of compound[a]				
			Type	Diameter						Ply	Thread count	Density	No. of sections	Speed		Life, pieces					
				Overall		Center		Arbor hole									No. of guns	Cycle,s		g per shot	oz per shot
				mm	in.	mm	in.	mm	in.					m/s	sfm			On	Off		
1	Sides (4)	1,2,3,4	Bias, air cooled	430	17	180	7	45	$1\frac{3}{4}$	. . .	86/93	2.4	20	40	7750	40,000	3	0.1	7	0.5	0.02
2	Corners (2)	5,6,7,8	Bias, 20-spoke sewed	430	17	180	7	45	$1\frac{3}{4}$	16	86/93	4	4	40	7750	35,000	1	0.1	7	0.5	0.02
3	Sides (2)	9,10,11,12	Bias, 20-spoke sewed	430	17	180	7	45	$1\frac{3}{4}$	16	86/93	4	4	40	7750	50,000	1	0.1	7	0.5	0.02
4	Sides (2)	13,14,15,16	Bias, 20-spoke sewed	430	17	180	7	45	$1\frac{3}{4}$	16	86/93	4	4	40	7750	35,000	1	0.1	8	0.5	0.02
5	Top	17	Bias, 45° spoke sewed	430	17	180	7	45	$1\frac{3}{4}$	16	86/93	4	15	40	7750	65,000	3	0.1	8	0.2	0.01
6	Top	18	Bias	430	17	180	7	45	1	12	86/93	8	18	40	7750	70,000	3	0.1	8	0.2	0.01

									3/4												
7	Top bias	19	Bias	430	17	180	7	45	1 3/4	12	86/93	8	18	40	7750	70,000	3	0.1	8	0.2	0.01
8	Top bias	20	Bias	410	16	125	5	45	1 3/4	14	64/68	2	19	37	7300	45,000	3	0.1	8	0.2	0.01
9	Corners (4)	21,22,23,24	Bias	430	17	180	7	45	1 3/4	12	86/93	8	4	40	7750	65,000	1	0.1	10	0.5	0.02
10	Sides (4)	25,26,27,28	Bias	430	17	180	7	45	1 3/4	12	86/93	8	4	40	7750	80,000	1	0.1	10	0.5	0.02
11	Top bias	29	Bias	410	16	125	5	45	1 3/4	14	64/68	2	15	23	4600	80,000	3	0.1	10	0.5	0.02
12	Sides (4)	30,31[b]	Domet flannel	430	17	180	7	70	2 3/4	20	[d]	[d]	40	20	4000	80,000	6	0.1	11	0.2	0.01
13	Top	32	Domet flannel[c]	430	17	180	7	40	1 5/8	32	[d]	[d]	24	25	4900	30,000	3	0.1	11	0.2	0.01
14	Top	33	Domet flannel[c]	430	17	180	7	40	1	32	[d]	[d]	24	18	3550	30,000	3	0.1	11	0.2	0.01

									$\frac{5}{8}$												

(a) Liquid tripoli compound applied to buffing heads No. 1 through 29; stainless steel buffing compound applied to heads No. 30 through 33.

(b) Each head buffs two sides.

(c) Domet flannel sections interleaved with 180 mm (7 in.) diam disks of Kraft paper.

(d) Inapplicable to flannel buff

Die-cast aluminum soleplates for steam irons (Table 8) were buffed to a bright finish on an automatic machine with eight buffing heads. The soleplates were made of alloy 380.0 and were prepolished with 320-mesh grit. A liquid buffing compound was applied by one gun per wheel for the first four heads and by two guns per wheel for the last four heads. The guns were on for 0.12 s and off for 13 s. The service life was 72,000 pieces for each buff of the first four heads, and 24,000 pieces for each buff of the last four heads.

Table 8 Automatic bright-finish buffing of aluminum soleplates

Operation	Area buffed	Buffing head No.	Buffing wheel										Application of compound[b]		
			Type	Size	Diameter[a]				No. of sections	Speed		Life, pieces			
					Overall		Arbor hole								
					mm	in.	mm	in.		m/s	sfm		No. of guns	g per shot	oz per shot
1	Side	1,2	Sisal	10 mm($\frac{3}{8}$ in.) spiral sewed	410	16	40	1 $\frac{1}{4}$	2	37	7350	72,000	1	0.5	0.02
2	Side	3	Bias	16-ply, 20-spoke sewed	430	17	45	1 $\frac{3}{4}$	2	40	7800	72,000	1	0.5	0.02
3	Side	4	Bias	16-ply, 20-spoke sewed	430	17	45	1 $\frac{3}{4}$	2	40	7800	72,000	1	0.5	0.02
4	Top	5	Sisal	10 mm ($\frac{3}{8}$ in.) spiral sewed	410	16	45	1 $\frac{3}{4}$	15	37	7350	24,000	2	3.0	0.1
5	Top	6	Sisal	10 mm ($\frac{3}{8}$ in.) spiral sewed	410	16	45	1 $\frac{3}{4}$	15	37	7350	24,000	2	3.0	0.1
6	Top	7, 8	Bias	16-ply, 20-spoke sewed	430	17	45	1	10	40	7800	24,000	2	3.0	0.1

(a) All wheels had 180 mm (7 in.) diam centers.

(b) Proprietary liquid compound was used. Cycle time: 0.12 s on, 13.0 s off

Satin Finishing

Mechanical satin finishing is an established method for obtaining an attractive surface texture on aluminum hardware items such as knobs, hinges, rosettes, and drawer pulls. Satin finishes are also used for architectural, appliance, and automotive trim. The satin finish results from small, nearly parallel scratches in the metal surface, which give the surface a soft, smooth sheen of lower reflectivity than that of polished or buffed surfaces.

Satin finishes can be applied by fine wire brushing. Other methods use a greaseless abrasive compound in conjunction with a conventional buffing head, tampico brush, cord brush, string buff, or brush-backed sander head. Abrasive-impregnated nylon disks mounted like buffs are also used, as are abrasive cloth sections mounted on a rotating hub. All of these methods produce about the same type of finish; the use of any particular one depends on the surface contour of the workpiece.

Surfaces of workpieces to be satin-finished should be free of grease and oil, and low contact pressures should be used. Wire brushes must be kept free of oxide and accumulations of aluminum metal. This is accomplished by frequently bringing a pumice stone or soft brick in contact with the rotating brush. A common wire brushing setup consists of a 250 mm (10 in.) diameter wheel having a surface speed of about 8.0 m/s (1600 sfm) and wires 0.4 mm (0.015 in.) in diameter. Undue pressure on a rotating wire wheel will bend the wires and cause excessive tearing of the aluminum surface.

Stainless steel wires are recommended, because other metals such as brass or steel may become embedded in the aluminum surface, producing discoloration or corrosion. If brass or steel wire wheels are used, the embedded particles can be removed by immersing the work in a nitric acid solution (1 part water to 1 part acid by volume) at room temperature.

The satin finish processes in which a greaseless abrasive compound is used are essentially dry. Water is required to soften the binder in the abrasive compound so that it will adhere to the surface of the buff. After the binder dries, the buff is ready for operation. At this stage a lubricant, such as a buffing compound or tallow, may be used to produce a higher reflection.

Table 9 describes the equipment and techniques employed in mechanical satin finishing processes. If the satin-finished parts are to be anodized, etching or bright dipping should not precede anodizing, because the satin appearance will be lost. Cleaning treatments that do not etch or that only slightly etch the metal should be used before anodizing.

Table 9 Methods, equipment, and conditions for mechanical satin finishing of aluminum

Method	Suitable equipment			Speed		Lubricant
	Buffing lathe	Portable power head	Power required	m/s	sfm	
Wire brushing[a]	Yes	Yes	[b]	6-11	1200-2250	None
Sanding with brush-backed head[c]	Yes	No	[d]	900-1800 rev/min	900-1800 rev/min	Optional
Tampico or string brushing[e]	Yes	No	[b]	15-31	3000-6000	Pumice[f]
Finishing with abrasive-coated cloth[g]	Yes	Yes	[d]	31-36	6000-7000	Optional
Finishing with nylon disks[h]	Yes	Yes	[i]	23-33	4500-6500	Optional

Buffing with compounds[j]	Yes	Yes	[b]	15-26	3000-5000	[k]

(a) 305 mm (12 in.) diam brush of stainless steel wire 0.125 mm (0.005 in.) in diameter.

(b) 1 hp per 25 mm (1 in.) of brush width.

(c) Using 60- to 600-mesh abrasive cloth loadings.

(d) 1 hp per head.

(e) 300 mm. (12 in.) diam brush.

(f) With oil or water; emery cake also may be used.

(g) Cloth is mounted radially on rotating hubs; coated with 50- to 320-mesh emery abrasive.

(h) Disks impregnated with silicon carbide abrasive, coarse to ultrafine.

(i) $\frac{1}{4}$ hp per 25 mm (1 in.) of disk width.

(j) Greaseless satin-finishing compounds containing aluminum oxide abrasive (200 or 240 mesh) used with unstitched or loosely stitched buffs (360 mm or 14 in.) or with string brush.

(k) Dry, or with buffing compound or grease stick

Chemical Cleaning

The cleanliness requirements for an aluminum surface are governed by the subsequent finishing operations. For example, plating or the application of chromate or another mild-reaction conversion coating requires cleaning procedures that are somewhat more stringent than for anodizing.

When establishing a cleaning cycle or when testing different cleaners or cleaning conditions, it is desirable to test the cleanliness of the processed surface. Wetting an aluminum surface with water, known as the water break test, does not always provide an indication of cleanliness if oxides are of concern, because oxide-coated surfaces free of oil or grease can be wetted uniformly. Also, a surface that has been processed with a detergent containing a wetting agent can be wetted even though not thoroughly clean, because the film of wetting agent remains on the unclean surface. Two other methods of testing aluminum for cleanliness are to:

- Spray or coat the work surface with, or dip a test panel into, an unheated aqueous solution containing 30 g/L (4 oz/gal) of cupric chloride and 29 mL/L (3.8 fluid oz/gal) of concentrated hydrochloric acid. Uniform gassing or a deposit of copper indicates that the surface is chemically clean.
- Spray or coat the work surface with, or dip a test panel into, an unheated chromate conversion coating bath of the acid type until an orange-colored film is formed. A uniform orange film indicates a

chemically clean surface.

Solvent Cleaning. The primary function of solvent cleaners is to remove oil and grease compounds. Organic solvents alone rarely provide sufficient cleaning to permit final finishing operations; solvents usually are used to remove large amounts of organic contaminants to minimize overloading of subsequently used alkaline cleaners.

Greases and oils vary as to solubility in specific solvents. Fish oils are more difficult to remove than other types of oils. In the dried condition, some oxidizing oils, such as linseed oil, form a leathery film that is difficult to remove with any solvent.

Polishing and buffing compounds are readily removed by most solvents when cleaning is performed immediately after buffing. If the compounds are permitted to harden, they may be difficult to remove. Heated solutions, agitation, or mechanical action (ultrasonics or physical force) may be required for satisfactory cleaning. To remove compounds burned in the surface, the parts must be soaked in a liquid using an organic degreaser. such as trichlorethylene or methylene dichloride (rather than vapor degreasing), or in an inhibited alkaline cleaner.

If polishing and buffing compounds cannot be removed immediately after buffing, the application of a neutral mineral oil over the buffed surface will maintain the compounds in a more soluble condition for subsequent removal by a solvent. The sequence of operations usually required for buffed aluminum surfaces is: solvent cleaning, rinsing, removal of surface oxides, rinsing, and finally the application of the desired finish. Some of these steps may be omitted, depending on the type and quality of the buffing compound, the quality of workmanship in buffing, and the quality of solvents and cleaners used.

Emulsifiable solvents also are used to clean aluminum. These are organic solvents, such as kerosene, Stoddard solvent, and mineral spirits, to which small amounts of emulsifiers and surfactants are added. In use, this type of cleaner emulsifies the oil or grease on the surface. The soil and cleaner are removed with water, preferably applied by spraying.

This type of degreasing is satisfactory prior to anodizing, etching, removal of surface oxides, chemical conversion coating, plating, or painting. In some instances, intermediate treatments are required, such as the removal of surface oxides before etching.

The emulsifiable solvent should have a pH of 8 or less; otherwise, it will stain or corrode the aluminum if permitted to remain on the surface prior to rinsing or additional cleaning. However, emulsifiable solvents with higher pH are more efficient cleaners, and they can be used if the surfaces are rinsed or are cleaned by additional methods within 2 or 3 min after degreasing.

A lower-cost cleaning solution can be obtained by adding water to the emulsifiable solvent. This less-efficient type of solution is limited to the removal of light oil and grease. It is now common practice to use alkaline cleaners to remove oil and grease instead of solvents, the use of which is under increasing scrutiny by the Environmental Protection Agency (EPA).

Alkaline cleaning is the most widely used method for cleaning aluminum and aluminum alloys. This method is easy to apply in production operations, and equipment costs are low. Aluminum is readily attacked by alkaline solutions. Most solutions are maintained at a pH between 9 and 11, and they are often inhibited to some degree to minimize or prevent attack on the metal. The most frequently used alkaline cleaner is the mildly inhibited type.

Cleaners of either the etching or nonetching type have some ability to emulsify vegetable and animal oils or greases, but not mineral oils or greases. Therefore, they can sometimes remove fresh buffing compounds and the lard oils used in spinning operations.

Nonetching cleaners can be classified as either silicated or nonsilicated. The silicated cleaners are based on aqueous solutions of sodium carbonate, trisodium phosphate, or other alkalis, to which small amounts of sodium silicate are added to inhibit etching. The main disadvantage of the silicated types, aside from their inability to emulsify and remove mineral oils, is that the silicate may react with the aluminum to form an insoluble aluminum silicate, especially when the temperature of the bath exceeds 80 °C (180 °F). However, lower operating temperatures decrease the efficiency of the solution for the removal of certain soils. Silicated alkaline cleaners are available that are used at 50 to 60 °C (120 to 140 °F) to reduce energy consumption.

Nonsilicated cleaners are often based on the use of relatively large concentrations of surfactants. High operating temperatures are required, but some cleaners used above 70 °C (160 °F) etch the aluminum surface. Cleaners containing a large quantity of surfactants, particularly those types that resist complete rinsing, must not be carried into baths used for bright dipping, anodizing, or chemical conversion coating.

Neither silicated nor nonsilicated cleaners remove aluminum oxide uniformly. Because oxide removal is essential for the application of decorative or functional finishes, the best procedure is to clean, remove oxide with an acid solution, and then proceed with finishing.

Nonetching cleaners may be used after solvent cleaning to produce water-wettable surfaces, or they may be used alone when soils are light and easily removed. The surfaces should be treated to remove oxides afterward. When sodium orthosilicate or sodium metasilicate is used, the concentration of carbonates must be kept at a minimum to minimize the formation of floc, which may redeposit on the work. Unlike sodium hydroxide, the alkali silicates have good wetting, emulsifying, and rinsing properties. The ratio of silicon dioxide to sodium oxide in the compound determines the effectiveness of the alkali silicates. Sodium orthosilicate has good detergency and is effective in the cleaner at a ratio of 1 to 2, whereas the ratio of sodium metasilicate should be 1 to 1.

Agitation of the cleaner increases the cleaning action and is best created by pumps, propellers, or movement of the work. Air agitation, although easier to install and convenient to operate, has the following disadvantages:

- Air can reduce the solution temperature.
- The additional oxygen may cause staining and tarnishing on some alloys.
- Air agitation introduces carbon dioxide, which may increase the carbonate content.

The work should be rinsed immediately after removal from the alkaline bath to prevent dry-on. Warm water is preferred; if low-temperature cleaners are used, then rinsing with cold water is satisfactory.

Aluminum surfaces sometimes contain areas of localized corrosion, referred to as atmospheric etch, caused by contaminants in the air during storage. The corroded areas are more visible after alkaline cleaning or etching than before. When corrosion spots are present, the work may be dipped in a sodium bisulfate solution of 45 g/L (6 oz/gal), or in a cold 70% nitric acid solution, to minimize the effect of the subsequent alkaline cleaning.

During alkaline cleaning, especially if etching occurs, some alloys containing copper, iron, manganese, or silicon develop a black smut on the surface. Compositions and operating conditions of common alkaline cleaners are given in Table 10.

Table 10 Alkaline cleaners used to clean aluminum surfaces

Constituent or condition	**Amount or value**
Etching cleaners	
Sodium hydroxide	22-75 g (3-10 oz)
Sodium phosphate	0.8-4 g (0.1-0.5 oz)
Water, to make	4 L (1 gal)
Temperature of bath	60-80 °C (140-180 °F)

Immersion time	30 s-10 min
Sodium hydroxide	2-6 g (0.25-0.75 oz)
Sodium phosphate	8-60 g (1-8 oz)
Sodium carbonate	8-60 g (1-8 oz)
Water, to make	4 L (1 gal)
Temperature of bath	60-80 °C (140-180 °F)
Immersion time	2-5 min
Nonetching cleaners	
Sodium pyrophosphate and sodium metasilicate	Total of 15-75 g (2-10 oz)
Water, to make	4 L (1 gal)
Temperature of bath	60-70 °C (140-160 °F)
Immersion time	2-5 min
Trisodium phosphate and sodium metasilicate	Total of 15-75 g (2-10 oz)
Water, to make	4 L (1 gal)
Temperature of bath	60-70 °C (140-160 °F)
Immersion time	2-5 min
Sodium carbonate	4-8 g (0.5-1 oz)
Sodium metasilicate	4-8 g (0.5-1 oz)
Water, to make	4 L (1 gal)
Temperature of bath	6-70 °C (140-160 °F)
Immersion time	2-5 min

Borax	22-38 g (3-5 oz)
Sodium pyrophosphate	4-8 g (0.5-1 oz)
Water, to make	4 L (1 gal)
Temperature of bath	60-70 °C (140-160 °F)
Immersion time	2-5 min

Electrocleaning is seldom used for cleaning aluminum and aluminum alloys, because it offers no advantage over an etching cleaner. However, a few processes are used in production operations. These use low voltage, usually in the range of 6 to 12 V. Cathodic cleaning, in which the work is the cathode, is more common than anodic cleaning. Common practice is to reverse the current during the last 5 to 10 s of the cleaning operation.

After removal from the cleaner, the work is rinsed in warm or hot water, dipped in acid to neutralize any residual alkali, and finally rinsed in cold water. The work can then be finished as desired. The composition of two solutions that are recommended for electrocleaning are:

Constituents	**Composition, %**
Solution A	
Sodium orthosilicate	85
Sodium carbonate (anhydrous)	10
Sodium resinate	5
Solution B	
Sodium carbonate (anhydrous)	46
Trisodium phosphate	32
Sodium hydroxide	16
Rosin	6

Note: For typical operating conditions, see text.

Acid Cleaning. Acid cleaners may be used alone or in conjunction with other acid, alkaline, or solvent cleaning systems. Vapor degreasing and alkaline cleaning may be required for the removal of heavy oils and grease from workpieces before they are immersed in an acid bath. One of the main functions of an acid cleaner is to remove surface oxides prior to resistance welding, painting, conversion coating, bright dipping, etching, or anodizing.

A mixture of chromic and sulfuric acids is commonly used to remove surface oxides, burnt-in oil, water stains, or other films, such as the iridescent or colored films formed during heat treating. This acid mixture cleans and imparts a slightly etched appearance to the surface, preparing it for painting, caustic etching, conversion coating, or anodizing. Nonpolluting, proprietary products free of chromic acid are available for acid cleaning and deoxidizing.

Oxide films must be thoroughly removed before spot welding. A mixture of phosphoric and chromic acids is another solution that can be used for this purpose. Because of the corrosive nature of the chlorides and fluorides in welding fluxes, the fluxes should be removed as soon as possible after welding. Mixtures of nitric and hydrofluoric acids are best for removing fluxes. Most fluxes can also be satisfactorily removed by a dilute (5 to 20 vol%) nitric acid solution.

Proprietary nonetching acid cleaners are available for cleaning aluminum and aluminum alloys. Operating temperatures of these solutions range from 55 to 80 °C (130 to 180 °F), and pH usually ranges from 4.0 to 5.7. Compositions and operating conditions for typical acid cleaning solutions are given in Table 11.

Table 11 Acid cleaners used to clean aluminum surfaces

Constituent or condition	Amount or value
Solution 1	
Chromic acid	45-90 g (6-12 oz)
Sulfuric acid (66° Bé)	150-190 mL (19-24 fluid oz)
Water, to make	4 L (1 gal)
Temperature of bath	45-80 °C (110-180 °F)
Immersion time	up to 20 min
Solution 2	
Nitric acid (42° Bé)	500-750 mL (64-96 fluid oz)
Hydrofluoric acid (48%)	25-190 mL (3-24 oz)
Water, to make	4 L (1 gal)
Temperature of bath	Room temperature
Immersion time	1-5 min

Solution 3	
Sulfuric acid (66° Bé)	100 mL (13 fluid oz)
Hydrofluoric acid (48%)	25 mL (3 fluid oz)
Chromic acid	40 g (5 oz)
Water, to make	4 L (1 gal)
Temperature of bath	65-70 °C (150-160 °F)
Immersion time	2-5 min
Solution 4	
Nitric acid (42° Bé)	38-125 mL (5-16 fluid oz)
Sodium sulfate (hydrate)	60-120 g (8-16 oz)
Water, to make	4 L (1 gal)
Temperature of bath	75-80 °C (170-175 °F)
Immersion time	4-8 min
Solution 5	
Phosphoric acid	70 mL (9 fluid oz)
Chromic acid	20 g (2.75 oz)
Water, to make	4 L (1 gal)
Temperature of bath	45-65 °C (110-150 °F)
Immersion time	1-5 min

Aluminum parts should be insulated from ferrous metal baskets or supports when immersed in acid cleaning solutions, because contact of these two metals can produce a galvanic action that causes corrosion. Materials such as vinyl plastisols, epoxy, polyethylene, and polypropylene may be used for insulation. When practical, baskets or rods should be of the same or similar material as the workpieces.

Chemical Brightening (Polishing)

Chemical brightening, also known as bright dipping and chemical polishing, smoothens and brightens aluminum products by making use of the solution potential of the aluminum surface in the various baths employed and of the local differences in potential on the aluminum surface.

In general, chemical brightening baths can be concentrated or dilute acid solutions that contain oxidizing agents. The acids commonly used are sulfuric, nitric, phosphoric, acetic, and, to a lesser extent, chromic and hydrofluoric. Ammonium bifluoride is used when it is desirable to avoid the hazards that attend the use of hydrofluoric acid. Fluoboric and fluosilicic acids may also be used as alternates to hydrofluoric acid. An alkaline bath, such as Alupol, can also be used for chemical etching. This bath consists of 20 kg (44 lb) sodium nitrate, 15 kg (33 lb) sodium nitrite, 25 kg (55 lb) sodium hydroxide, and 20 kg (44 lb) water. An aluminum part is immersed for 1 to 5 min at a bath temperature of 90 to 140 °C (195 to 285 °F). Protrusions, valleys, and scratches are eliminated, and reflectance is increased.

Phosphoric-Nitric Acid Baths. Among the various types of concentrated baths, the phosphoric-nitric acid baths are the most widely used in the United States. Compositions and operating conditions for two commercial baths of this type are given below:

Constituent or condition	Range
Phosphoric-nitric[(a)]	
Phosphoric acid (85%)	45-98 wt%[(b)]
Nitric acid (60%)	0.5-50 wt%[(b)]
Water	2 to 35 wt%
Temperature	85-110 °C (190-230 °F)
Immersion time	30 s to 5 min
Phosphoric-acetic-nitric[(c)]	
Phosphoric acid (85%)	80 vol%
Acetic acid (glacial, 99.5%)	15 vol%
Nitric acid (60%)	5 vol%
Temperature	85-110 °C (190-230 °F)
Immersion time	30 s to 5 min

(a) U.S. Patent 2,729,551 (1956).

(b) Recommended volumetric make-up consists of 93.5 parts of 85% phosphoric acid and 6.5 parts of 60% nitric acid.

(c) U.S. Patent 2,650,157 (1953)

Additionally, certain proprietary chemical bright dips can be operated at 75 to 80 °C (170 to 180 °F), which is significantly lower than the normal 85 to 110 °C (190 to 230 °F) for conventional baths. The low-temperature baths, however, are limited in allowable water drag-in from prior rinse operations. Excessive water drag-in results in poor brightening.

Alkali nitrates may be used as substitutes for nitric acid. Acetic acid, copper salts, and other additives are used in some phosphoric-nitric acid baths. As additive content increases, solution control becomes more complex.

For economy, some phosphoric-nitric acid baths are operated with an aluminum phosphate content near the tolerable maximum of 10 to 12%, with a dissolved aluminum content of about 40 g/L (5 oz/gal). This is close to the saturation point, at which precipitation of this compound on the work produces etch patterns.

The addition of surfactants increases the amount of metal removed under a given set of operating conditions. Surfactants help to enhance the chemical polishing as well as to suppress the evolution of fumes. Acetic and sulfuric acids alter the physical property/composition relationship in the concentrated acid baths and also complicate control problems. Acetic acid volatilizes rapidly from the bath.

Small concentrations of heavy metals in the bath enhance the brightening effect, particularly on alloys with negligible copper content. Copper can be introduced into the bath by one of three methods: the direct dissolution of a small amount of copper; the addition of a small amount of a copper compound, such as 0.01 to 0.02% cupric nitrate; or the use of racks made of aluminum-copper alloys. Copper is added to the bath when brightening aluminum alloys such as 2024 and 7075, which contain high percentages of copper. Excess copper can plate out of the bath. In some baths, however, excess copper causes etching, and sometimes nickel or zinc is used instead.

Phosphoric-nitric acid baths are not recommended for brightening alloys that contain silicon. Excessive dissolution causes dispersion of undissolved silicon, which deposits on the work surfaces and is difficult to remove by rinsing. When high-silicon alloys are used, the addition of 1 to 2% hydrofluoric acid to the bath is recommended. The gradual buildup of other metals in the bath from the aluminum alloys processed usually causes no difficulty unless the amount of aluminum dissolved exceeds the solubility limit. When this occurs, excess aluminum precipitates and causes coprecipitation of trace elements, which may be difficult to remove from the work.

Contamination of the bath by more than trace amounts of buffing or polishing compounds and other soils should be avoided. These compounds may cause the bath to foam excessively and may interfere with its polishing action. Food-grade or National Formulary phosphoric acid should be used. Lower grades contain fluorides, arsenic, and other impurities that are harmful to the process.

Close control of the nitric acid and water contents, necessary for optimum chemical brightening, is difficult because of the rapid volatilization of these liquids and because of the time required for chemical analysis of the bath. A control method based on an electronic device that monitors the nitric acid content and on the physical measurement of specific gravity and viscosity has been developed.

Drag-out is a major factor in the cost of chemical brightening. The amount of solution and the weight of chemicals lost by drag-out are related to the specific gravity and viscosity of the solution. Drag-out can be minimized by operating the bath at higher temperatures, but this condition may increase the amount of transfer etch while moving to the rinse tank, as well as the rate of aluminum dissolution and the rate of evaporation of nitric acid and water. However, transfer etch can be avoided by rapid transfer into the rinse, and the rate of aluminum dissolution can be minimized by a shorter period of immersion. In general, an operating temperature in the range of 85 to 100 °C (190 to 212 °F) is satisfactory, provided an

optimum bath composition, including additives, is maintained. Also, evaporation of nitric acid and water is not excessive at this temperature. Acetic acid also reduces transfer etch, but this acid volatilizes rapidly from the bath.

Surfactants are employed in some baths to suppress the evolution of fumes; however, they may cause foaming and increase the amount of drag-out. Surfactants also increase the rate of workpiece dissolution. The generation of heat accompanying high dissolution rates must be considered when providing for the control of bath temperatures within the specified range.

Agitation is useful for maintaining a uniform temperature and composition throughout the bath, and for fast removal of reaction products and replenishment of reactants at the surfaces of the work. The most satisfactory method is mechanical agitation and movement of the work in an elliptical pattern. Air agitation is commonly used, but it must be properly controlled. Small air bubbles cause excessive loss of volatile acids by evaporation and an excess of nitrous oxide fumes. Large air bubbles sufficient to create uniform bath temperature provide satisfactory agitation. Excessive solution agitation can cause pitting and streaking on work, so the agitation should always be moderate.

The bath must be well vented to remove the noxious fumes; an exhaust of about 90 m^3/min per square meter (300 ft^3/min per square foot) of bath surface is recommended. Fumes evolved during transfer of the parts to the first rinse tank should likewise be vented, and it is good practice also to vent the first rinse tank, for which an exhaust of about 60 m^3/min per square meter (200 ft^3/min per square foot) of water surface is satisfactory. Water should be warm and air-agitated.

The fumes can be exhausted by fan or steam jet. Fume separators are required when the fumes cannot be exhausted into the atmosphere. Dilute caustic soda solutions are used to scrub the fumes and neutralize the acid.

Phosphoric and Phosphoric-Sulfuric Acid Baths. Concentrated solutions of phosphoric acid at operating temperatures above 80 °C (175 °F) were the first baths used for brightening aluminum. A more effective bath, which combines some smoothening or polishing with brightening action, is one containing 75 vol% phosphoric acid and 25 vol% sulfuric acid. This bath, which is operated at 90 to 110 °C (195 to 230 °F) for 30 s to 2 min, produces a diffuse but bright finish.

Under some conditions of composition and bath temperature, a white film of phosphate salts remains on the metal after treatment in either of these baths. The film must be removed by using a hot (60 to 70 °C, or 140 to 160 °F) aqueous solution of chromic and sulfuric acids. The composition of this acid solution is not critical and may range from 2 to 4% CrO_3 and 10 to 15% H_2SO_4 by weight.

Electrolytic Brightening (Electropolishing)

Electrolytic brightening, also known as electrobrightening and electropolishing, produces smooth and bright surfaces similar to those that result from chemical brightening. After pretreatment (which consists of buffing, cleaning in an inhibited alkaline soak cleaner, and thorough rinsing) the work is immersed in the electrobrightening bath, through which direct current is passed. The work is the anode.

Solution compositions and operating conditions for three commercial electrolytic brightening processes, as well as for suitable post-treatments, are given in Table 12. Operating conditions for electrolytes used in electrobrightening are selected to produce the desired selective dissolution and may vary for optimum results on different aluminum alloys.

Table 12 Electrolytic brightening and polishing solutions and processes for use on aluminum and aluminum alloys

Bath	Percentage	Temperature		Duration, min	Voltage, V	Current density		Film thickness		Appearance properties	Remarks
		°C	°F			A/dm^2	A/ft^2	μm	mils		
Seignette salt brightener (alkaline process)											

Sodium potassium tartrate	15 wt%	38-42	100-108	2-15	10	3-5	30-50	. . .	. . .	High luster, mirror-like reflectivity	For pure aluminum, Raffinal, Reflektal, and for jewelry and reflectors
Sodium hydroxide	1.2 wt%										
Aluminum powder	0.2 wt%										
Water	83.6 wt%										
Acid brightening											
Sulfuric acid	70 vol%	75-85	167-185	2-10	10-20	10-15	100-150	. . .	. . .	High luster, mirror-like reflectivity	For pure aluminum, and its alloys and for reflectors, architectural and structural shapes, and appliance parts
Phosphoric acid	15 vol%										
Nitric acid	1 vol%										
Water	14 vol%										
VAW brightener											
Sodium bisulfate	20 wt%	87-93	188-199	8-10	8-10	10-15	100-150	. . .	. . .	Colorless, transparent oxide film with effect on reflectivity	Used as a post-treatment after conventional anodizing is accomplished
Sodium sulfate	10 wt%										
Sodium hydroxide	1 wt%										
Water	69 wt%										
Smudge remover											
Sodium carbonate	2 wt%	92-97	198-207	. . .	. . .	. . .	. . .	. . .	. . .	Preserve reflectivity	For removing the thin film produced on the aluminum

Water	96.5 wt%										reflectivity
Anodic post-treatments											
Sulfuric acid	71 wt%	23-27	74-81	10	12	1	10	4	0.1	Colorless, transparent film	Without anodizing good results; best results with anodizing
Water	93 wt%										
Sulfuric acid	10-20 wt%	18-22	64-72	10	12	1	10	4	0.1	Colorless, transparent film	Without anodizing good results; best results with anodizing
Water	90-80 wt%										
Sodium bisulfate	20 wt%	33-37	91-98	10	10	0.5	5	2	0.08	Colorless, transparent film	Without anodizing good results; best results with anodizing
Water	80 wt%										

Fluoboric acid electrobrightening operating conditions and suitable post-treatments are given in Table 13. This process can be used for specular and diffuse reflectors, products made of super-purity aluminum (99.99%) in combination with up to 2% Mg, and products made of high-purity aluminum (99.7 to 99.9%).

Table 13 Fluoboric acid electrobrightening of aluminum and aluminum alloys

Constituent or condition	Amount or value
Electrobrightening[(a)]	
Fluoboric acid	2.5 wt%
Temperature of bath	30 °C (85 °F)
Current density	1-2 A/dm^2 (10-20 A/ft^2)
Voltage	15-30 V
Immersion time	5-10 min
Agitation	None
Smut removal	

Phosphoric acid	1.0 wt%
Chromic acid	0.5 wt%
Temperature of bath	90-95 °C (190-200 °F)
Immersion time	30 s
Anodizing	
Sulfuric acid	7-15 wt%
Current density	1.3 A/dm^2 (12 A/ft^2)
Temperature of bath	20 °C (70 °F)
Immersion time	10 min
Sealing	
Distilled water	100%
Temperature of bath	95-100 °C (200-212 °F)
Immersion time	10 min

(a) U.S. Patent 2,108,603 (1938)

Sodium carbonate electrobrightening can be used for specular reflectors, automotive trim, decorative ware, and jewelry. It can also be used for products made of super-purity aluminum in combination with up to 2% Mg, products made of high-purity aluminum, and products made of the following commercial alloys (in approximate order of decreasing quality of finish): 5457, 5357, 6463, 6063, 5052, 1100, 5005, 3003, and 6061. Sodium carbonate electrobrightening operating conditions and suitable post-treatments are given in Table 14.

Table 14 Sodium carbonate electrobrightening of aluminum and aluminum alloys

Constituent or condition	Amount or value
Electrobrightening	
Sodium carbonate (anhydrous)	15 wt%

Trisodium phosphate	5 wt%
pH	10.5
Temperature of bath	80-82 °C (175-180 °F)
Current density	2-3 A/dm^2 (20-30 A/ft^2)
Voltage	9-12 V
Initial immersion without current	20 s
Immersion time with current	5 min
Agitation	Work rod only
Anodizing[(b)]	
Sodium bisulfate	20 wt%
Temperature of bath	35 °C (95 °F)
Current density	0.5 A/dm^2 (5 A/ft^2)
Voltage	10 V
Immersion time	15 min
Smut removal[(a)]	
Sulfuric acid	10 vol%
Temperature of bath	20-25 °C (70-80 °F)
Immersion time	15-30 s
Sealing	
Distilled water	100%
Temperature of bath	85 °C (185 °F)

Immersion time	20 min

(a) Smut may also be removed mechanically.

(b) The anodizing treatment in the preceding list may be used as an alternative.

Sulfuric-phosphoric-chromic acid electrobrightening operating conditions and suitable post-treatments are given in Table 15. This process is used primarily for macrosmoothening to replace mechanical polishing wholly or in part. Other applications include architectural trim, decorative ware, jewelry, and products made of commercial alloys.

Table 15 Sulfuric-phosphoric-chromic acid electrobrightening of aluminum and aluminum alloys

Constituent or condition	**Amount or value**
Electrobrightening[(a)]	
Sulfuric acid	4-45 wt%
Phosphoric acid	40-80 wt%
Chromic acid	0.2-9.0 wt%
Trivalent metals	6 wt% max
Temperature of bath	70-95 °C (160-200 °F)
Viscosity of bath at 82 °C (180 °F)	9-13 cP
Current density	2.5-95 A/dm^2 (25-950 A/ft^2)
Voltage	7-15 V
Agitation	Mechanical
Smut removal	
Phosphoric acid	3.5 wt%
Chromic acid	2.0 wt%
Temperature of bath	90-95 °C (190-200 °F)

Anodizing	
Sulfuric acid	7-15 wt%
Current density	1.2 A/dm^2 (12 A/ft^2)
Temperature of bath	20 °C (70 °F)
Immersion time	10-20 min
Sealing	
Distilled water	100%
Temperature of bath	95-100 °C (200-212 °F)
Immersion time	10 min

(a) U.S. Patent 2,550,544 (1951)

Selection of Chemical and Electrolytic Brightening Processes

Chemical and electrolytic brightening are essentially selective-dissolution processes, in which the high points of a rough surface are attacked more rapidly than the depressions. An important feature of these processes is their ability to remove a surface skin of metal that is contaminated with oxides and with traces of residual polishing and buffing compounds, or other inclusions, while at the same time brightening the surface.

Metallurgical Factors. The composition, orientation, and size of the individual grains within a workpiece have a direct effect on the uniformity of dissolution during brightening. Fine-grain material is the most desirable for chemical or electrolytic brightening. Best results are obtained with alloys that are of uniform chemical composition and that do not precipitate constituents of different potential from the matrix during any necessary heating or heat treatment. Also, the alloys should be such that forming operations cause only relatively minor detrimental effects.

Mill operations must be controlled to produce material that can be brightened satisfactorily. It is important that the material be fine-grain and that surfaces be free of imperfections, such as segregation, oxide inclusions, laps, die marks, and stains.

Optical Factors. In general, the highest total and specular reflectance of a brightened surface is obtained on pure aluminum having a fine grain structure. Reflectance, both total and specular, decreases as alloy content increases; however, at a given alloy content the decrease will vary with the process. Magnesium has a very small effect on reflectance. The effect of alloying elements varies greatly with different brightening processes.

In a few applications, chemically or electrolytically brightened surfaces are protected by a clear organic coating. However, most surfaces brightened by these methods are anodized to produce a clear, colorless, protective oxide coating. For many decorative uses, the anodic coating is subsequently dyed.

Applications of chemical and electrolytic brightening processes are functional and decorative. They include jewelry, razor parts, automotive trim, fountain pens, searchlight reflectors, natural-finish or brightly colored giftware, architectural trim, household appliances, and thermal reflectors for components of space vehicles.

Chemical and electrolytic brightening may be used before or after buffing, as an intermediate operation, or to replace buffing either completely or partly. In processes where brightening is used to replace buffing completely, aluminum is dissolved at relatively rapid rates, and 25 μm (1 mil) or more of metal is removed. In processes where brightening is used as the final operation of the finishing sequence, metal is dissolved more slowly, and total metal removal usually ranges from about 3 to 13 μm (0.1 to 0.5 mil). Such procedures are used primarily on super-purity aluminum with up to 2% Mg and on high-purity aluminum.

Chemical versus Electrolytic Brightening. Because of improvements in chemical brightening processes, brightening results are equivalent to those obtained by the electrolytic processes, with the exception of reflector-type finishes on super-purity and high-purity aluminum.

Initial and operating costs for equipment are lower for chemical brightening than for electrolytic brightening, because electrical power and associated equipment are not required. Chemical brightening can be used on a variety of alloys.

Electrobrightening processes can have low chemical costs, because the chemicals used are less expensive and because baths operate well at high levels of dissolved aluminum. Other advantages of some baths used in electrobrightening are chemical stability of the solution and the ability of the bath to operate continuously for long periods at optimum efficiency with relatively simple control.

Advantages over Buffing. In performance and economy, chemical and electrolytic polishing processes offer the following advantages over buffing:

Performance

- Contaminants are not introduced into the metal surface. Chemical or electrolytic processes remove trace amounts of contaminants initially present in the surface skin or embedded in the metal during prior operations. Surfaces brightened by these processes have better total and specular reflectance.
- Anodized and dyed surfaces that have been chemically or electrolytically brightened have a brilliance, clarity, and depth not attainable with buffed surfaces. Anodizing reduces the reflectance values of chemically or electrolytically brightened surfaces less than it reduces the reflectance of buffed surfaces.
- Chemical or electrolytic brightening of aluminum prior to electroplating provides better adhesion and continuity of the plated deposits. This improves corrosion resistance and serviceability.

Economy

- Labor costs are lower than for buffing.
- Processes are readily adaptable to high-production parts that, because of their shape, cannot be finished on automatic buffing machines, and to parts that require buffing of a large percentage of the total surface area. Modification of automatic buffing machines to accommodate parts of different shapes may be more expensive than changes in racking for chemical or electrolytic brightening of these parts.
- Incorporation of processes into an automatic anodizing or electroplating line can result in economies in terms of space, equipment, and operations, and it may eliminate one or more cleaning or pickling operations in the pretreatment cycle. Deburring can sometimes be completely eliminated because of the high rate of metal removal on edges and corners.

Chemical Etching

Chemical etching, using either alkaline or acid solutions, produces a matte finish on aluminum products. The process may be used for final finishing, but it is more often used as an intermediate step prior to lacquering, conversion coating, anodizing, or other finishing treatments. Chemical etching also is used extensively in conjunction with buffing or chemical brightening.

The advantages of etching with alkaline or acid solution prior to anodizing are that it removes oxide films and embedded surface contaminants that otherwise would discolor the anodic coating; roughens the surface slightly, to produce a less glossy anodized surface and to minimize slight differences in the mill finish of different production lots; and minimizes

color-matching differences, which are more apparent with glossy or specular surfaces. Matte finishes are readily produced by chemical etching on the following wrought and cast aluminum alloys:

Wrought alloys

- *Sheet and plate:* 1100, 2014, 2024, 3003, 5005, 5052, 5457, 6061, 7075
- *Extrusions:* 2014, 2024, 6061, 6063, 6463, 7075

Casting alloys

- 242, 295, 514, A514, B514, F514, 518, 510

Cleaning prior to etching is recommended for attainment of the highest-quality finish. The need for prior cleaning, however, is determined by the amount and type of soil present on the surface of work being processed. In many instances, the etching solution serves as both a cleaner and a finishing medium.

Post-Treatments. Subsequent treatments, such as anodizing or chromate conversion coating, are required for protection against corrosion and against mechanical damage to the soft, easily marred surface. Clear lacquer may be applied to protect the matte finish produced by the etching process. Before being lacquered, the work must be cleaned of etching smut, thoroughly rinsed in clean cold water, and dried in warm air. Lacquering or painting should be done as soon as possible in a clean atmosphere.

Alkaline Etching

Alkaline etching reduces or eliminates surface scratches, nicks, extrusion die lines, and other imperfections. However, some surface contaminants, if not removed before the work enters the etching solution, may accentuate these imperfections during etching. Oxides, rolled-in dirt, and many other surface contaminants can sometimes be eliminated by deoxidizing the work with a 2 to 4 wt% chromic acid/10 to 15 wt% sulfuric acid etchant at 60 to 70 °C (140 to 160 °F) prior to alkaline etching. This treatment removes stains resulting from heat treatment and other causes without removing much metal.

Solution Makeup and Control. A hot (50 to 80 °C, or 120 to 180 °F) solution of sodium hydroxide, potassium hydroxide, trisodium phosphate, or sodium carbonate is used for alkaline etching. The solution may contain more than one alkali. The use of uninhibited alkaline solutions (such as sodium hydroxide solutions) is not recommended for high-strength 7*xxx* and 2*xxx* aluminum alloys in certain artificially aged tempers because of the danger of intergranular attack.

Sequestrants, such as gluconic acid, sodium gluconate, the glucamines, and sorbitol, are added to alkaline solutions to prevent the formation of hydrated alumina. If permitted to form, this compound coats tank walls and heating coils with a difficult-to-remove scale. Sequestrants increase the life of the bath by preventing the formation of scale and by reducing the accumulation of sludge in the tank. They are added in concentrations of 1 to 5%.

Sodium hydroxide is the alkali most commonly used. Its reaction with aluminum is exothermic, produces hydrogen gas and sodium aluminate, and may increase the temperature of the bath, depending on the relationship between rate of metal removal and tank volume. Uniform finishes may thus be more difficult to obtain with large loads or rapid dissolution rates in small tanks, because the increase in temperature causes faster etching and more rapid depletion of the chemical constituents in the bath.

The concentration of sodium hydroxide in the etching solution usually ranges from 15 to 60 g/L (2 to 8 oz/gal). For most applications, a concentration of 30 to 45 g/L (4 to 6 oz/gal) is adequate. The choice of concentration is influenced by the finish desired, the operating temperature of the bath, the quality of water, the transfer time between the etchant and rinse, and the amount of drag-out.

Solution control is guided by regular titration of samples to determine free sodium hydroxide and sodium aluminate (aluminum). In a common method of operation, the concentration of free sodium hydroxide is not permitted to fall below

26 or 30 g/L (3.5 or 4 oz/gal) when a uniform, medium-deep etch is required. The normal working concentration of aluminum is about 30 g/L (4 oz/gal), or about 2.5 wt%. When the aluminum content of the solution approaches 55 to 75 g/L (7 to 10 oz/gal) and the free sodium hydroxide content about 40 g/L (5 oz/gal), the finish may become brighter and more reflective, indicating that the solution is nearly exhausted and should be partly or completely replaced.

Determination of specific gravity also is useful in solution control. A solution that has a specific gravity of 1.15 to 1.18 while maintaining a free sodium hydroxide content of 30 to 38 g/L (4 to 5 oz/gal) is considered to be approaching exhaustion. When this condition is reached, the finish being produced should be carefully observed for nonuniform etching and shiny appearance. As the aluminum content of the solution increases, the solution becomes more viscous, which may result in poor rinsing and greater drag-out. Special proprietary rinse additives are available that help to reduce the drag-out and streaking problems caused by high viscosity of the etchant.

Environmental regulations have led to the development of waste recovery technology for used caustic etching solutions. These baths can be operated without any chelating agents, such as sodium gluconate. Recovery processes depend on a controlled precipitation of dissolved aluminum with an accompanying regeneration of free sodium hydroxide. Closed-loop recovery systems of this type also reduce chemical costs and provide more uniform etching. Because of the high capital investment required, these recovery processes are most feasible for large installations.

Equipment and Operating Procedures. Tanks and heating coils for alkaline etching may be made of low-carbon steel. Ventilation is required for the etching tanks, because the mistlike fumes generated are a health hazard to personnel, and because alkali-contaminated air can corrode or etch unprotected aluminum in the work area, especially during periods of high humidity. Efficient venting should be provided to exhaust the fumes and spray generated during the transfer of the parts to the first rinse tank.

Sometimes a blanket of foam on the solution is used to reduce the amount of mist. Foam is usually created by the addition of surface-active, or wetting, agents to the bath. A layer of 25 or 50 mm (1 or 2 in.) of foam on the surface of the bath is usually adequate.

Work to be processed may be placed on appropriate racks or loaded in baskets for immersion in the etching solution. Dipping is the method most often used for etching, although in some instances spray etching has been used. Workpieces to be bulk-processed in baskets must be positioned to prevent the formation of air or gas pockets. For best results, it is desirable to agitate the solution by air or by movement of the work.

Racks and baskets are usually used when etching is followed by subsequent treatments, such as chemical brightening or conversion coating. Stainless steel is a suitable material for bulk-etching baskets, because it withstands the corrosive conditions of the various solutions used in the cleaning and finishing processes. Baskets for bulk etching cannot be used for anodizing because an electrical contact cannot be made. Bulk parts must be transferred to specially designed containers with a pressure contact prior to anodizing.

In general, bath temperatures range from 50 to 80 °C (120 to 180 °F). Specific operating temperature is determined by the final finish desired, the time cycle, available equipment, and the concentration of the bath constituents.

After etching, the work should be rinsed immediately. A high etching temperature and a long transfer time from the etching tank may cause dry-on of the etchant. This condition produces a nonuniform finish characterized by cloudy, pitted, or stained areas.

An air-agitated rinse is beneficial, as is a double rinse in cold water flowing in a countercurrent. The latter method uses smaller tanks, uses less water, and produces better rinsing than the use of warm water or only one rinse tank. Warm water may cause staining as a result of postetching, especially when only one rinse tank is used. The work should not remain too long in the first rinse tank following etching, because the tank usually contains sufficient residual sodium hydroxide to cause staining or a cloudy finish.

Spot welds, riveted areas, and folded edges may contain small cracks or crevices that entrap the alkaline solution. Rinsing may not remove the entrapped solution; the alkaline solution will subsequently bleed out and leave a residue of white powder after the finishing process is completed. Bleed-out also can occur after anodizing. Bleed-out is unattractive and can cause failure of organic films, such as lacquers and paints, applied for added protection.

Dimensional Changes. Etching in alkaline solutions can remove a considerable amount of metal. Figure 1 shows the dimensional changes that occurred when sheet materials of various aluminum-base alloys were etched for 1, 2, or 3 min in air-agitated sodium hydroxide solution (5 wt% NaOH) operated at 70 ± 5 °C (160 ± 5 °F). When clad materials are being treated, the etching cycle must be carefully controlled to prevent loss of the cladding.

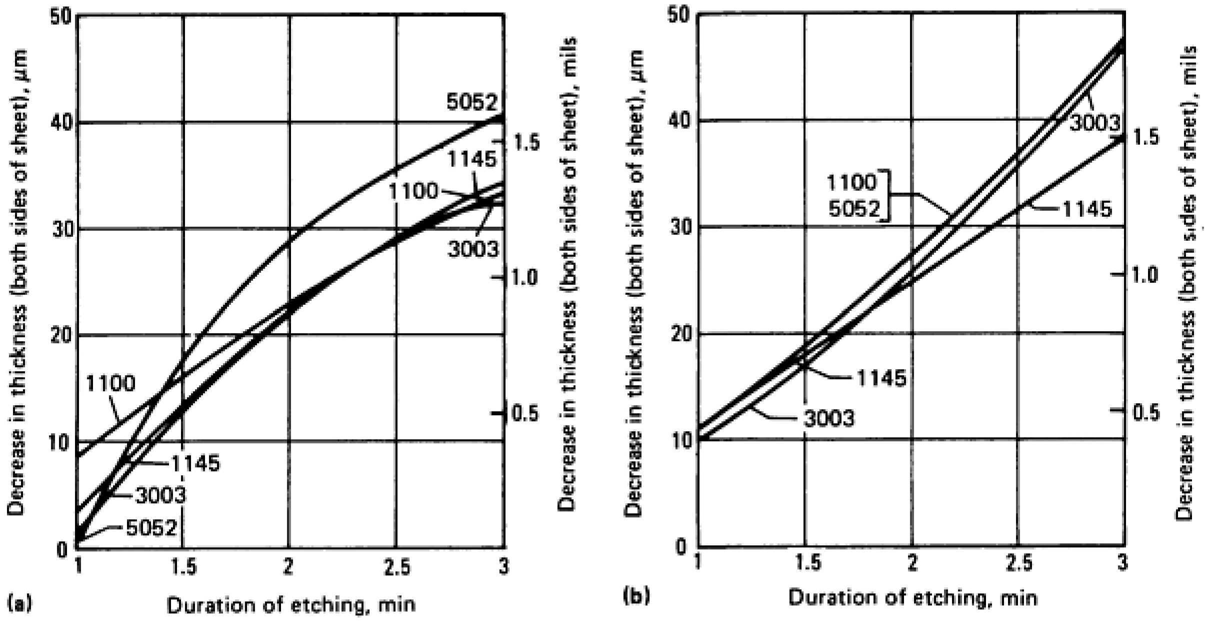


Fig. 1 Effect of time on the amount of metal removed from aluminum alloys during alkaline etching. (a) By micrometer measurement. (b) Calculated from loss in weight. Both solutions contain 5 wt% NaOH at 70 ± 5 °C (160 ± 5 °F).

Desmutting. During the cleaning and etching operation, smut (a gray-to-black residual film) is deposited on the surface of the work. This deposit usually consists of iron, silicon, copper, or other alloying constituents (in an aluminum-base material) that are insoluble in sodium hydroxide. When etching is to be followed by anodizing, the smut can sometimes be removed by the anodizing solution (current flowing); however, this practice generally cannot be controlled to produce a finish of uniform appearance. Copper and iron smuts dissolved in the anodizing electrolyte can accumulate until they make necessary premature disposal of the electrolyte. The recommended procedure is to remove the smut in a solution prepared specifically for this purpose.

A nitric acid solution (10 to 15 vol% HNO_3 or more) will remove smut. A solution containing 0.5 to 1 wt% chromic acid plus 4 to 6 wt% sodium bisulfate is similarly effective. Solutions of proprietary compounds that are nonchromated and hence nonpolluting are also used. Fluorides are usually added to solutions to aid the removal of smut from high-silicon aluminum alloys and aluminum die castings. Good results have been obtained with a room-temperature solution of 3 parts nitric acid and 1 part hydrofluoric acid.

The following example describes the solution to a problem encountered in the desmutting of die castings of a high-silicon alloy that was etched in a sodium hydroxide solution.

Because of the high silicon content of alloy 380.0 (7.5 to 9.5% Si), desmutting to obtain an attractive, uniform finish on the die castings was difficult. A chromate-type desmutting solution had been used after etching in sodium hydroxide, but it had not been entirely effective. The addition of an acid fluoride etch provided the desired finish. The sequence of operations used was as follows:

1. Soak in nonetching aluminum cleaner at 60 to 65 °C (140 to 150 °F) for 5 to 10 min.
2. Rinse in cold water.
3. Etch for 60 to 90 s in a sodium hydroxide etching solution at 60 to 65 °C (140 to 150 °F).
4. Rinse in cold water.

5. Remove part of the smut by immersing in an air-agitated, chromate-type desmutting solution at room temperature.
6. Rinse in cold water.
7. Immerse in a room-temperature acid etching solution containing fluoride and nitric acid for 30 to 60 s to remove the remaining smut.
8. Rinse in cold water.

After being prepared in this manner, the castings were chromate-conversion coated and dipped in lacquer.

Proprietary chromic-sulfuric acid desmutting solutions generally require a tank made of type 302 or 304 stainless steel, although some solutions may require type 316 or 347. They are usually operated at room temperature and normally do not require ventilation. This is an advantage over nitric acid solutions. A disadvantage of some proprietary solutions is the need for treatment of the wastes to remove the harmful effects of chromium salts before the wastes are discharged from the plant. EPA regulations and local ordinances regulate the disposition of waste solutions.

Hexavalent chromium compounds and nitric acid are especially undesirable from an EPA environmental viewpoint. As a result, these traditionally effective oxidizing agents are frequently replaced with such compounds as ferric salts, persulfates, and peroxides. (Additional information is available in the article "Chromium Elimination" in this Volume.)

Acid Etching

Acid solutions are commonly used for finished castings, especially those made of high-silicon alloys. Acid etching can be done without heavy smut problems, particularly on aluminum die castings. Hydrochloric, hydrofluoric, nitric, phosphoric, chromic, and sulfuric acids are used in acid etching.

Combinations of these acids and mixtures of acids and salts are often used for specific applications. Sulfuric-chromic acid solutions remove heat-treating stains with little etching of the metal; dilute hydrofluoric-nitric acid solutions produce bright, slightly matte-textured surfaces; and hydrochloric acid containing sodium chloride and ferric chloride is used for deep etching of designs. Additions of cobalt and nickel salts to the hydrochloric acid solution accelerate etching, but they do not affect the ability of the solution to produce a sufficiently smooth surface. Alloys containing silicon, such as sand castings, should be acid-etched with a 2 to 5% aqueous solution of hydrofluoric acid prior to anodizing.

Compositions and operating conditions for three acid etching solutions are:

Solution 1	
Nitric acid	3 parts by vol
Hydrofluoric acid	1 part by vol
Temperature of bath	20 °C (70 °F) max
Immersion time	15 s to 1 min
Solution 2	

Chromic acid	80 g (10.5 oz)
Sulfuric acid	675 mL (22.4 fluid oz)
Water, to make	4 L (1 gal)
Temperature of bath	60-70 °C (140-160 °F)
Immersion time	30 s to 2 min
Solution 3	
Chromic acid	175 g (23.5 oz)
Sulfuric acid	75 mL (2.5 fluid oz)
Water, to make	4 L (1 gal)
Temperature of bath	60-70 °C (140-160 °F)
Immersion time	30 s to 2 min

Figure 2 is a flow chart of the operations used in acid etching.

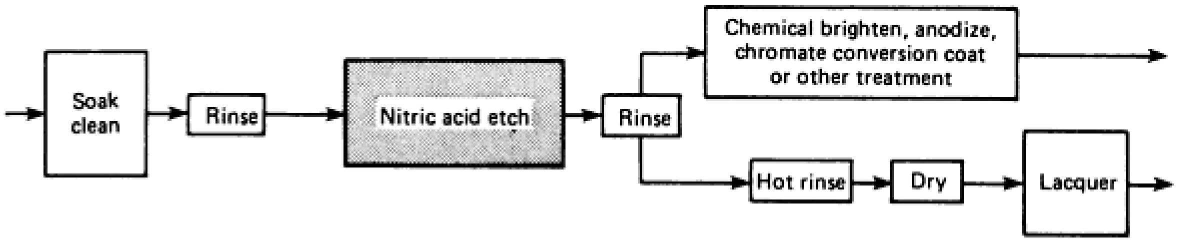


Fig. 2 Operations used in etching of aluminum and aluminum alloys

Fumes from most acid etching solutions are corrosive, and the mist or spray carried up by the gases generated constitutes a health hazard. Ventilation is required, even for solutions operated at room temperature. Tanks are made of stainless steel or plastic, or are plastic lined; plastic or plastic-lined tanks are used with solutions containing hydrochloric or hydrofluoric acid. Cooling coils may be required, because etching generates heat. Heating coils are required for solutions operated at elevated temperatures.

Acid etching is often used alone, but sometimes it may either precede or follow alkaline etching. It is usually used before alkaline etching when oxides are to be removed and after alkaline etching when smut removal is a problem. Acid etching solutions, especially those containing fluorides, are excellent smut and scale removers. After acid etching and thorough rinsing, the work is ready for further processing (Fig. 2).

Anodizing

The basic reaction in all anodizing processes is the conversion of the aluminum surface to aluminum oxide while the part is the anode in an electrolytic cell. Aluminum surfaces are anodized for a number of reasons, including to:

- Increase corrosion resistance
- Increase paint adhesion
- Prepare the surface for subsequent plating
- Improve adhesive bonding
- Improve decorative appearance
- Provide electrical insulation
- Permit application of photographic and lithographic emulsions
- Increase emissivity
- Increase abrasion resistance
- Permit detection of surface flaws

The three principal types of anodizing processes are:

- *Chromic anodizing,* in which the agent is chromic acid
- *Sulfuric anodizing,* in which the active agent is sulfuric acid
- *Hard anodizing,* in which the agent is sulfuric acid, alone or in combination with additives

Other processes, used less frequently or for special purposes, employ sulfuric-oxalic, phosphoric, oxalic, boric, sulfosalicylic, or sulfophthalic acid solutions. Except for those produced by hard anodizing processes, most anodic coatings range in thickness from 5 to 18 μm (0.2 to 0.7 mil). The succession of operations typically employed in anodizing is illustrated in Fig. 3.

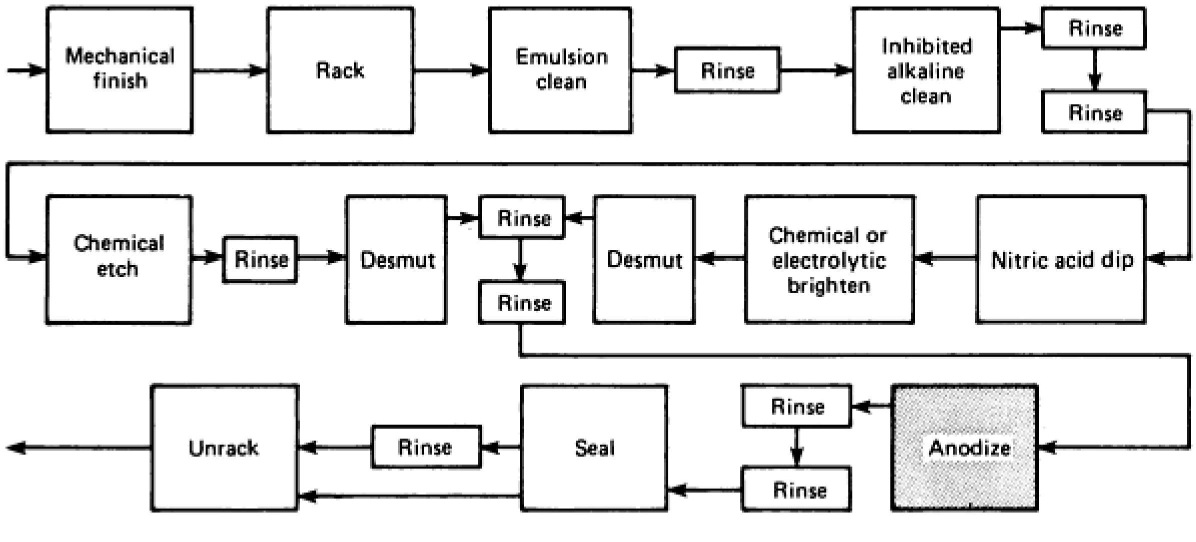


Fig. 3 Typical sequence of operations for anodizing aluminum alloys

The three major anodizing processes, as well as anodizing equipment, applications, troubleshooting, and coating evaluation, are described in detail in the article "Anodizing" in this Volume.

Chemical Conversion Coating

Chemical conversion coatings are adherent surface layers of low-solubility oxide, phosphate, or chromate compounds produced by the reaction of suitable reagents with the metallic surface. These coatings affect the appearance, electrochemical potential, electrical resistivity, surface hardness, absorption, and other surface properties of the material. They differ from anodic coatings in that conversion coatings are formed by a chemical oxidation-reduction reaction at the surface of the aluminum, whereas anodic coatings are formed by an electrochemical reaction. The reaction that takes place in chemical conversion coating involves the removal of 0.3 to 2.5 μm (0.01 to 0.1 mil) of the material being treated.

Conversion coatings are excellent for:

- Corrosion retardation under supplementary organic finishes or films of oil or wax
- Improved adhesion for organic finishes
- Mild wear resistance
- Enhanced drawing or forming characteristics
- Corrosion retardation without materially changing electrical resistivity
- Decorative purposes, when colored or dyed

Conversion coatings are used interchangeably with anodic coatings in organic finishing schedules. One use of conversion coating is as a spot treatment for the repair of damaged areas in anodic coatings. Because of their low strength, conversion coatings should not be used on surfaces to which adhesives will be applied. Anodic coatings are stronger than conversion coatings for adhesive bonding applications.

The simplicity of the basic process, together with the fact that solutions may be applied by immersion, spraying, brushing, wiping, or any other wetting method, makes conversion coating convenient for production operations. Some applications using chemical conversion coatings on various aluminum alloys are given in Table 16. In most installations, conversion coating offers a cost advantage over electrolytic methods. Moreover, unlike some anodic coatings, chemical conversion coatings do not lower the fatigue resistance of the metal treated.

Table 16 Applications of aluminum using chemical conversion coatings

Application	Aluminum alloy	Subsequent coating
Oxide conversion coatings		
Baking pans[(a)]	1100, 3003, 3004, 5005, 5052	Silicone resin
Phosphate conversion coatings		
Screen cloth	5056	Clear varnish
Storm doors	6063	Acrylic paint[(b)]
Cans	3004	Sanitary lacquer
Fencing	6061	None applied
Chromate conversion coatings		

Aircraft fuselage skins	7075 clad with 7072	Zinc chromate primer
Electronic chassis	6061-T4	None applied
Cast missile bulkhead	356-T6	None applied
Screen	5056 clad with 6253	Clear varnish
Extruded doubler	6061-T6	Clear lacquer

(a) Baking pans of these alloys may alternatively be chromate conversion coated prior to the application of silicone resin.

(b) Thermosetting

Procedure. The sequence of operations for applying a satisfactory conversion coating to aluminum-base materials is as follows:

- Removal of organic contaminants
- Removal of oxide or corrosion products
- Conditioning of the clean surface to make it susceptible to coating
- Conversion coating
- Rinsing
- Acidulated rinsing (recommended if supplementary coating is to be applied)
- Drying
- Application of a supplementary coating when required

Surface preparation entails the same procedures as are used in preparation for anodizing. However, the cleaning procedure for preparing aluminum for conversion coating is much more critical than for anodizing. After cleaning, removal of the natural oxide film is accomplished in any of the standard aqueous solutions, such as chromate-sulfate, chromate, or phosphate.

Pretreatment immediately prior to the coating operation is required for the development of extremely uniform conversion coatings. Either acid or alkaline solutions are used. Subsequent to the above operations, the work is subjected to the conversion coating solution. The addition of a wetting agent, such as sodium alkyl aryl sulfonate, to the solution helps to produce a uniform and continuous coating. After coating, the work is thoroughly rinsed and dried. The final rinse is usually hot (60 to 80 °C, or 140 to 180 °F) to aid drying. Drying is important in order to prevent staining. Drying at temperatures higher than 65 °C (150 °F) usually dehydrates the coatings and thus increases hardness and abrasion resistance.

Supplementary coatings of oil, wax, paint, or other hard organic coatings frequently are applied. If the conversion coating is intended to improve subsequent forming or drawing, the final supplementary coating may be soap or a similar dry-film lubricant.

Oxide Coating Processes. The modified Bauer-Vogel (MBV), Erftwerk (EW), and Alrok processes are the principal methods for applying oxide-type conversion coatings. Nominal compositions of the solutions used and typical operating conditions are given in Table 17. The MBV process is used on pure aluminum as well as on aluminum-magnesium, aluminum-manganese, and aluminum-silicon alloys. The coating produced varies from a lustrous light gray to a dark gray-black color. The EW process is used for alloys containing copper. The film produced is usually very light gray. The

Alrok process is for general-purpose use with all alloys, and it is often the final treatment for aluminum products. Coatings vary in color from gray to green and are sealed in a hot dichromate solution.

Table 17 Process conditions for oxide conversion coating of aluminum

Process	Bath composition	Amount		Temperature		Duration, min	Uses
		g/L	oz/gal	°C	°F		
I MBV	Sodium chromate	15	1.7	96	205	5-10 or 20-30	Corrosion protection or foundation for varnishes or lacquers
	Sodium carbonate	50	5.7				
II MBV	Sodium chromate	15	1.7	65	150	15-30	In situ treatment of large objects with paint brush or spray. When 8 g/L (0.9 oz/gal) sodium hydroxide is added, MBV oxidation may be carried out at 35 °C (95 °F) for 30 min
	Sodium chromate	50	5.7				
	Sodium hydroxide	4	0.5				
EW	Sodium carbonate	56	6.4	88-100	190-212	8-10	For copper-containing alloys
	Sodium chromate	19	2.2				
	Sodium silicate	0.75-4.5	0.09-0.5				
Alrok	Sodium carbonate	20	2.3	88-100	190-212	20	Final treatment for aluminum products
	Potassium dichromate	5	0.6				

Phosphate Coating Process. The range of operating conditions and a formula for a standard solution for phosphate coating are given below:

Specific formulations

Ammonium dihydrogen phosphate ($NH_4H_2PO_4$)	61.7%
Ammonium bifluoride (NH_4HF_2)	22.9%
Potassium dichromate ($Kr_2Cr_2O_7$)	15.4%
Operating temperature	45-50 °C (110-120 °F)
Treatment time	1-5 min
Desired operating range	
Phosphate ion	20-100 g/L (2.6-13.2 oz/gal)
Fluoride ion	2-6 g/L (0.26-0.80 oz/gal)
Dichromate ion	6-20 g/L (0.80-2.6 oz/gal)
Operating temperature	18-50 °C (65-120 °F)
Treatment time	1.5-5 min

Each liter (gallon) of solution contains 75 to 150 g (10 to 20 oz) of a mixture consisting of the above formulations (U.S. Patent 2,494,910, 1950).

Phosphate coatings vary in color from light bluish-green to olive green, depending on the composition of the aluminum-base material and the operating conditions of the bath. The phosphate-chromate conversion coatings are used extensively on aluminum parts or assemblies to provide galvanic protection from components of different kinds of materials, such as bushings or inserts made of steel.

Chromate Coating Process. Solution compositions and operating conditions for two chromate conversion coating processes are given in Table 18. Chromate coatings vary from clear and iridescent to light yellow or brown, depending on the composition of the aluminum-base material and the thickness of the film. Chromate coatings are used when maximum resistance to corrosion is desired.

Table 18 Process conditions for chromate conversion coating of aluminum

Process	Solution composition	Amount		pH	Temperature		Treatment time
		g/L	oz/gal		°C	°F	
Process A[a]	CrO_3	6[b]	0.80[b]	1.2-2.2	16-55	60-130	5 s-8 min
	NH_4HF_2	3	0.40				

	$SnCl_4$	4	0.6				
Process B[c]	$Na_2Cr_2O_7 \cdot 2H_2O$	7[b]	1[b]	1.2-2.2	16-55	60-130	5 s-8 min
	NaF	1	0.1				
	$K_3Fe(CN)_6$	5	0.7				
	HNO_3 (48° Bé)	[d]	[d]				
Process C[e]	H_3PO_4	64	8.5	1.2-2.2	40-80	105-175	1-10 min
	NaF	5	0.6				
	CrO_3	10	1.3				

(a) U.S. Patents 2,507,959 (1950) and 2,851,385 (1958).

(b) Desired range of hexavalent chromium ion, 1 to 7 g/L (0.13 to 0.90 oz/gal).

(c) U.S. Patent 2,796,370 (1957).

(d) 3 mL (0.1 fluid oz).

(e) Process for Alodine, Alochrome, and Bonderite

Chromate coatings exhibit low electrical resistivity. At a contact pressure of 1380 kPa (200 psi), in a direct-current circuit, the resistivity of a normal chromate film varies from 0.30 to 3.0 $\mu\Omega/mm^2$ (200 to 2000 $\mu\Omega/in.^2$). This resistivity is low enough so that a chromate-coated article can be used as an electrical ground. The conductivity of the films at radio frequencies is extremely high. This permits the use of a chromate film on electrical shields and wave guides. Thus, chromate conversion coating is widely used for treatment of aluminum articles for the electronics industry.

Processing equipment for conversion coating solutions must be made from acid-resistant materials. Tanks may be made of type 316 stainless steel or of low-carbon steel if lined with polyvinyl chloride or another suitably protective material. Tanks for solutions that do not contain fluorides can be constructed of acid-resistant brick or chemical stoneware. Racks can be made of low-carbon steel but must be coated with an acid-resistant compound. Heating coils or electrical immersion heaters should be made of stainless steel or stainless-clad material.

Some conversion coating solutions cause a sludge to form in the bottom of the tank. To prevent contact between the sludge and the workpieces, the tank may be equipped with a false bottom through which sludge can fall.

Adequate ventilation must be provided to remove vapors. The inhalation of fluoride vapors is dangerous. Solutions should not contact the skin; if they do, the affected area should be washed immediately with running water and then be treated by a physician. Respirators, goggles, and gloves should be worn when handling all chemicals used to make up solutions. Brushes used to apply solutions should have natural bristles; synthetic bristles are attacked by solutions.

Control of Solution. Most users of conversion coating solutions purchase prepared formulations for makeup and solution adjustment. In general, the solutions require control of both pH and the concentration of the critical elements. Direct measurement of pH is made with a glass-cell electric pH meter. The percentage concentration of active ion is obtained by direct titration with a suitable base.

Solution control becomes more critical as the size of the bath decreases with respect to the amount of work treated. Experienced operators of a conversion coating process can detect changes in the composition of the solution by observing the color and appearance of the treated work. A skilled operator often can control the bath by this method alone.

During use, coating solutions are depleted by drag-in, drag-out, and consumption of the basic chemicals. In one plant, drag-in of alkaline cleaner into the conversion coating bath adversely affected the appearance of the conversion coating. Details of this problem and the method adopted for correcting it are given in the following example.

Aluminum screen cloth made from wires of alloy 5056 clad with alloy 6253 had a rejection rate as high as 3% because of the presence of sparklers on the product after chemical conversion coating. Sparklers, also known as shiners, are areas that have higher metallic reflectance than the rest of the conversion-coated surface; they are merely an appearance defect and do not affect the adherence of organic coatings. The following processing cycle was being used:

1. Alkaline cleaning for 1 min in an inhibited solution at 70 °C (160 °F)
2. Rinsing for 30 s in overflowing cold water
3. Conversion coating for $2\frac{1}{2}$ min in a phosphate-chromate solution at 40 to 45 °C (100 to 115 °F)
4. Rinsing for 30 s in overflowing cold water
5. Second rinsing for 30 s in overflowing cold water
6. Drying
7. Application of a clear varnish (baked at 135 °C, or 275 °F for $1\frac{1}{2}$ to 2 min) or of a gray pigmented paint. (For material to be painted, conversion coating required only $1\frac{1}{2}$ min.)

The coating defects were found to be caused by contamination (and neutralization) of the acid conversion coating solution by drag-in from the alkaline cleaner. The use of a rotating beater to shake droplets of cleaning solution out of the screen openings had reduced drag-out from that bath, but it had not eliminated it.

To prevent neutralization of the acid conversion coating solution by contamination with alkali from step 1, the slightly acid overflow from the rinse in step 4 was piped back into the rinse tank in step 2, thus keeping it slightly acid. Rejects were eliminated. This procedure also reduced the amount of overflow rinse water needed to operate the line.

Control of Coating Quality. A properly applied coating should be uniform in color and luster and should show no evidence of a loose or powdery surface. Poor luster or powder surfaces are caused by low pH, improper cleaning and rinsing, excessive treatment temperature or treatment time, a contaminated bath, or insufficient agitation. Light and barely visible coatings are caused by high pH, low operating temperatures, insufficient treatment times, or high ion concentrations. Usually, the quality of a conversion coating is established on the basis of its appearance, corrosion resistance, hardness, and adherence. These qualities may be determined by the ASTM test methods described in the standards listed below:

Corrosion resistance

- Salt spray: B 117
- Copper-accelerated acetic acid salt spray (fog): B 368
- Evaluation of painted or coated specimens subjected to corrosive exposure: D 1654

Resistance to blistering

- Evaluation of blistering of paints: D 714

Adherence

- Elongation of attached organic coatings with conical mandrel apparatus: D 522

Hexavalent chromium compounds are especially effective components of solutions that form conversion coatings on aluminum. However, environmental regulations often make the handling of chromate-containing rinses a high-cost operation. Two types of technology address this problem. One is a dried-in-place chromate coating system, which eliminates the need for subsequent rinsing. The second involves the use of chromium-free treatments that form oxide films containing selected metal ions. The use of either of these processes, when possible, eliminates the need for expensive chrome destruction.

Electroplating

Aluminum-base materials are more difficult to electroplate than the common heavier metals because aluminum has a high affinity for oxygen, which results in a rapidly formed, impervious oxide film, and because most metals used in electroplating are cathodic to aluminum, so that voids in the coating lead to localized galvanic corrosion. Following are comparisons between the electrolytic potentials of several common metals and those of pure aluminum:

Metal	**Potential, mV[(a)]**
Magnesium	-850
Zinc	-350
Cadmium	-20 to 0
Aluminum (pure)	0
Aluminum-magnesium alloys	+100
Aluminum-copper alloys	+150
Iron, low-carbon steel	+50 to 150
Tin	+300
Brass	+500
Nickel	+500

Copper	+550
Silver	+700
Stainless steel	+400 to 700
Gold	+950

Note: Metals above aluminum in this list will protect it; those below cause aluminum to corrode preferentially. Cathode and anode polarization, however, can cause a reversal of these relationships.

Source: *Metal Finishing,* Nov 1956

(a) In a 6% sodium chloride solution.

Electrodeposits of chromium, nickel, cadmium, copper, tin, zinc, gold, or silver are used for various decorative and functional applications. For example, automotive aluminum bumpers get a zincate treatment, copper strike, and a plating of copper, nickel, and chromium. A copper strike coated with cadmium and chromate or by flowed tin enables the soft soldering of electrical terminals to an aluminum chassis. Brass enhances the bonding of rubber to aluminum. Silver, gold, and rhodium provide specific electrical and electronic surface properties. Examples of applications of plated aluminum with typical finishing sequences are given in Table 19.

Table 19 Applications using electroplated coatings on aluminum products

Product	**Form**	**Preplating treatment**	**Electroplating system**	**Thickness**		**Reason for plating**
				µm	**mils**	
Automotive applications						
Bearings	Sheet	None	Pb-Sn-Cu alloy	6-32	0.25-1.25	Prevent seizing
Bumper guards	Castings	Buff and zincate	Cu + Ni + Cr	2.5 + 51 + 0.8	0.1 + 2 + 0.03	Appearance; corrosion resistance
Lamp brackets; steering-column caps	Die castings	Buff and zincate	Cu + Ni + Cr	0.8 + 20 + 1.3	0.03 + 0.8 + 0.05	Appearance; corrosion resistance
Tire molds	Castings	None	Hard Cr	51	2	Appearance; corrosion resistance
Aircraft applications						
Hydraulic parts; landing gears; small engine pistons	Forgings	Machine and zincate	Cu flash + Cu + hard Cr	2.5 + 25 + 76	0.1 + 1 + 3	Wear resistance

Propellers	Forgings	Conductive rubber coating	Ni	203	8	Resistance to corrosion and erosion
Shell	Extrusion	Double zincate	Cu flash + Cd[(a)]	8-13[(a)]	0.3-0.5[(a)]	Dissimilar-metal protection
Electrical and electronics applications						
Busbars; switchgears	Extrusions	Zincate	Cu flash + Cu + Ag[(b)]	8 + 5[(b)]	0.3 + 0.2[(b)]	Nonoxidized surface; solderability; corrosion resistance
Intermediate-frequency housings	Die castings	Zincate	Cu flash + Cu + Ag + Au[(c)]	13 + 13 + 0.6[(c)]	0.5 + 0.5 + 0.025[(c)]	Surface conductivity; solderability; corrosion resistance
Microwave fittings	Die castings	Zincate	Cu flash + Cu + Ag + Rh	0.25 + 13 + 0.5	0.01 + 0.5 + 0.02	Smooth, nonoxidized interior; corrosion resistance of exterior
Terminal plates	Sheet	Zincate	Cu flash	. . .	. . .	Nonoxidized surface; solderability; corrosion resistance
General hardware						
Screws; nuts; bolts	Castings	Buff and zincate	Cd (on threads)	13; 0.5 on threads	0.5; 0.2 on threads	Corrosion resistance
Die cast spray guns and compressors	. . .	Buff and zincate	Hard Cr	51	2	Appearance
Die cast window and door hardware	. . .	Barrel burnish and zincate	Brass[(d)]	8[(d)]	0.3[(d)]	Appearance; low cost
Household appliances						
Coffee maker	Sheet	Buff and zincate	Cr	5	0.2	Appearance; cleanness; resistance to food contamination
Refrigerator handles; salad makers; cream dispensers	Die castings	Buff and zincate	Cu + Ni + Cr	2.5 + 13 + 0.8	0.1 + 0.5 + 0.03	Appearance; cleanness; resistance to food contamination
Personal products						
Compacts; fountain pens	Sheet	Buff and	Cu flash + brass	5	0.2	Appearance; low cost

		zincate				
Hearing aids	Sheet	Zincate	Cu flash + Ni + Rh	19 + 0.25	0.75 + 0.01	Nonoxidizing surface; low cost
Jewelry	Sheet	Buff and zincate	Brass + Au	8 + 0.25	0.3 + 0.01	Appearance; low cost

(a) Chromate coating applied after cadmium plating.

(b) Soldering operation follows silver plating.

(c) Baked at 200 °C (400 °F) after copper plating and after silver plating. Soldering operation follows gold plating.

(d) Brass plated in barrel or automatic equipment

Effect of Substrate Characteristics on Plating Results. Each aluminum alloy, according to its metallurgical structure, behaves differently from others during electroplating. Alloying elements may be in solid solution in the aluminum, or they may be present in discrete particles or as intermetallic compounds. These microconstituents have different chemical or electrochemical reactivities, and their surfaces do not respond uniformly to treatment. Variations in response also occur between different lots or product forms of the same alloy.

Surface Preparation Methods. The three established methods for surface preparation prior to electroplating are surface roughening, anodizing, and immersion coating in zinc or tin solutions.

Surface roughening, which is accomplished either by mechanical abrasion or by chemical etching, assists in mechanically bonding the electrodeposits to the aluminum surface. Surface roughening is sometimes used in preparation for the application of hard chromium to aluminum engine parts, such as pistons. A water blast of fine quartz flour may be used to remove surface oxides and to abrade the surface. The adherent wet film protects the aluminum surface from further oxidation before plating. The quartz film is dislodged by the evolution of hydrogen that occurs during plating. Chemical etching produces undercut pits that provide keying action for the electrodeposited metal. In general, mechanical bonding of electrodeposits is not reliable, particularly for applications involving temperature variations. Therefore, preparation by surface roughening is not recommended.

Anodizing is sometimes used as a method of surface preparation prior to electroplating. However, the adherence of the subsequent electrodeposit is limited; plated deposits over anodic films are highly sensitive to surface discontinuities, making the time, temperature, and current density of the anodizing process critical. Phosphoric acid anodizing has been used for the aluminum alloys listed in Table 20; the sequence of operations is:

1. Vapor degreasing or solvent cleaning
2. Mild alkaline cleaning
3. Rinsing
4. Etching for 1 to 3 min in a solution containing sodium carbonate (23 g/L, or 3 oz/gal) and sodium phosphate (23 g/L, or 3 oz/gal), at 65 °C (150 °F)
5. Rinsing
6. Dipping in nitric acid solution (50% HNO_3 by volume) at room temperature
7. Rinsing
8. Phosphoric acid anodize according to the conditions given in Table 20; the anodic coating should not be sealed.
9. Rinsing

10. Electroplating in a copper pyrophosphate or nickel sulfamate bath

Table 20 Conditions for anodizing aluminum alloys prior to electroplating

Electrolyte solution of aqueous H_3PO_4

Alloy[(a)]	Specific gravity	Temperature		Voltage	Time, min
		°C	°F		
1100	1.300	30	87	22	5
3003	1.300	29	85	22	5
5052	1.300	29	85	22	10
6061	1.300	29	85	22	7

(a) With special care, phosphoric acid anodizing may be used also for aluminum-copper or aluminum-silicon alloys.

Immersion coating in a zincate solution is a traditional method of preparing aluminum surfaces for electroplating. It is simple and low in cost, but it is also critical with respect to surface pretreatment, rinsing, and the strike sequence used. The principle of zincating is one of chemical replacement, whereby aluminum ions replace zinc ions in an aqueous solution of zinc salts. Thus, a thin, adherent film of metallic zinc is deposited on the aluminum surface. Adhesion of the zinc film depends almost entirely on the metallurgical bond between the zinc and the aluminum. The quality and adhesion of subsequent electrodeposits depend on obtaining a thin, adherent, and continuous zinc film. The electrolytic Alstan strike is coming into general use as a more dependable method than the zincate process for obtaining good adhesion. It is followed by a bronze strike.

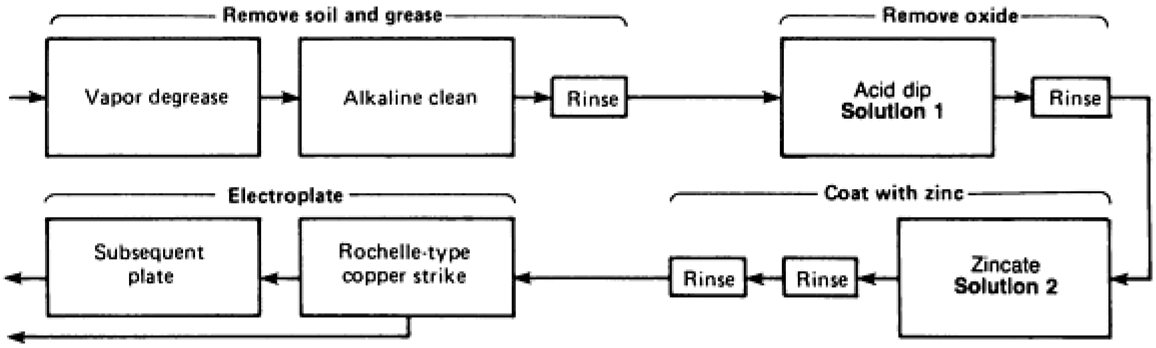
Another immersion process is based on the deposition of tin from a stannate solution. This offers improved corrosion resistance because of the more favorable electrolytic potential of tin versus zinc in chloride solutions.

Immersion Procedures. To obtain consistently good results with zinc or tin immersion procedures, it is essential that cleaning and conditioning treatments produce a surface of uniform activity for deposition. Vapor degreasing or solvent cleaning followed by alkaline cleaning is used for removing oil, grease, and other soils. The alkaline cleaner may be a mild etching solution of water containing 23 g/L (3 oz/gal) each of sodium carbonate and sodium phosphate. The solution temperature should range from 60 to 80 °C (140 to 180 °F), and the material should be immersed for 1 to 3 min and then be thoroughly rinsed. After cleaning, the material is further treated to remove the original oxide film as well as any microconstituents that may interfere with the formation of a continuous film or that may react with the subsequent plating solutions.

Castings present special problems, because their surfaces are more porous than those of wrought products. Solutions entrapped in pores are released during subsequent processing, resulting in unplated areas, staining, or poor adhesion of the electrodeposit. Sometimes the trapped solutions become evident much later, during storage or further processing (such as heating for soldering). Furthermore, even if pores are free of solution, the deposit may not bridge them, thus creating a point of attack for corrosion of the base metal. This is of particular significance in the electroplating of aluminum castings: The electrodeposited metal is electrolytically dissimilar to aluminum, and thus every opening in a casting surface will be a source of corrosion. To circumvent these problems, it is essential when preparing cast aluminum surfaces for electroplating that all processing steps be carefully controlled to avoid surfaces with excessive porosity.

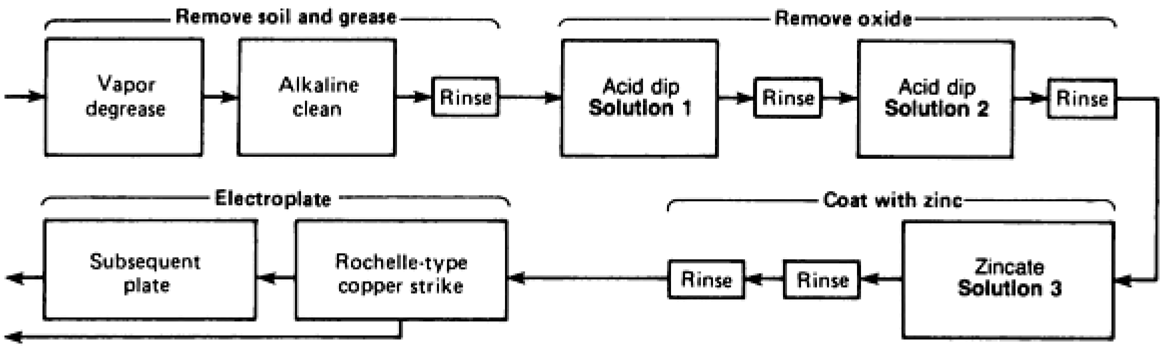
In zincating, the procedures used for removal of the original oxide film and for application of a zinc film depend to a considerable degree on the aluminum alloy. Several methods are available for accomplishing this surface conditioning, and some alloys can be conditioned by more than one procedure. In such instances, the order of preference follows the order of discussion of these procedures in the following paragraph.

Wrought alloys without interfering microconstituents and casting alloys containing high silicon are prepared for electroplating according to the procedure shown by the flow chart in Fig. 4. The flow chart in Fig. 5 represents the procedure for alloys that contain interfering microconstituents; this procedure is suitable for all wrought alloys, most casting alloys, and especially aluminum-magnesium alloys. Figure 6 indicates the procedure for treating most casting alloys, wrought alloys that contain less than approximately 3% Mg, and alloys of unknown composition.



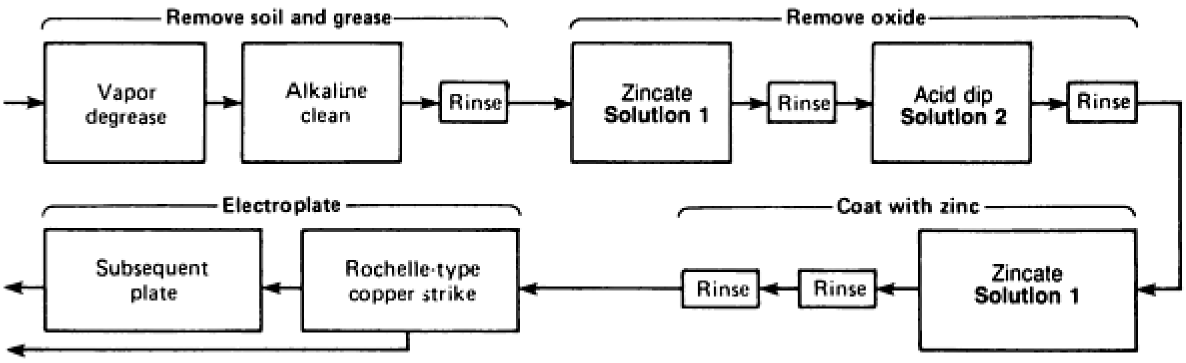
Solution No.	Type of solution	Composition	Amount	Operating temperature		Cycle time, s
				°C	°F	
Alloys 1100 and 3003						
1	Acid dip	HNO_3	50 vol%	Room	Room	15
2	Zincating	NaOH	525 g/L (70 oz/gal)	16-27	60-80	30-60
		ZnO	98 g/L (13 oz/gal)			
Alloys 413, 319, 356 and 380						
1	Acid dip	HNO_3	75 vol%	Room	Room	3-5
		HF	25 vol%			
2	Zincating	NaOH	525 g/L (70 oz/gal)	16-27	60-80	30 max
		ZnO	98 g/L (13 oz/gal)			

Fig. 4 Preplating surface preparation procedures suitable for wrought aluminum alloys that contain high amounts of silicon or do not contain interfering microconstituents (e.g., 1100 and 3003) and for aluminum casting alloys 413, 319, 356, and 380



Solution No.	Type of solution	Composition	Amount	Operating temperature		Cycle time, s
				°C	°F	
1	Acid dip	H_2SO_4	15 vol%	85 min	185 min	120-300
2	Acid dip	HNO_3	50 vol%	Room	Room	15
3	Zincating	NaOH	525 g/L (70 oz/gal)	16-27	60-80	30-60
		ZnO	100 g/L (13 oz/gal)			

Fig. 5 Preplating surface preparation procedures suitable for all wrought aluminum alloys, for most aluminum casting alloys, and for magnesium-containing aluminum alloys with interfering microconstituents. Applicable alloys include 1100, 3003, 3004, 2011, 2017, 2024, 5052, 6061, 208, 295, 319, and 355.



Solution No.	Type of solution	Composition	Amount	Operating temperature	Cycle time, s

				°C	°F	s
1	Zincating	NaOH	525 g/L (70 oz/gal)	16-27	60-80	30-60
		ZnO	100 g/L (13 oz/gal)			
2	Acid dip	HNO_3	50 vol%	Room	Room	15

Fig. 6 Preplating surface preparation procedures suitable for most aluminum casting alloys, for wrought aluminum alloys containing less than approximately 3% Mg (e.g., 1100, 3003, 3004, 2011, 2017, 2024, 5052, and 6061), and for aluminum alloys whose identities are not known

Table 21 gives details of three zincating solutions that may be used alternatively to the solution indicated in the tables that accompany Fig. 4, 5, and 6. The modified solution in Table 21 is recommended when double-immersion zincating (Fig. 6) is required; it is not essential for alloys 2024 and 7075. This solution produces more uniform coverage than the unmodified solution and also imparts greater corrosion resistance to the treated work. Dilute solution No. 1 in Table 21 is recommended when there are problems in rinsing and drag-out. Dilute solution No. 2 provides a greater reserve of zinc for high-production operations, but at a slight sacrifice in effectiveness of rinsing. In some special operations, triple zincate treatment is used. This involves essentially stripping the second zinc film formed in double zincate and adding a zincate from a third solution. Triple zincate provides an even more uniform and fine-grain zinc coating than double zincate.

Table 21 Zincating solutions for use with aluminum alloys

Solution type	Sodium hydroxide		Zinc oxide		Ferric chloride crystals		Rochelle salt		Sodium nitrate		Operating temperature		Processing time,s
	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	°C	°F	
Modified[(a)]	525	70	100	13	1.00	0.13	9.8	1.3	. . .	. . .	15-27	60-80	30-60
Dilute 1[(b)]	50.3	6.7	5	0.7	2.03	0.30	50	6.7	0.98	0.13	21-24	70-75	30 max

(a) U.S. Patent 2,676,916 (1954).

(b) U.S. Patents 2,676,916 (1954) and 2,650,886 (1953)

If correct procedures are followed, the resulting zinc deposit is uniform and firmly adherent to the aluminum surface. The appearance of the surface will vary with the alloy being coated, as well as with the rate at which the coating forms. The weight of zinc deposit should be from 1.5 to 5.0 mg/dm^2 (0.1 to 0.3 mg/in.^{2}). Generally, it is desirable to limit the deposit to 3 mg/dm^2 (0.2 mg/in.^{2}).

The thinner and more uniform zinc deposits are the most suitable for plating preparation and for the service performance of plated coatings. Heavy zinc deposits usually are spongy, less adherent, and undesirable from the standpoint of corrosion resistance.

Plating Procedures. Copper is one of the easiest metals to electrodeposit on zincated aluminum surfaces. For this reason, it is used extensively as an initial strike over which other metals may be subsequently deposited. An advantage of the copper strike is that it protects the thin zinc film from attack by the plating solutions. Penetration of the zinc film and attack of the underlying aluminum surface by the plating solutions result in a poorly bonded electrodeposit.

The copper strike bath should be a Rochelle-type copper cyanide solution. The composition and operating conditions recommended for this bath are:

Copper cyanide	4 g/L (5.5 oz/gal)
Total sodium cyanide	50 g/L (6.5 oz/gal)
Free sodium cyanide	4 g/L (0.5 oz/gal) max
Sodium carbonate	30 g/L (4.0 oz/gal)
Rochelle salt	60 g/L (8.0 oz/gal)
Operating temperature	40-55 °C (100-130 °F)
pH	Varies with alloy; see Table 22

Table 22 Conditions for electroplating various metals on zincated aluminum surfaces

Electroplate	Minimum deposit		Plating time, min	Bath temperature		Current density		Type of electrolyte
	µm	mils		°C	°F	A/dm^2	A/ft^2	
Copper:								
1 Copper strike[(a)]	7.5	0.3	2[(b)]	34-54	100-130	2.4[(b)]	24[(b)]	Rochelle cyanide[(c)]
2 Brass strike[(a)]	7.5	0.3	2-3	27-32	80-90	0.5	5	Cyanide
3 Copper plate[(d)]	12.5	0.5	40 s-2 min	76-83	170-180	3-6	30-60	High-speed NaCN or KCN
Brass	12.5	0.5	3-5	27-32	80-90	1	10	Cyanide

Cadmium:								
1 Copper strike[a]	12.5	0.5	2[b]	34-54	100-130	2.4[b]	24[b]	Rochelle cyanide[c]
2 Cadmium plate	12.5	0.5	8-20	21-35	70-95	1.4-4.5	14-45	Cyanide
Chromium, decorative:								
1 Copper strike[a]	7.5	0.3	2[b]	34-54	100-130	2.4	24[b]	Rochelle cyanide[c]
2 Brass strike[a]	7.5	0.3	2-3	27-32	80-90	0.5	5	Cyanide
3 Nickel undercoat	2.5-5	0.1-0.2	[e]	[e]	[e]	[e]	[e]	[e]
4 Chromium plate	25-50	0.01-0.02	10-12	43-46	110-115	0.07-0.15	0.7-1.5	Conventional
Chromium, decorative (direct on zincate)	0.75	0.03	5-10	18-21	65-70	0.07-0.15	0.7-1.5	Conventional
Chromium, hard:								
1 Copper strike	7.5	0.3	2[b]	34-54	100-130	2.4[b]	24[b]	Rochelle cyanide[c]
2 Chromium plate	1.25	0.05	5	54	130	0.07-0.15	0.7-1.5	Conventional
Chromium, hard (direct on zincate)	1.25	0.05	10-20; then 54[f]	18-21; then 130[f]	65-70	0.07-0.15; then 0.3[f]	0.7-1.5; then 3 A in.^{2}	Conventional
Chromium, hard (for corrosion protection):								
1 Copper strike	7.5	0.3	2[b]	34-54	100-130	2.4[b]	24	Rochelle cyanide[c]
2 Brass strike	7.5	0.3	2-3	27-32	80-90	0.5	5	Cyanide
3 Nickel undercoat	25-50	1-2	[e]	[e]	[e]	[e]	[e]	[e]
4 Chromium plate	2.5-5	0.1-0.2	10-12	43-46	110-	0.07-0.15	0.7-1.5	Conventional

					115			
Gold:								
1 Copper strike	7.5	0.3	2[b]	34-54	100-130	2.4[b]	24[b]	Rochelle cyanide[c]
2 Brass strike	7.5	0.3	2-3	27-32	80-90	0.5	5	Cyanide
3 Nickel undercoat	17.5	0.7	[e]	[e]	[e]	[e]	[e]	[e]
4 Gold plate	0.625	0.025	10 s-1 min	49-71	120-160	0.5-1.5	5-15	Potassium cyanide
Nickel (for minimum corrosion protection):								
1 Copper strike	7.5	0.3	2[b]	34-54	100-130	2.4[b]	24[b]	Rochelle cyanide[c]
2 Brass strike	7.5	0.3	2-3	27-32	80-90	0.5	5	Cyanide
3 Nickel plate	7.5-12.5	0.3-0.5	[e]	[e]	[e]	[e]	[e]	[e]
Nickel (for maximum corrosion protection):								
1 Copper strike	7.5	0.3	2[b]	34-54	100-130	2.4[b]	24[b]	Rochelle cyanide[c]
2 Brass strike	7.5	0.3	2-3	27-32	80-90	0.5	5	Cyanide
3 Nickel plate	25-50	0.3-0.5	[e]	[e]	[e]	[e]	[e]	[e]
Silver:								
1 Double silver strike	0.625	0.025	10 s[g]	30[g]	80[g]	1.5-2.5[g]	15-25[g]	Cyanide[h]
2 Silver plate	1.25-2.5	0.05-0.1	18-35	27-32	80	0.5	5	Cyanide
Silver (alternative method):								

1 Copper strike	7.5	0.3	2[(b)]	34-54	100-130	2.4[(b)]	24[(b)]	Rochelle cyanide[(c)]
2 Silver strike	0.50	0.02	10 s	27-32	80	1.5-2.5	15-25	Cyanide[(i)]
3 Silver plate	1.25-2.5	0.05-0.1	18-35	27-32	80	0.5	5	Cyanide
Tin:								
1 Copper strike	7.5	0.3	2[(b)]	34-54	100-130	2.4[(b)]	24[(b)]	Rochelle cyanide[(c)]
2 Tin plate[(j)]	17.5	0.7	15-30	93-99	200-210	4.5-6.5	45-65	Sodium stannate
Zinc:								
1 Copper strike	7.5	0.3	2[(b)]	34-54	100-130	2.4[(b)]	24[(b)]	Rochelle cyanide[(c)]
2 Zinc plate	12.5	0.5	18-45	24-30	75-86	1-3	10-30	Pyrophosphate
Zinc (direct on zincate)	12.5	0.5	10	24-35	75-95	0.5-5[(k)]	5-50[(k)]	Pyrophosphate

(a) An initial cyanide copper strike is generally used to achieve complete metal coverage of zincated aluminum parts prior to plating, because of the excellent throwing power of the copper electrolyte. A copper strike is not, however, recommended as the initial coating for alloys 5056, 214, 218, and others that contain substantial amounts of magnesium; these will achieve a better initial coverage in a brass strike. Neither copper strike nor brass strike should be used as a final finish; both should always have an electroplated top coat.

(b) The copper strike is achieved during the first 2 min while the current density of the electrolyte is maintained at 2.4 A/dm^2 (24 A/ft^2). Instead of being transferred from the strike bath to a high-speed sodium or potassium electrolyte for subsequent copper plating, the work may be allowed to remain (3 to 5 min) in the Rochelle-type electrolyte to be copper plated, provided the current density is lowered to 1.2 A/dm^2 (12 A/ft^2).

(c) Colorimetric pH of electrolyte is 12.0 for all treatable alloys except 5052, 6061, and 6063, for which pH is 10.2 to 10.5

(d) Work for which copper strike plating may be used may be left in the copper strike for copper plating, instead of being transferred to the high-speed sodium or potassium cyanide electrolyte (see footnote c).

(e) As discussed in the article on nickel plating, various electrolytes are used, depending on the specific purpose of the plated deposit. If the nickel is to be deposited directly on the zincated surface, a bath must be selected that is suitable for application over zinc (examples of such baths are fluoborate and sulfamate nickel electrolytes).

(f) The transition from low-temperature to high-temperature plating may be accomplished either by heating the electrolyte to 54 °C (130 °F) after deposition has started at 18 to 21 °C (65 to 70 °F) or by transferring the work (without rinsing) from an electrolyte at 18 to 21 °C (65 to 70 °F) to one at 54 °C (130 °F) and holding the work in the high-temperature electrolyte without current until the work reaches bath temperature. Current density is 0.07 to 0.15 A/dm^2 (0.7 to 1.5 A/in.^{2}) in the electrolyte at 18 to 21 °C (65 to 70 °F). 1935 AS/mm^2 (3 A/in.^{2}) at 54 °C (130

°F).

(g) Each bath.

(h) First strike bath contains 1 g (0.11 oz) of AgCN and 90 g (10.2 oz) of NaCN per litre (gallon); second bath, 5.3 g (0.60 oz) of AgCN and 67.5 g (7.7 oz) of NaCN per litre (gallon).

(i) Contains 5.3 g (0.60 oz) of AgCN and 67.5 g (7.7 oz) of NaCN per litre (gallon).

(j) After the aluminum material has been copper strike plated, tin may be applied also by immersion for 45 min to 1 h in a sodium stannate solution at 49 to 74 °C (120 to 165 °F). Time and temperature depend on solution used.

(k) Current is applied as work is being immersed in electrolyte.

A brass strike is sometimes used in place of copper; however, a bronze strike is frequently used on a tin immersion coating. Table 22 gives operating conditions for the electrodeposition of different metals on zincated aluminum surfaces. Environmental considerations sometimes necessitate substitution for cyanide-containing solutions. Nickel strikes, which are successful as a result of careful control of composition and operation conditions, permit this.

Immersion Plating

Immersion plating refers to processes in which another metal is deposited from solution on an aluminum surface under the influence of the potential that exists between the solution and the immersed aluminum material. An external potential is not required. Deposits produced by immersion plating are thin and of little protective value.

Zincating, the procedure used for coating aluminum surfaces with zinc prior to electroplating (see the preceding section), is an example of immersion plating. Brass deposits can be produced by adding copper compounds to the sodium zincate solutions used in zincating.

Tin can be deposited from solutions containing potassium stannate, stannous chloride, or stannous sulfate-fluoride. The lubricating qualities of these tin deposits are desirable for aluminum alloy piston and engine components. Immersion tin coatings also are used to facilitate soft soldering and as a base coating for building up electrodeposits. The composition and operating conditions of a successful immersion tin bath are given below:

Potassium stannate	100 g/L (13.40 oz/gal)
Zinc acetate	2 g/L (0.27 oz/gal)
m-Cresol sulfonic acid	35 g/L (4.40 oz/gal)
Temperature of solution	60 °C (140 °F)
Immersion time	2 min

Degreasing is the only pretreatment required. The thickness of the tin coating is about 1.3 μm (0.05 mil); solution life is about 0.75 m^2/L (30 ft^2/gal).

Electroless Plating

Electroless plating, often called chemical plating, refers to nonelectrolytic processes that involve chemical reduction, in which the metal is deposited in the presence of a reducing agent. Deposition may take place on almost any type of material, even the container of the solution. For a variety of applications in the aircraft industry, nickel is chemically plated on aluminum parts of shapes for which electroplating is not practical. However, electroless plating is too expensive to be used when conventional electroplating is feasible. The composition and operating conditions of a bath for the successful deposition of nickel are given below:

Nickel chloride	30 g/L (4 oz/gal)
Sodium hypophosphite	7.5 g/L (1 oz/gal)
Sodium citrate	72 g/L (9.60 oz/gal)
Ammonium chloride	48 g/L (6.40 oz/gal)
Ammonium hydroxide (0.880 sp gr)	13 g/L (1.75 oz/gal)
pH	10
Temperature of solution	80-90 °C (180-190 °F)
Immersion time	1 h

Deposits produced contain about 6 wt% P and usually are not considered suitable as a base for chromium plate. The immersion time given is for deposits 50 μm (2 mil) or more thick.

Silver can be plated using the electroless process on anodized aluminum-base materials. The procedure consists of degreasing the anodized surface, dipping in dilute hydrochloric acid, water rinsing, and then immersing the object in a silvering solution. A mixture of two solutions is required for silvering. The first consists of 3.33 mL (0.113 fluid oz) of a 10% solution of silver nitrate to which a 7.5 vol% solution of ammonium hydroxide is added until the precipitate first formed just redissolves, after which an excess of 40 mL (1.3 fluid oz) of ammonium hydroxide solution is added. The second solution is made by adding 80 g (3 oz) of Rochelle salt or 40 g (1.4 oz) of potassium citrate to water, to a total volume of 330 mL (11 fluid oz). Solutions are filtered and mixed immediately before use.

Additional information on electroless plating processes is available in the Section "Plating and Electroplating" in this Volume.

Painting

The difference between painting of aluminum and painting of iron or steel lies primarily in the method of surface preparation. Aluminum is an excellent substrate for organic coatings if the surface is properly cleaned and prepared. For

many applications, such as indoor decorative parts, the coating may be applied directly to a clean surface. However, a suitable prime coat, such as a wash primer or a zinc chromate primer, usually improves the performance of the finish coat.

For applications involving outdoor exposure, or for indoor applications that expose the part to impact or abrasive forces, a surface treatment such as anodizing or chemical conversion coating is required prior to the application of a primer and a finish coat. These processes were discussed above.

Anodizing in sulfuric or chromic acid electrolytes provides an excellent surface for organic coatings. Usually, only thin anodic coatings are required as a prepaint treatment. Decorative parts for home appliances generally are anodized before painting to ensure good paint adhesion over an extended period. Sulfuric acid anodic coatings are used when painting of only part of the surface is required for decorative effects; the anodic coating protects the unpainted portions of the surface.

Conversion coatings usually are less expensive than anodic coatings, provide a good base for paint, and improve the life of the paint by retarding corrosion of the aluminum substrate material. Adequate coverage of the entire surface by the conversion coating is important for good paint bonding.

The article "Painting" in this Volume contains additional information on surface preparation, paint formulations, and application procedures.

Porcelain Enameling

Porcelain enamels are glass coatings applied to products to improve appearance and protect the metal surface. Porcelain enamels are distinguished from other ceramic coatings by their predominantly vitreous nature and the types of applications for which they are used. They are distinguished from paint by their inorganic composition and the fusion of the coating matrix to the substrate metal.

Aluminum products, including tanks and vessels, architectural panels, cookware, and signs, may be finished by porcelain enameling to enhance appearance, chemical resistance, or weather resistance. The common porcelain enameling alloys for the various forms of aluminum are:

- *Sheet:* 1100, 3003, and 6061
- *Extrusions:* 6061
- *Casting alloys:* 443 and 356

Of the wrought alloys, only 6061 alloy is heat-treatable. Because of its higher strength, 6061 alloy has better handling characteristics before and during porcelain enameling, and it is stronger after porcelain enameling. The non-heat-treatable alloys are easier to form before porcelain enameling and are used for small parts for which the amount of distortion and low strength encountered after firing are acceptable. However, non-heat-treatable alloys are unsuitable for more than one coat of porcelain because of the crazing that occurs after a second firing.

Frits. The basic material of the porcelain enamel coating is frit, a special glass of small friable particles produced by quenching a molten glassy mixture. Because porcelain enamels are usually designed for specific applications, the compositions of the frits from which they are made vary widely.

Enamel frits for aluminum are usually based on lead silicate and on cadmium silicate, but they may be based on phosphate or barium. Table 23 gives the compositions of several frits used for aluminum.

Table 23 Melted-oxide compositions of frits for porcelain enameling of aluminum

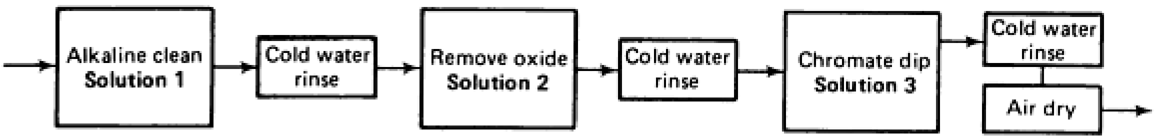
Constituent	Composition, wt%		
	Lead-base enamel	Barium enamel	Phosphate enamel

PbO	14-45	. . .	. . .
SiO_2	30-40	25	. . .
Na_2O	14-20	20	20
K_2O	7-12	25	. . .
Li_2O	2-4	. . .	4
B_2O_3	1-2	15	8
Al_2O_3	. . .	3	23
BaO	2-6	12	. . .
P_2O_5	2-4	. . .	40
F_2	. . .	. . .	5
TiO_2	15-20	(a)	(a)

(a) TiO_2, 7 to 9 wt%, added to frit during mill preparation of the enamel slip

The high-lead enamels for aluminum have a high gloss, good acid and weather resistance, and good mechanical properties. The phosphate enamels generally are not alkali-resistant or water-resistant, but they may have good acid resistance. They melt at relatively low temperatures and are useful in many applications. The barium enamels are not as low-melting as the lead or phosphate glasses, but they do have good chemical durability.

Surface Preparation. The preparation of heat-treatable aluminum alloy parts for porcelain enameling involves the removal of soil and surface oxides and the application of a chromate coating. Figure 7 shows the sequence of these surface preparation treatments and gives operating conditions. Final drying removes all surface moisture; drying must be accomplished without contaminating the cleaned surface. Parts made of non-heat-treatable aluminum alloys require only the removal of soil, which can be done by alkaline cleaning or vapor degreasing.



No.	Type	Composition of solution		Operating temperature		Cycle time, min
		Constituent	wt%	°C	°F	
1	Alkaline cleaner[a]	[b]	[b]	60-82	140-180	2-5
2	Oxide removal	Chromic acid	3.5	82	180	3-10
		Sulfuric acid	18.0			
3	Chromate dip	Chromic sulfate	0.2	Ambient		1-6
		Potassium dichromate	14.4			
		Sodium hydroxide	7.75			

(a) Vapor degreasing may be used instead of alkaline cleaning.

(b) Either inhibited or mildly etching (uninhibited) cleaners can be used

Fig. 7 Process for preparing heat-treatable aluminum alloys for porcelain enameling

Because enamel ordinarily is applied to aluminum to only about half the thickness to which it is applied to steel, freedom from surface scratches, burrs, and irregularities is doubly important for aluminum. Most shaping of aluminum is done before enameling, but the thin coating permits some bending, shearing, punching, and sawing of the enameled part.

Surfaces to be enameled should have generous inside radii of not less than 4.8 mm ($\frac{3}{16}$ in.) and outside radii of not less than 1.6 mm ($\frac{1}{16}$ in.). Attachments should be welded to the unenameled back side of enameled heavy-gage aluminum sheet or extrusions. The visible metal surfaces must not be overheated; overheating causes the aluminum to blister and alters the color and gloss of the enamel. Welding can be done before enameling, provided that the weld area is cleaned properly before coating.

Additives and Application. Porcelain enamel is usually applied to aluminum as a suspension of finely milled frit in water. Mill additions for wet process enamel frits for aluminum consist of boric acid, potassium silicate, sodium silicate, and other additives. These materials are used to control the wet suspension of the frits, and they contribute to the characteristics of the fired enamel. Titanium dioxide and ceramic pigments can also be added to produce opacity and the desired color, respectively.

Porcelain enamel slips for aluminum usually are applied by spraying, using either manual or automatic equipment with agitated pressure tanks. Slips for aluminum are not self-leveling and thus must be deposited smoothly in an even thickness and without runs or ripples.

Many aluminum parts are coated satisfactorily by the one-coat/one-fire method. Although the heat-treatable alloys can be recoated one or more times, the opacity and color of the coating will change with the thickness of the porcelain and with

repeated firing. The desirable minimum fired enamel thickness is 65 μm (2.5 mil), and the desirable maximum is 90 μm (3.5 mil).

Furnaces. Forced convection is the preferred method of heating furnaces for firing porcelain enamel on aluminum. The heat is provided by electric package heaters, quartz-tube electric heaters, or metal-sheath heaters, all specially designed for operation at high ambient air temperature. Quartz-tube and metal-sheath heaters are adapted to the furnace so that radiant heat is available in the firing zone along with forced circulation. Package heaters are placed remote from the firing zone; this is the most effective method of eliminating direct radiation and hot spots. Heat imparted to the work from the package heater is derived completely from adequate air circulation to maintain a uniform temperature throughout the furnace of ±1% of the nominal operating temperature.

Forced-convection heating is also accomplished with gas-fired radiant tubes as the heat source. The tubes are baffled from the work or firing zone so that air circulation provides the same advantages as in electric-package forced-convection heating.

Furnace construction for aluminum enameling generally requires the use of stainless steel inner liner sheets, low-density wall insulation, and plain-carbon steel exterior shell. This type of fabrication eliminates long heat-up and cool-down periods.

Firing of enamel on aluminum is accomplished between 525 and 550 °C (980 and 1020 °F); cycles are shown in Table 24. To control color and gloss of the enamel within acceptable limits, the temperature throughout the work must be held to 1.5 °C (2.5 °F).

Table 24 Cycles for firing procelain enamel on aluminum

Type of part	Section thickness, 0.025 mm (0.001 in.)	Firing time, min	Firing temperature	
			°C	°F
Any configuration	26-40	5-6 $\frac{1}{2}$	540	1000
Any configuration	51-64	7-8	540	1000
Extrusions	125	10	550	1020

Detailed information about porcelain enamel coatings is available in the article "Porcelain Enameling" in this Volume.

Shot Peening

Shot peening is a method of cold working in which compressive stresses are induced in the exposed surface layers of metallic parts by the impingement of a stream of shot, which is directed at the metal surface at high velocity under controlled conditions. It differs from blast cleaning in primary purpose and in the extent to which it is controlled to yield accurate and reproducible results. Cast steel shot is the most widely used peening medium, but glass beads often are used for peening aluminum and other metals that might be contaminated by steel shot.

Although shot peening cleans the surface being peened, this function is incidental. The major purpose of shot peening is to increase fatigue strength. For example, the fatigue strength of several aluminum alloys peened with cast steel shot can

be improved by 23 to 34%. The process has other useful applications, such as relieving tensile stresses that contribute to stress-corrosion cracking (SCC), and forming and straightening metal parts.

Peening action improves the distribution of stresses in surfaces that have been disturbed by grinding, machining, or heat treating. Shot peening is especially effective in reducing the harmful stress concentration effects of notches, fillets, forging pits, surface defects, and the heat-affected zones of weldments.

The surface tensile stresses that cause SCC can be effectively overcome by the compressive stresses induced by shot peening with either steel shot or glass beads. In one application, test bars were cut in the short transverse direction from a 7075-T6 aluminum alloy hand forging and stressed to 75% of the yield strength. During alternate immersion tests in 3.5% sodium chloride solution, unpeened specimens failed in 1, 5, 17, and 28 days. Specimens peened in the unstressed condition with cast steel shot lasted 365 and 730 days, when failure occurred in the unpeened grip outside the test area. During exposure to an industrial atmosphere, similar unpeened test bars failed in 20, 37, 120, and 161 days, whereas a peened specimen under the same conditions was uncracked when it was removed from testing after an exposure of $8\frac{1}{2}$ years.

Additional information is provided in the article "Shot Peening" in this Volume.

Designation System for Aluminum Finishes

Finishes used on aluminum are categorized as mechanical or chemical finishes or as coatings. Types of coatings that can be applied include anodic coatings, resinous and other organic coatings, and vitreous coatings. In addition, laminated, electroplated, or other metallic coatings can be used on aluminum.

In the designation system developed by the Aluminum Association, each of these categories is assigned a letter, and the various finishes in each category are designated by two-digit numerals. Specific finishes of the various types thus are designated by a letter followed by two numbers, as shown in Table 25. Two or more designations can be combined into a single designation to identify a sequence of operations covering all the important steps leading to a final complex finish.

Table 25 Designations for aluminum finishes

Designation[a]	**Finish**
Mechanical finishes--M	
As fabricated:	
M10	Unspecified
M11	Specular finish as fabricated
M12	Nonspecular finish as fabricated
M1X	Other (to be specified)
Buffed:	
M20	Unspecified

M21	Smooth specular
M22	Specular
M2X	Other (to be specified)
Directional textured:	
M30	Unspecified
M31	Fine satin
M32	Medium satin
M33	Coarse satin
M34	Hand rubbed
M35	Brushed
M3X	Other (to be specified)
Nondirectional textured:	
M40	Unspecified
M41	Extra fine matte
M42	Fine matte
M43	Medium matte
M44	Coarse matte
M45	Fine shot blast
M46	Medium shot blast
M47	Coarse shot blast

M4X	Other (to be specified)
Chemical finishes[(b)]--C	
Nonetched cleaned:	
C10	Unspecified
C11	Degreased
C12	Inhibited chemical cleaned
C1X	Other (to be specified)
Etched:	
C20	Unspecified
C21	Fine matte
C22	Medium matte
C23	Coarse matte
C2X	Other (to be specified)
Brightened:	
C30	Unspecified
C31	Highly specular
C32	Diffuse bright
C3X	Other (to be specified)
Chemical coatings:	
C40	Unspecified

C41	Acid chromate-fluoride
C42	Acid chromate-fluoride-phosphate
C43	Alkaline chromate
C44	Nonchromate
C45	Nonrinsed chromate
C4X	Other (to be specified)
Anodic coatings--A	
General:	
A10	Unspecified
A11	Preparation for other applied coatings
A12	Chromic acid coatings
A13	Hard, wear- and abrasion-resistant coatings
A1X	Other (to be specified)
Protective and decorative:	
(Less than 10 μm, or 0.4 mil)	
A21	Clear (natural)
A22	Integral color
A23	Impregnated color
A24	Electrolytically deposited color
A2X	Other (to be specified)

Architectural Class II(c):	
(10 to 18 μm, or 0.4 to 0.7 mil)	
A31	Clear
A32	Integral color
A33	Impregnated color
A34	Electrolytically deposited color
A3X	Other (to be specified)
Architectural Class I[c]:	
(18 μm, or 0.7 mil)	
A41	Clear (natural)
A42	Integral color
A43	Impregnated color
A44	Electrolytically deposited color
A4X	Other (to be specified)
Resinous and other organic coatings[d]--R	
R10	Unspecified
R1X	Other (to be specified)
Vitreous (porcelain and ceramic) coatings[d]--V	
V10	Unspecified
V1X	Other (to be specified)

Electroplated and other metal coatings[d]--E	
E10	Unspecified
E1X	Other (to be specified)
Laminated coatings[d]--L	
L10	Unspecified
L1X	Other (to be specified)

(a) All designations are preceded by the letters "AA," to identify them as Aluminum Association designations. Examples of methods of finishing are given in the Aluminum Association publication from which the presentation here is derived.

(b) Includes chemical conversion coatings, chemical or electrochemical brightening and cleaning treatments.

(c) Classification established in Aluminum Association Standards for Anodically Coated Aluminum Alloys for Architectural Applications, October 1978.

(d) These designations may be used until more complete series of designations are developed for these coatings.

When designations for chemical coatings are used alone, other processing steps normally used ahead of these finishes are at the option of the processor. Where a finish requires two or more treatments of the same class, the class letter is repeated, each time being followed by the appropriate two-digit numeral.

Designations for specific coatings have been developed only for the anodic coatings. Coatings of the four other classes may be tentatively designated by the letters respectively assigned for them; detailed designations for these four categories may be developed and added to the system later.

The examples that follow show how the designation system for aluminum finishes is used. Each designation is preceded by the letters "AA" to identify it as an Aluminum Association appellation. More detailed information can be found in the Association document titled "Designation Systems for Aluminum Finishes, 1980."

Smooth Specular Finish. A finish can be obtained by polishing aluminum with an aluminum oxide compound according to the following schedule. Begin with grits coarser than 320; follow with 320-grit and a wheel speed of 30 m/s (6000 ft/min); complete polishing by buffing with tripoli-based buffing compound at 35 to 41 m/s (7000 to 8000 ft/min). The designation for this finish is AA-M21 (Table 25).

Architectural Building Panel. A matte-anodized finish for a building, such as that produced by giving aluminum a matte finish, then chemical cleaning followed by architectural class II natural anodizing, would be designated as AA-M32C12A31:

AA	Aluminum Association
M32	Mechanical finish, directional textured, medium satin appearance
C12	Chemical treatment, inhibited alkaline cleaning
A31	Anodic coating, architectural class II (10 to 18 μm, or 0.4 to 0.7 mil thick), clear (natural)

Architectural Aluminum with Anodized Integral Color. An anodized panel with an integral color for architectural application would be designated as AA-M10C22A42:

AA	Aluminum Association
M10	Unspecified as-fabricated finish
C22	Chemically etched medium matte finish
A42	Anodic coating, architectural class I (18 μm, or 0.7 mil or thicker), integral color

Chromium-Plated Aluminum Panel. The finish for a chromium-plated aluminum panel that is first given a highly specular mechanical finish, then a nonetch chemical cleaning, followed by a thin anodic coating produced in phosphoric acid, and finally direct chromium plating, would be designated as AA-M21C12A1XE1X:

AA	Aluminum Association
M21	Mechanical finish, polished, smooth specular (see smooth specular finish, (above)
C12	Inhibited alkaline cleaned
A1X	Specify exact anodizing process
E1X	Specify exact chromium plating method

Introduction

COPPER and copper alloys constitute one of the major groups of commercial metals. They are widely used because of their excellent electrical and thermal conductivities, outstanding resistance to corrosion, ease of fabrication, and good strength and fatigue resistance. They are generally nonmagnetic. They can be readily soldered and brazed, and many coppers and copper alloys can be welded by various gas, arc, and resistance methods. For decorative parts, standard alloys having specific colors are readily available. Copper alloys can be polished and buffed to almost any desired texture and luster. They can be plated, coated with organic substances, or chemically colored to further extend the variety of available finishes.

Pure copper is used extensively for cables and wires, electrical contacts, and a wide variety of other parts that are required to pass electrical current. Coppers and certain brasses, bronzes, and cupronickels are used extensively for automobile radiators, heat exchangers, home heating systems, panels for absorbing solar energy, and various other applications requiring rapid conduction of heat across or along a metal section. Because of their outstanding ability to resist corrosion, coppers, brasses, some bronzes, and cupronickels are used for pipes, valves, and fittings in systems carrying potable water, process water, or other aqueous fluids.

The elements most commonly alloyed with copper are aluminum, nickel, silicon, tin, and zinc. Other elements and metals are alloyed in small quantities to improve certain material characteristics, such as corrosion resistance or machinability. Copper and its alloys are divided into nine major groups. These major groups are:

- *Coppers,* which contain a minimum of 99.3% Cu
- *High-copper alloys,* which contain up to 5% alloying elements
- *Copper-zinc alloys (brasses),* which contain up to 40% Zn
- *Copper-tin alloys (phosphor bronzes),* which contain up to 10% Sn and 0.2% P
- *Copper-aluminum alloys (aluminum bronzes),* which contain up to 10% Al
- *Copper-silicon alloys (silicon bronzes),* which contain up to 3% Si
- *Copper-nickel alloys,* which contain up to 30% Ni
- *Copper-zinc-nickel alloys (nickel silvers),* which contain up to 27% Zn and 18% Ni
- *Special alloys,* which contain alloying elements to enhance a specific property or characteristic, for example, machinability

Many copper alloys have common names, such as oxygen-free copper (99.95% Cu min), beryllium copper (0.2 to 2.0% Be), Muntz metal (Cu-40Zn), Naval brass (Cu-39.25Zn-0.75Sn), and commercial bronze (Cu-10Zn).

A more standardized system of identification is the unified Numbering System (UNS). In this system, wrought alloys of copper are designated by numbers 1*xxxx* to 7*xxxx*, and cast alloys are designated 8*xxxx* to 9*xxxx*; thus, the same alloy can be produced as a wrought and cast product.

Additional information about the classification, metallurgy, properties, and applications of copper and copper alloys is available in *Properties and Selection: Nonferrous Alloys and Special-Purpose Materials,* Vol 2 of *ASM Handbook.*

The selection of surface treatments for copper and copper alloys is generally based on application requirements for appearance and corrosion resistance. These treatments range from simple low-cost chemical processes that provide a uniform surface appearance, to expensive electroplates that provide maximum corrosion resistance. This article describes the cleaning, finishing, and coating processes used with copper and copper alloys.

Acknowledgements

This article was adapted from Robert M. Paine and Bob Srinivasan, Cleaning and Finishing of Copper and Copper Alloys, *Surface Cleaning, Finishing, and Coating,* Volume 5, 9th Edition, *Metals Handbook,* American Society for Metals, 1982, p 611-627. It was revised for this edition by Andrew J. Brock, Olin Corporation.

Cleaning and Finishing

Prior to subsequent processing or the application of a protective or decorative coating, the copper or copper alloy surface must be prepared by suitable cleaning procedures. The severity of these cleaning procedures will depend on the past processing history of the metal. Copper and copper alloys obtained from major materials suppliers should be received reasonably clean (free from heat treat scale or tarnish) and should only require minimal cleaning prior to further processing.

Heat treating of copper and copper alloys in air results in the formation of copper oxides; further cleaning will be necessary to remove these oxides, as discussed below. The need for such cleaning can be prevented by heat treating in reducing atmospheres, such as nitrogen with 1 to 4% H, in which the formation of copper oxides will be completely suppressed. Such atmospheres will not, however, prevent the oxidation of reactive alloying constituents such as aluminum, silicon, or zinc.

Pickling and Bright Dipping

Pickling in solutions containing 4 to 15 vol% sulfuric acid or 40 to 90 vol% hydrochloric acid is used for the removal of oxides formed on the surface of copper-base materials during mill processing and fabricating operations. The sulfuric acid solution is used to remove black copper oxide scale on brass extrusions, forgings, and machined parts; oxide on copper tubing, forgings, and machined parts; and light annealing scale or tarnish. The hydrochloric acid solution is primarily used for finishing, but is also used to remove scale and tarnish from brass forgings and machined parts, and oxide on copper forgings and machined parts. Conditions for pickling copper-base metals with sulfuric acid and hydrochloric acid are shown in Table 1. Sometimes no additional surface preparation is necessary to produce the uniformity of appearance required for further finishing of copper; however, heavily scaled material may need a bright dip or color dip after pickling.

Table 1 Pickling conditions for copper-base materials

Constituent or condition	Amount or value
Sulfuric acid bath	
Sulfuric acid[(a)]	15-20 vol%
35% hydrogen peroxide	3-5 vol%
Water	bal
Temperature of solution	Room temperature to 60 °C (140 °F)
Immersion time	15 s to 5 min
Hydrochloric acid bath	
Hydrochloric acid[(b)]	40-90 vol%
Water	bal
Temperature of solution	Room temperature

Immersion time	1-3 min

(a) 1.83 sp gr. The bath needs additives to stabilize peroxide and accelerators to maintain etch rate. Proprietary products are available from metal finishing suppliers.

(b) 1.16 sp gr

Except for bright annealed material, copper alloys must be pickled after each annealing treatment, completely descaled, and bright dipped to produce a natural surface color and luster suitable for other finishing treatments such as electroplating or painting. Scale dip and bright dip solutions are given in Table 2. Bright dips for copper-base materials consist of sulfuric and nitric acids in varying proportions with a small amount of water and hydrochloric acid. Proprietary pickle and bright dips, using sulfuric acid and stabilized hydrogen peroxide, are also available. Whereas the conventional bright dips use highly concentrated acids, this sulfuric acid-hydrogen peroxide bath is dilute and reduces worker safety hazards.

Table 2 Scale dip and bright dip conditions for copper-base metals

These solutions remove scale that is not removed by sulfuric or hydrochloric acid solutions; lower concentrations of nitric acid and higher concentrations of sulfuric acid produce a bright lustrous finish; these solutions can remove 0.0255 mm (0.001 in.) of metal and should not be used when close dimensional tolerances must be maintained. Solutions are used at room temperature.

Solution	**Sulfuric acid, vol%[(a)]**	**Nitric acid, vol%[(b)]**	**Hydrochloric acid[(c)]**		**Water, vol%**	**Immersion time,s**
			g/L	**oz/gal**		
Scale dip						
Solution A	0	50	4	$\frac{1}{2}$	50	15-60
Solution B	25-35	35-50	4	$\frac{1}{2}$	35-40	15-60

(a) 1.83 sp gr.

(b) 1.41 sp gr.

(c) 1.16 sp gr. Excess hydrochloric acid spots brass. Wood soot and activated charcoal are added to the solution to prevent this condition.

After bright dipping and thorough rinsing in cold running water, stain or tarnish may be removed by dipping in a cyanide solution. Some proprietary bright dips, incorporated with corrosion inhibitors, eliminate the use of toxic cyanides and chromates and are easy to waste treat.

When a semibright finish is satisfactory, a dichromate color dip is less expensive and more convenient to use than the conventional acid dip. Color dip should not be used if parts are to be plated or soldered. The following conditions for color dipping include a solution that removes red copper oxide and imparts a film that resists discoloration during storage and work:

Sodium dichromate	30 to 90 g/L (4 to 12 oz/gal)
Sulfuric acid, 1.83 sp gr	5 to 10 vol%
Water	bal
Immersion time	30 s
Temperature of solution	Room temperature

Extruded yellow brass rod may be pickled, usually in dilute sulfuric acid, to remove light oxide prior to drawing, forging, or machining. Yellow brass forgings are similarly treated for the removal of oxide scale and forging lubricant. Hydrochloric acid solutions may be used instead of sulfuric acid in some applications. Bright dipping follows pickling to complete the removal of all oxide. The yellow brass is then given a color dip to produce a uniform cartridge-brass color. Although brass sand castings are seldom pickled, a solution similar to that used for forgings may be used when pickling is indicated.

A typical acid treatment cycle for copper-base materials is given in the following list. The cycle may be terminated after any water rinse if the desired finish and color have been obtained:

- Pickling
- Cold water rinse
- Scale dip or bright dip
- Cold water rinse (repeat once)
- Color dip
- Cold water rinse (repeat once)
- Hot water rinse
- Air-blast dry

Aluminum bronzes form a tough, adherent aluminum oxide film during hot fabrication. This film can be removed or loosened by the following strong alkaline solution:

Sodium hydroxide	10 wt%
Water	bal

Temperature of solution	75 °C (170 °F)
Immersion time	2 to 6 min

After this treatment the material can be treated in acid solutions by some of the same cycles used for other copper-base materials.

Alloys containing silicon may form oxides of silicon that are removable only by hydrofluoric acid. Proprietary fluorine-bearing compounds are also available for this purpose. If a dull brown-to-gray appearance is not objectionable, the material may be pickled in the conventional sulfuric acid solution to remove the copper oxides. If a brighter finish is required, one of the solutions in Table 3 may be used.

Table 3 Pickling conditions for copper alloys containing silicon

Solutions are used at room temperature.

Constituent or condition	Solution A	Solution B
Sulfuric acid[(a)]	5-15 vol%	40-50 vol%
Hydrofluoric acid[(b)]	$\frac{1}{2}$-15 vol%	$\frac{1}{2}$-5 vol%
Nitric acid[(c)]	. . .	15-20 vol%
Water	bal	bal
Immersion time	$\frac{1}{2}$-10 min	5-45 s

(a) 1.83 sp gr.

(b) 52%.

(c) 1.41 sp gr

Alloys containing beryllium that have been heat treated at relatively low temperatures (below 400 °C, or 750 °F) can be pickled or bright dipped as any other copper alloy; however, alloys containing beryllium that have been heat treated at temperatures above 400 °C (750 °F) in operations such as solution annealing and those that have been bright annealed will generally possess a surface oxide that contains beryllium oxide as a major constituent. This oxide can be difficult to remove if present in a thickness greater than 0.04 to 0.05 μm (1.6 to 2.0 μin.). A 1 or 2 min soak in a solution of 50% sodium hydroxide at 130 °C (265 °F) before acid pickling facilitates removal of any beryllium oxide.

Nickel silvers and copper-nickel alloys do not respond readily to the pickling solution usually used for brasses, because nickel oxide has a limited solubility in sulfuric acid. Heavy scaling of these alloys should be avoided during annealing by using a reducing atmosphere. For example, the annealing of 18% nickel silver in a rich reducing atmosphere

results in a slight tarnish that is easily removed in the sulfuric acid pickle and dichromate solutions ordinarily used for descaling brass. Controlling the atmosphere during annealing produces a bright metal finish.

Tubing made of 30% copper-nickel may be annealed in a reducing atmosphere, but not in a brightening atmosphere, to produce a clean surface that does not require acid treatment; 18% nickel silver wire is pretreated in a proprietary hot alkaline cleaning solution and then annealed in a controlled atmosphere furnace to produce a clean and bright surface. The wire is subsequently pickled in sulfuric acid and treated in a dichromate solution to remove zinc sweat. The wire is then finish pickled in 10 to 15% sulfuric acid solution at 60 °C (140 °F).

Tarnish Removal. Tarnish, the surface discoloration formed on copper-base materials during exposure to the atmosphere or to alkaline cleaning, usually consists of a thin film of oxide or sulfide. One of the most commonly used dips for removing tarnish is an aqueous solution of 8 to 60 g/L (1 to 8 oz/gal) of sodium cyanide. The metal to be cleaned is immersed for 1 to 2 min in the cyanide solution at room temperature. Steel tanks are used to contain the solution. Thorough rinsing is required after the dip treatment.

Extreme safety precautions must be followed when cyanide solutions are being used, because cyanide is highly poisonous. To prevent the formation of ammonia, metal previously cleaned in an alkaline solution must be thoroughly rinsed before it is brought into contact with the cyanide solution. Cyanide must not come in contact with acid because lethal hydrocyanic acid is produced. Despite the strict safety precautions that are necessary, cyanide solutions are commonly used.

A solution containing 5 to 10 vol% hydrochloric or sulfuric acid may also be used to remove tarnish from copper-base materials. Immersion time is a few seconds in either of these solutions at room temperature. Thorough rinsing in water is required after the treatment. The hydrochloric acid solution may be contained in a vitrified crock, or in a rubber-lined or glass-lined tank. A vitrified crock or lead-lined tank may be used as a container for the sulfuric acid solution. Plastics such as polypropylene or polyvinyl chloride are also suitable containers for hydrochloric and sulfuric acid solutions. These materials are resistant to 50% sulfuric acid and 37% hydrochloric acid up to 65 to 70 °C (150 to 160 °F).

Another noncyanide solution sometimes used for removing tarnish consists of 10% citric acid at 70 to 80 °C (160 to 175 °F). This solution removes most tarnish stains and poses no health or ecological hazards.

Tarnish Prevention. Tarnishing of copper alloys after pickling or degreasing operations is accelerated when the metal is inadequately dried following rinsing and can be particularly rapid if the final rinse solution is contaminated with the cleaning solutions. Significant resistance to tarnishing after cleaning can be rendered by incorporating benzotriazole (BTA) or tolyltriazole (TTA) into the final rinse. Typical concentrations are 0.1 to 0.5% with the rinse water being used at 40 to 60 °C (104 to 140 °F).

Pickling Equipment. Equipment requirements for the automatic pickling of brass forgings of various sizes are given in Table 4. The automatic pickling machine is similar to automatic plating equipment. Solution conditions for automatic pickling of brass forgings are as follows:

- Hydrochloric acid solution at room temperature
- Nitric-sulfuric acid solution, 38 °C (100 °F) maximum
- Sodium dichromate solution, room temperature
- Cold water rinse, 2300 L/h (600 gal/h)
- Hot water rinse, 66 to 82 °C (150 to 180 °F), 4 L/h (1 gal/h)

Table 4 Production capacity of equipment for automatic pickling of brass forgings

Immersion time, 40 s; total cycle time, 6 min

Item or condition	Size of forgings		
	Small	Medium	Large

Number of pieces per hour	2500	500	250
Pieces per basket	250	50	25
Pounds pickled per hour	2500	2500	2500
Configuration of forgings	Irregular	Irregular[(a)]	Irregular[(a)]

(a) May contain cavities; require hand loading into baskets

Compositions of pickling tanks are determined by the type of solution used, such as:

Solution	**Tank material**
Hydrochloric acid	Plastic-lined steel
Nitric-sulfuric acid	Type 316 stainless steel
Color dip (dichromate solution)	Plastic-lined steel
Cold water rinse (four tanks)	Steel
Hot water rinse	Steel or rubber-lined steel

Work baskets require type 316 stainless steel or plastic composition with dimensions of 330 by 635 by 155 mm (13 by 25 by 6 in.) and 610 by 205 by 180 mm (24 by 8 by 7 in.). Equipment requirements for pickling brass tubes or rods and the equipment for pickling brass tubing are listed in Table 5.

Table 5 Equipment requirements for pickling brass tubes or rods

Oxide scale is removed from 25 mm (1 in.) diam brass tubing and rods that are 1.9 to 21 m (6 to 70 ft) in length; immersion time varies from 5 to 30 min; the source of heat is steam, 105,000 kJ (100,000 Btu)

Tanks[(a)]	**Material**	**Solution**	**Temperature**		**Overflow**[(b)]
			°C	**°F**	
Acid tank	Stainless steel	10% sulfuric acid	38-60	100-140	. . .
Cold water rinse tank	Wood	. . .	. . .	. . .	380 L/h (100 gal/h)

Hot water rinse tank	Wood	. . .	54-71	130-160	38 L/h (10 gal/h)

(a) All tanks measure 1.1 by 0.9 by 21 m (3.5 by 3 by 70 ft) and hold 6738 L (1780 gal) for a 0.6 m (2 ft) depth of solution.

(b) Connected to bottom of tank

Tanks for sulfuric acid may be lined with natural rubber. Tanks intended to contain nitric and hydrofluoric acids may be lined with polyvinyl chloride or polypropylene. Additional information on materials and construction of acid tanks is given in the article "Acid Cleaning" in this Volume.

Defects from Pickling. By far the most common defect encountered in pickling brass is the presence of red stain on the metal. Caused by cuprous oxide, this defect may be removed by pickling in a solution of 10% sulfuric acid containing 98 g/L (13 oz/gal) of ferric sulfate at temperatures up to 60 °C (140 °F), or in a solution of 12% sulfuric acid containing 45 g/L (6 oz/gal) of sodium dichromate at room temperature. Alternatively, sulfuric acid-hydrogen peroxide solution can be used. Red stains may result from the presence of metallic iron in the pickling solution, causing copper to plate out on the parts when the parts come in contact with iron or steel. This is because iron is anodic to copper. Care must be taken to prevent any stray pieces of iron, such as nails or tools, from entering the pickling solution. Red stains can also result from the reaction of sulfuric acid on cuprous oxide (Cu_2O), forming cupric oxide (CuO) and copper. This can be removed in any of the above oxidizing acids.

Oil and lubricants remaining on formed metal must be removed before pickling and dipping. If formed material is to be bright dipped, it should first be degreased, or the lubricant remaining will prevent the bright dip from being effective. If the work is to be annealed and pickled, it should be degreased, usually in a hot water rinse, because the oil may cause excess cuprous oxide and unwanted red staining to form during annealing. In extreme instances, the more volatile constituents of the oil burn off readily, leaving a carbonaceous deposit that must be removed mechanically.

Acid stains will appear on the metal if it is not thoroughly rinsed and cleansed of all remaining acid after pickling or dipping. At least two separate washings in water or one thorough running water wash should be used before drying. Dipping in a soap solution or a buffered salt solution will neutralize traces of acid.

The metal is etched or pitted if it is immersed for too long in a pickling solution or dip, or if the solution is too strong or too hot. The proper time, temperature, and concentration of solution may be determined quickly during trial runs.

Safety Practices. Acids, even in dilute solution, can cause serious injuries to the eyes and other portions of the body. Operators should wear face shields, rubber boots, and rubber aprons for protection. Eye fountains and showers adjacent to acid tanks, for use in the event of an accident, should be provided. Adequate ventilation and suitable hoods for the tanks are recommended.

Extreme caution should be exercised when adding acid to a water solution, especially if sulfuric acid is used. Sulfuric acid should be added slowly and only while stirring the solution.

Abrasive Blast Cleaning

Abrasive cleaning is used to remove molding, core sand, and investment material from the exterior and interior surfaces of copper-base castings. Selection of the proper kind and particle size of grit determines the type and color of the finish. The coarser grits clean faster but give a rougher finish.

Dry abrasive cleaning of beryllium copper is usually confined to castings. Steel shot is used for general cleaning to remove sand and slight surface imperfections from the casting after mold shakeout. Sands are used to blend in surface areas, to remove heat treat scale and to produce a uniform surface texture. Graded bronze chips, together with the regular commercial abrasives, are used in some applications to impart a better color and finish. Abrasive blast cleaning is seldom used to produce decorative finishes on copper alloys.

Wet blasting offers a means of cleaning previously blasted and machined surfaces without damaging the finished or threaded areas. Wet blasting produces various degrees of satin finish. The process is ideal for removing oxide film acquired during brazing, soldering, welding, or heat treating and for removing smudges, stains, and finger marks. For example, bronze castings that have been machined and brazed often are wet blasted with quartz (140-grit) for $\frac{1}{2}$ to 5 min to remove braze discoloration and shop dirt. The parts are normally degreased before wet blasting. After the castings are wet blasted, they are cleaned ultrasonically, inspected, and assembled.

Surfaces cleaned by wet blasting are uniform in appearance, although their color is not the same as original grit-blasted surfaces because of the abrasive used. Cleaning action is gentle but effective because water is the carrier.

Mass Finishing

Mass finishing is best suited for stamped, formed, or machined parts. Castings with remnants of gates and parting lines; forgings with heavy scale, flash lines, or die marks; and heavily burred, pitted, or dented parts are not well suited for mass finishing. Light burrs can sometimes be removed by a prior bright dip, after which tumbling may be used for radius blending, polishing, and burnishing. High thin burrs of soft alloys are likely to peen over. Mass finishing of soft alloys at excessive speeds with insufficient amounts of solution can result in roughened and indented surfaces. Dry tumbling is generally restricted to small parts of simple shape and maximum dimension less than 50 mm (2 in.).

Abrasives. Aluminum oxide, silicon carbide, limestone, and flintstone are the abrasive materials most often used in mass finishing of copper and copper alloys. Combinations of these abrasives may be used for specific applications. For example, a blend of aluminum oxide and silicon carbide of mesh size 46 to 150 produces a reasonably fine matter surface on parts with heavy burrs. Aluminum oxide has a cutting action, and silicon carbide has a planing action.

Preshaped abrasives of various sizes and shapes also may be used. Although more expensive than material in its natural form, preshaped abrasives permit a more constant and uniform polishing action, are more effective in holes and recesses, and retain their effective cutting shape for a longer period of use.

Compounds. Parts heavily coated with grease or oil or contaminated with dirt or chips should be degreased before mass finishing, preferably in a separate barrel, dip tank, or degreaser. A better practice is to clean parts in the barrel when progressing from rough to finishing cycles and to bright dip before burnishing. A sulfuric-nitric acid or sulfuric acid-hydrogen peroxide bright dip should be used if plating follows burnishing.

Soft water and neutral compounds are preferred for mass finishing copper and copper alloys. The use of liquid soap-free alkaline compounds for mass finishing highly leaded, free-cutting brasses prevents the formation of lead soaps that impair the effectiveness of the operation.

Compounds for mass finishing are classified according to the following categories and are purchased as proprietary materials:

- *Cleaning compounds* possess high detergency and buffering action for removing oils, greases, and residues.
- *Descaling compounds* are used to remove tarnish from copper alloys; neutralizing cycles usually follow the use of these compounds.
- *Grinding compounds* are used with abrasive mediums for softening the water, saponifying oils, and keeping chips clean; these compounds inhibit tarnish and improve the color of parts.
- *Abrasive compounds* contain grits such as aluminum oxide, silicon carbide, emery, quartz sand, or pumice.

Surface Finishes. Although mass finishing produces the final finish for many parts, it is used more extensively for cleaning prior to plating and painting or for deburring and polishing before a final finish is applied. Examples of mass finishing applications are given in Table 6.

Table 6 Operating conditions for mass finishing

Material	Medium	Size of abrasive particles		Tumbling time, h	Finish
		mm	in.		
Heavy cutting					
Brass or bronze castings	Aluminum oxide	6.4-19	0.25-0.75	6-16	Matte
Moderate cutting					
Brass stampings	Aluminum oxide	6.4-19	0.25-0.75	1-6	Light matte
Brass screw-machine parts	Aluminum oxide or granite	6.4-19	0.25-0.75	$\frac{1}{2}$-6	Light matte or bright
Light cutting[(a)]					
Brass stampings or screws[(b)]	Limestone	3.2-13	0.13-0.50	2-6	Bright

(a) Submerged tumbling is used for fragile and precision parts.

(b) Screw-machine parts

Bright rolling or water rolling in a barrel is an economical bulk method of finishing small parts. The finishes may be dull, semibright, or of high luster. This operation consists of tumbling the parts in water containing a suitable additive. The water acts as the carrier for the fine burnishing materials. Selection of additive and cycle time controls the surface roughness, stock removal, color, and reflective luster. Examples of water rolling applications are given in Table 7.

Table 7 Operating conditions for bright rolling or water rolling

Solutions are used at room temperature. Time, 20-60 min. Resulting surface has bright finish.

Parts	Weight of load		Additive[(a)]	Water		Speed, rev/min
	kg	lb		L	gal	
Blanks or buttons, copper[(b)]	363-408	800-900	Cream of tartar	95	25	32
Gripper post, nickel over brass	136	300	Proprietary[(c)]	95	25	32
Fragile tubular part, brass[(d)]	18	40	Proprietary	20	5	7

(a) 9 g/L (1 oz/gal).

(b) Removal of burrs.

(c) Additive containing sodium bicarbonate, cream of tartar, sodium acid pyrophosphate, sodium sulfite, and a wetting agent.

(d) Wall thickness is 0.150 mm (0.006 in.).

A prime consideration for successful water rolling is the cleanness of the parts. Oil, grease, scale, and dirt should be removed before rolling for luster. Basic cleaning and pickling operating conditions used before water rolling are given in Table 8.

Table 8 Operating conditions for cleaning and pickling in water rolling barrels

Barrel is made of Type 304 stainless steel. Speed of rotation, 7-32 rev/min; cycle time, 15-20 min. Parts are thoroughly rinsed in hot water after cycle is finished

Solution	Concentration	Temperature	
		°C	°F
Alkaline cleaner[a]	15-20 g/L (2-3 oz/gal)	71	160
Pickling solution[b]	1-2%	54	130

(a) Sodium hydroxide or proprietary compound.

(b) H_2SO_4

For economy, cleaning and pickling should be done in the same barrel by the same operator. For example, oily gripper parts from eyelet machines are placed in an oblique stainless steel barrel and cleaned by a suitable alkaline cleaner. After rinsing, the parts are pickled in a 1 to 2% sulfuric acid solution and rinsed. Clear water and additives, burnishing compounds, are added, and the parts are rolled until the desired finish is obtained. If the work appears to darken during water rolling, the medium should be dumped, the barrel and parts rinsed and then charged with a fresh burnishing compound. Parts suitable for water rolling to a bright finish include posts, sockets, studs, tack buttons, and zipper parts.

Vibratory finishing is particularly effective for deburring, forming radii, descaling, and removing flash from castings and molded parts. It may also be used for burnishing. Vibratory finishers deburr parts 50 to 75% faster and are more versatile than rotary tumbling barrels. There is no cascading of parts, with the attendant possibility of damage by impact. The process is adaptable to both light castings and formed parts. Vibratory finishing is also effective on internal surfaces and recesses that are not usually worked by rotary tumbling.

The mediums for vibratory finishing of copper and copper alloys are similar to those used for rotary tumbling. Dry mediums are used occasionally, but usually a liquid is added to provide lubrication, suspension of worn-off particles, and a more gentle cleaning action. The selection of medium is frequently by trial and error. Conditions for vibratory finishing are given in Table 9.

Table 9 Operating conditions for vibratory finishing

Machined part diam		Material	Medium	Parts per load	Ratio of medium to parts[(a)]	Vibrations per min	Time, min	Purpose
mm	in.							
25	1	Nickel silver	Steel pins and quartz sand	650	4 to 1	1500	40	Deburr
38	$1\frac{1}{2}$	Brass	Steel wire brads	500	2 to 1	1300	60	Deburr and form radii
75	3	Brass	Arkansas stone	150	10 to 1	1500	35	Deburr and finish

(a) 0.03 m^3 (1 ft^3) bowl

Additional information is contained in the article "Mass Finishing" in this Volume.

Polishing and Buffing

Copper alloy parts are polished after scale removal and dressing or rough cutting, but before final finishing operations, which include buffing, burnishing, or honing. Rough castings normally require two polishing operations before buffing. Forgings and stampings require one polishing operation before buffing. Pipe, tubing, and some stampings can be buffed without previous polishing. Buffing is not required when a brushed or satin finish is desired as the final finish.

Because copper-base materials are softer than steel, fewer stages of successively finer polishing are required to achieve a uniformly fine surface finish. For many parts, especially those having machined surfaces or those free of defects, a single-stage polishing operation using 180- to 200-grit abrasive on a lubricated belt or setup wheel may be all that is required before buffing. Poor-quality surfaces require preliminary rough polishing on a dry belt or wheel with 80- to 120-grit abrasive. Surfaces of intermediate quality may be given a first-stage polishing with 120- to 160-grit abrasive, either dry or lubricated. Belt polishing is generally advantageous for high-production finishing except when special shapes are processed. These are best handled by the contoured faces of setup polishing wheels.

Buffing of copper and copper alloys is usually accomplished with standard sectional cloth wheels operating at moderate speeds of 1200 to 1800 rev/min. Typical wheel speeds for various finishes are:

Finish	Wheel speed	
	m/min	ft/min
Dull[(a)]	915-1675	3000-5500
Satin	1220-1830	4000-6000

Cutting and coloring	1675-2135	5500-7000
High luster[(b)]	2135-2440	7000-8000

(a) Using 120- to 200-grit aluminum oxide.

(b) Using tripoli, lime, and silica with no-free-grease binder

When it is necessary to mush a buff to the contour of a complicated part, buffing speeds may range between 200 and 1000 rev/min.

Neutral compounds that are free of sulfur must be used to avoid staining in the plating operation when polishing and buffing precede electroplating. Excessively high temperatures during polishing and buffing may cause difficulties in subsequent cleaning and plating operations. When flawless chromium-plated surfaces are required, it is necessary both to buff and color buff the polished copper alloy surfaces before plating. Chromium reproduces all imperfections in the underlying plating or base metal, and because chromium is hard and has a high melting point, it is more resistant to flow and is not readily buffed by normal methods. A good chromium-plated surface can be obtained without the color buff operation, by only polishing and cut-down buffing. An example of offhand belt polishing and wheel buffing operations is given in Table 10.

Table 10 Offhand belt polishing and wheel buffing operations for sand cast red brass parts

Sand cast lavatory fittings made of red brass are finished in a sequence of six operations in preparation for decorative chromium plating; sequential finishing of spout with flat surfaces

Operation	**Type of contact wheel**	**Wheel speed, rev/min**	**Pieces per hour**	**Type of abrasive belt**	**Belt life, pieces**	**Polishing lubricant or buffing compound**
Rough polishing	Cloth[(a)]	2100	23	80-grit silicon carbide	29	None or light application of grease stick
Final polishing	Cloth[(a)]	2100	30	220-grit Al_2O_3	49	Grease stick
Spot polishing	Cloth[(a)]	2100	46	220-grit Al_2O_3	77	Grease stick
General buffing	Spiral-sewn, treated cloth sections with intermediate airway[(b)]	2400	32	. . .	. . .	Tripoli
Spot buffing	Spiral-sewn, treated cloth sections with intermediate airway[(b)]	2400	115	. . .	. . .	Tripoli
Color buffing	Spiral-sewn, treated cloth sections with intermediate airway[(b)]	1700	75	. . .	. . .	Silica compound

(a) 355 mm (14 in.) diam, 45 mm (1 $\frac{3}{4}$ in.) width, 90 density.

(b) 355 mm (14 in.) diam, 60.3 mm (2 $\frac{3}{8}$ in.) width, 18 ply, 86/93

Scratch brushing is used to produce a contrasting surface adjacent to a bright reflective surface; to produce an uneven surface for better paint adherence; to remove metal during final finishing of parts with intricate recesses that are inaccessible to polishing and buffing wheels; and to remove impacted soil and buffing compounds from previous finishing operations, prior to subsequent finishing in some applications.

Various types of scratching mediums are used to produce different finishes, such as butler, satin, directional, sunburst (or circular), and matte. These mediums are as follows:

- *Wire wheels* are used on copper or brass grill work to clean intricate recesses, holes, or ribbed areas and to produce a decorative noncontinuous scratch pattern on ornamental parts such as vases, lamps, and kitchenware.
- *Emery cloth or paper* is a common medium for producing a series of linear or circular parallel lines on flat objects with no sudden changes in contour. This type of decorative finish is applied to fireplace accessories, automotive hub caps, and kitchenware and appliances.
- *Polishing wheels headed with greaseless compounds* produce scratch-brush finishes with parallelism of the directional pattern. Decorative items such as jewelry, building paneling, and built-in refrigerator and stove parts can be finished in this manner.
- *Soft tampico and manila brushes* remove soil from scrollwork and embossed areas on ornate tableware serving sets and jewelry prior to final processing.

Table 11 gives the sequence of operations and mediums for scratch-brush finishing several copper alloy products.

Table 11 Suggested sequence of operations for scratch brushing of copper alloy parts

Part	Finish desired	Abrasive	Type of wheel	Size of wheel		Speed, rev/min
				mm	in.	
Black fuse body, yellow brass[(a)]	Dull, smooth, black	None	Tampico	80 diam by 75 thick, 5 rows wide	7 diam by 3 thick, 5 rows wide	1200
Silver-plated red brass lipstick case[(b)]	Semibright	Solution of soap bark and cream of tartar	Nickel-silver wire, 0.100 mm (0.004 in.) diam	150 diam by 75 thick, 6 rows wide	6 diam by 3 thick, 6 rows wide	850
Black-on-bronze bookends, highlights relieved[(b)]	Black background with colored copper highlights	Pumice in water	Cloth, sewn sections	180 diam by 13 wide	7 diam by $\frac{1}{2}$ wide	850
Silver-plated lipstick	Satin	Greaseless rouge,	Loose cloth wheel	150 diam by	6 diam by 2	1800

cap[c]		proprietary		51 wide	wide	
Nickel-plated refrigerator panels or stove parts[d]	Satin	Greaseless compound	Loose cloth wheel	305 diam by 50-510 wide	12 diam by 2-20 wide	1800

(a) Clean brush often by running pumice stone across face of wheel.

(b) Lacquer after scratch brushing.

(c) Lacquer after finishing.

(d) Chromium plate after finishing

Although scratch-brush finishing is useful for producing eye-appealing finishes and as a mechanical means for preparing surfaces for subsequent processing, certain hazards must be recognized. Extreme care and control are required when the part being worked contains patterns with sharp corners or embossments, because the sharpness of detail may be destroyed. In salvage or rework operations, it is difficult and sometimes impossible to blend the original brush pattern into a repaired area from which a defect has been removed by grinding.

Chemical and Electrochemical Cleaning

During fabrication, copper alloys may become coated with lubricating oils, drawing compounds, greases, oxides, dirt, metallic particles, or abrasives. These must be removed by cleaning. The selection of the cleaning process depends on the type of lubricant and other materials to be removed, the equipment available, the environmental restrictions, and the degree of cleanness required. The nature and size of the pieces also influence the selection of equipment or process.

Where permissible, mechanical scrubbing, accomplished by turbulent boiling, pressure spraying, or agitating, aids in the removal of any substances that are not exceptionally adherent. Occasionally, hand brushing may be used for small production quantities.

Lubricants made from animal or vegetable oils or greases, such as tallow, lard oil, palm oil, and olive oil, can usually be removed by saponification. In this process, the parts are immersed in an alkaline solution where the oil reacts with the alkali to form water-soluble soap compounds. Mineral oils that are not saponifiable, such as kerosine, machine oil, cylinder oil, and general lubricating oils, are usually removed from the metal by emulsion cleaning.

Dirt particles, abrasives, metal dust, and inert materials are removed by one or both of these processes. To remove undesirable materials by saponification, emulsification, or similar means, it is necessary to use particular chemicals or combinations of chemicals.

Solvent Cleaning and Vapor Degreasing. Solvent cleaning of copper alloys involves immersion in special naphthas with flash points over 38 °C (100 °F) for the removal of light grease and light oil. An example of this type of naphtha is Stoddard solvent. These solvents are preferred to kerosine and to the naphthas used in paints, because less residue remains on the work after the special naphthas have evaporated.

The straight-chain naphthas are not effective for complete removal of heavy grease, burned-on hydrocarbons, pigmented drawing compounds, and oils containing solid contaminants. Buffing compounds containing tallow, stearic acid, and metallic soaps require cyclic hydrocarbons such as toluol and xylol for effective cleaning. Table 12 gives cycles for solvent cleaning of copper alloys.

Table 12 Cycles for cleaning copper alloy parts with a solvent cleaner

Part	Solvent cleaner	Temperature of solvent		Immersion time, min	Soil removed
		°C	°F		
Dose cap[(a)]	Stoddard solvent or mineral spirits	RT to 49	RT to 120	2	Heavy drawing compound
Brass retainer ring[(a)]	Stoddard solvent or mineral spirits	RT to 49	RT to 120	2	Eyelet machine lubricant
Brass rods	Sawdust, dampened with Stoddard solvent or mineral spirits	RT	RT	5[(b)]	Mill lubricant

RT, room temperature.

(a) Hand cleaning necessary with fragile parts.

(b) Tumbled in barrel

Chlorinated solvents such as methylene chloride (boiling point, 40 °C, or 104 °F), trichloroethylene (boiling point, 90 °C, or 189 °F), and perchloroethylene (boiling point, 120 °C, or 250 °F) have been used instead of naphtha. These compounds are less of a fire hazard than straight petroleum solvents but are much more toxic. Because of environmental constraints their use is gradually being curtailed.

Vapor degreasing effectively removes many soils from copper alloys. Stabilized trichloroethylene is used extensively in vapor degreasing because it does not attack copper alloys during degreasing and because it has high solvency for the oils, greases, waxes, tars, lubricants, and coolants in general use in the copper and brass industry. Perchloroethylene is used especially for removing high-melting pitches and waxes, for drying parts by vaporizing entrapped moisture, and for degreasing thin-gage materials.

Vapor degreasing or solvent cleaning is not effective for removing inert materials and inorganic soils such as metal salts, oxides, or compounds that are not generally soluble in chlorinated solvents. Similarly, vapor degreasing for removal of hard and dry buffing compounds could leave behind the insoluble and hard-to-clean abrasives. Solvent emulsion cleaners, although slow, are highly effective for complete removal of buffing compounds.

Solid particles of metal dust or chips that are held on the surface by organic soil can be removed mechanically by the washing action of the solvent. Removal of these particles is accelerated and accomplished better with solvent sprays or by immersion in boiling solvent than with the vapor phase of the degreaser.

Emulsion and Alkaline Cleaning. Parts with heavy soils such as machine oils, grease, and buffing compounds are treated first with emulsion cleaners to remove most of the soil. After the parts have been rinsed, the remaining soil is removed by alkaline soak or electrolytic cleaning. Precleaning reduces the contamination of the alkaline solution, extending the life of the solution. Thorough alkaline cleaning must follow the emulsion cleaning cycle before the subsequent acid cycles. Extreme caution must be exercised to avoid dragging emulsifiers through the rinses and into a plating solution, especially an acid solution.

Emulsion cleaning may be accomplished by soaking the work for 3 min or less in a mildly agitated solution. Spraying is helpful only when all surfaces being cleaned can be thoroughly contacted. The thin film of oil remaining after emulsion cleaning acts as a temporary tarnish preventive. Some parts may be stored after drying, depending on the composition of the solution and the metal being cleaned; however, brass may become pitted by prolonged exposure to certain emulsifier

films. When emulsion-cleaned zinc-bearing brass parts are cleaned electrolytically by alkalines, sufficient time should be allowed for the dispersal of the emulsifier in the alkaline solution to avoid pitting.

The environmental restrictions placed on the use of chlorinated solvents have resulted in the industry turning more and more to alkaline cleaners for degreasing copper and its alloys. Table 13 lists typical compounds from which these are formulated. A great number of these cleaners, which usually contain proprietary additives, are available on the market. Selection of a cleaner is best achieved by a test program in which several cleaners are evaluated. However, the most critical factor in their effective use is to ensure vigorous flow of the cleaner across the parts being cleaned. Additional information is available in the article "Vapor Degreasing Alternatives" in this Volume.

Table 13 Compounds used for formulating alkaline cleaners

Component	Soak cleaners, %	Electrolytic cleaners, %
Sodium hydroxide	10-20	10-15
Sodium polyphosphates	5-20	5-20
Sodium orthosilicate, sesquisilicate, metasilicate	30-50	30-50
Sodium carbonate, bicarbonate	0-25	0-25
Resin-type soaps	5-10	None
Organic emulsifiers, wetting agents, chelating agents	2-10	1-3

Solutions for soak cleaning usually contain 30 to 60 g/L (4 to 8 oz/gal) of cleaner and are operated at 60 to 88 °C (140 to 190 °F). For every 6 °C (10 °F) rise in temperature above 60 °C (140 °F), the cleaning time is reduced by about 25%. Regardless of the concentration of the cleaning solution, there is a practical limit to the amount of contamination a given volume can accommodate without redepositing soil on the metal. In this condition, the solution should be discarded even though analysis reveals unused cleaner.

Dissolved air in fresh cleaning solutions is frequently the cause of tarnishing of copper alloys. The air can be eliminated by heating the solution to the boiling point for about $\frac{1}{2}$h before use. This procedure may not be advisable with every proprietary cleaner because of constituents that break down at the boiling temperature. Some uninhibited alkaline cleaners may also cause a slight darkening or tarnishing of the work surface. The darkening may be removed by dipping in dilute hydrochloric acid or in cyanide solution.

Electrolytic alkaline cleaning is the most reliable method for cleaning parts for plating. The work is the cathode, and steel electrodes are the anodes. Reverse-current anodic cleaning cannot be used for more than a few seconds because copper dissolves in the solution. Copper alloys will tarnish readily during exposure to the oxygen that is released at the anode, but this can be minimized by the addition of inhibitors. In many electroplating operations, anodic cleaning for a few seconds is used to develop tarnish, because it indicates that all soil has been removed. The small amount of metal dissolved by anodic cleaning exposes a more active surface for electroplating, and the light tarnish formed is readily dissolved by a mild hydrochloric or sulfuric acid solution. Current density during anodic electrocleaning of brass should be about 3 A/dm^2 (30 A/ft^2) at 3 to 4 V. Use of high currents will etch the brass and cause dezincification.

Copper-base materials are electrolytically cleaned by cathodic cleaning followed by short-time anodic cleaning, or by soak cleaning followed by anodic cleaning. Positively charged particles plated onto the work during cathodic cleaning

cause smut, which may lead to blistering and poor adhesion of the plated metal if not completely removed. To avoid this condition, a short period of anodic cleaning should follow the cathodic electrocleaning.

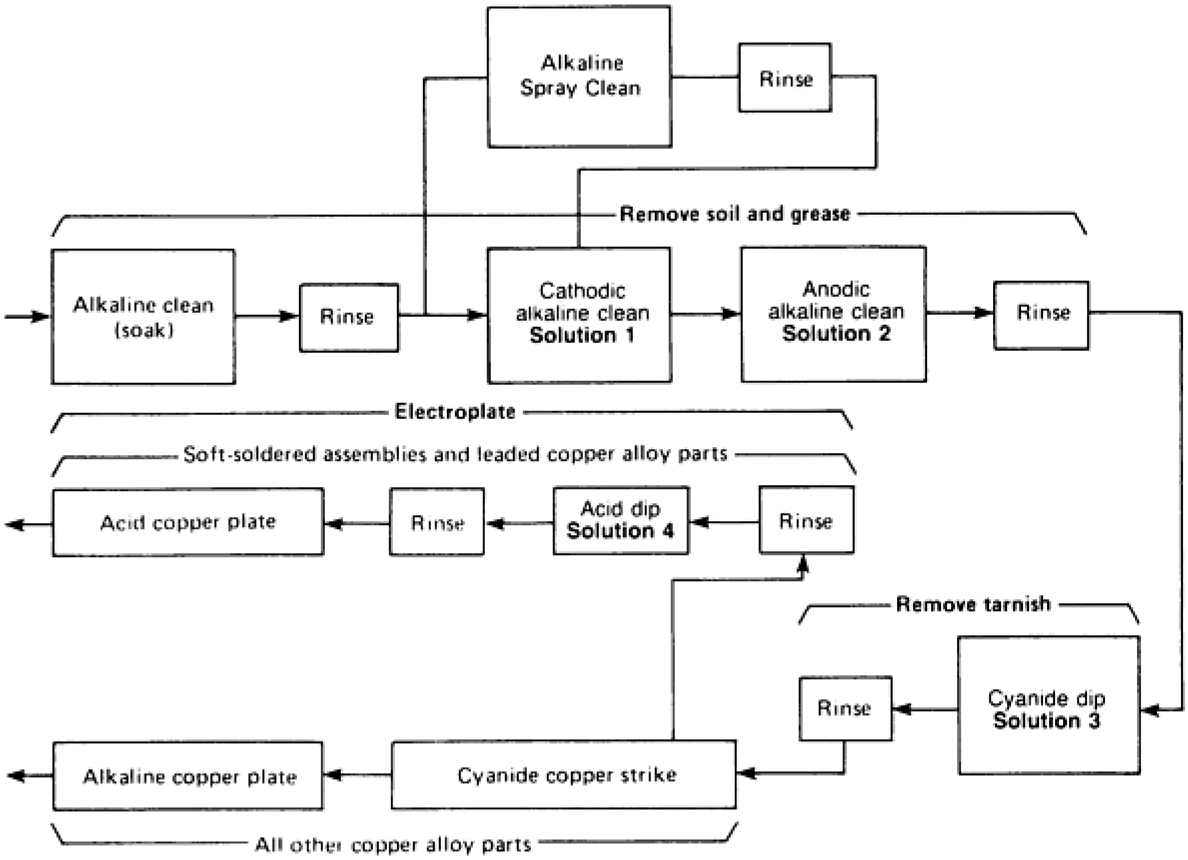
Racks and baskets that are used during the application of chromate chemical conversion coatings should not be used in alkaline cleaning solutions. Contamination of the cleaning solution with as little as 10 ppm of hexavalent chromium can cause poor adhesion and blistering of subsequent metal deposits. To avoid the effects of accidental contamination when chromate treatments are used, sodium hydrosulfite should be added to the cleaning solution at the rate of 14 g ($\frac{1}{2}$ oz) per 380 L (100 gal). The sodium hydrosulfite reduces hexavalent chromium to trivalent chromium, which does not affect subsequent plating. Periodic additions are required because trivalent chromium is reoxidized to hexavalent by the oxygen released at the anode.

Ultrasonic cleaning of copper-base materials is used when the size of particles remaining on the surface is less than 5 to 10 μm (0.2 to 0.4 mils) in any one direction and for removing dirt and chips that cause smudge, as indicated by a white cloth wipe test. Remove much of the surface contamination by other more economical cleaning procedures before ultrasonic cleaning. This increases the life of the ultrasonic cleaning solution and maintains production efficiency. After ultrasonic cleaning, the parts may be rinsed in deionized or distilled water and dried with warm filtered air or in a vacuum oven.

Ultrasonic cleaning is used with alkaline cleaning solutions, solvents, vapor degreasing solutions, or acid pickling solutions to increase the rate of cleaning or to complete the removal of soil from areas not completely cleaned by soak or spray procedures. An example of the need for ultrasonic assistance is the cleaning of fine internal threads on brass parts. An alkaline solution containing 15 to 30 g/L (2 to 4 oz/gal) of cleaner may be used for ultrasonic cleaning of such parts.

Plating and Coating

Preparation for Plating. Before copper alloys are plated, surface oxides are removed and the surfaces chemically activated for adherence of the plate. Heavy oxide scales are usually removed at the mill, so descaling is not normally a part of the preplate treatment. Figures 1 and 2 show sequences of operations required for preparing the surfaces of copper alloys. These operations apply to both lead-free and leaded materials and to soft-soldered assemblies. For many plating operations, where the copper alloy is relatively clean, free of oils, and uncontaminated by buffing compounds, the process can be simplified by eliminating the alkaline soak. If the surface contains buffing compounds, it may require precleaning by soaking in emulsion cleaners. Many plating processes do not use the anodic alkaline clean, especially when an acid dip is used after the cathodic alkaline clean. The acid dip suffices to remove any smut or stain. An acid dip may be simply 15% sulfuric acid or, if the surface needs additional pickling, a bright dip may be used. There are a number of bright dips for copper alloys on the market based on the sulfuric acid-hydrogen peroxide system (see Table 1), in addition to the example in Fig. 2. A chromate bright dip should not be used before plating because of possible chromium contamination of the plating bath, which could lead to blistering, pitting, and peeling of the electrodeposit.



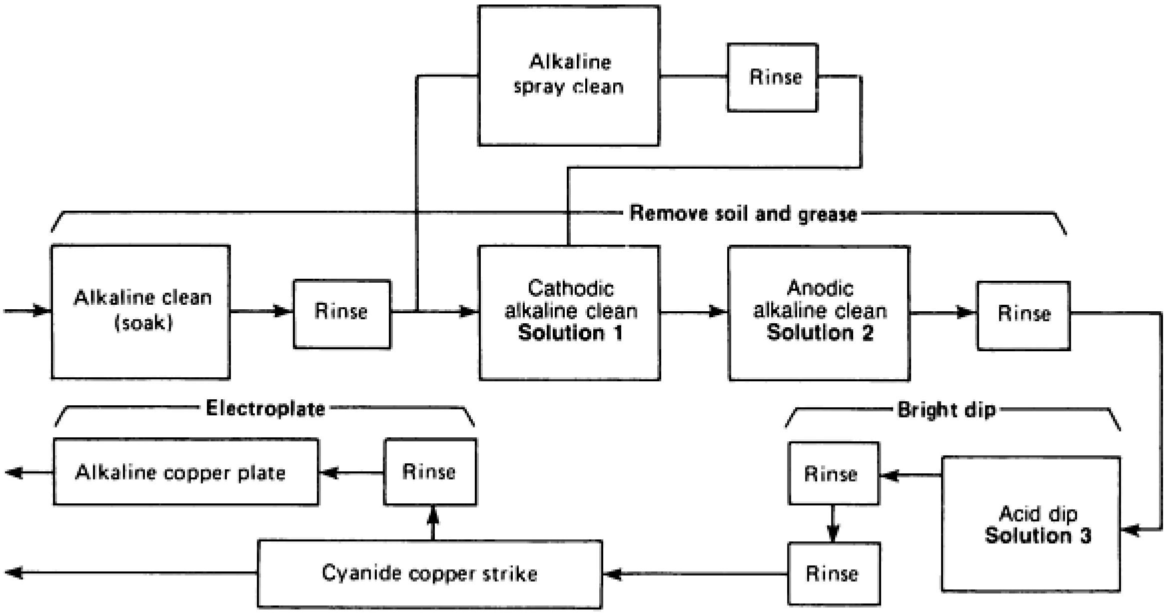
Solution No.	Type of solution	Composition of solution[(a)]	Operating temperature		Cycle time,s
			°C	°F	
1	Cathodic alkaline cleaner[(b)]	$Na_2CO_3H_2O$, 40-50%; $Na_3PO_4 \cdot 12H_2O$, 25-40%; NaOH, 10-25%; Na_2SiO_3, 15-40%	60-71	140-160	60-180
2	Anodic cleaner[(b)]	Same as Solution 1	60-71	140-160	5-10
3	Cyanide dip	NaCN, 15-45 g/L (2-6 oz/gal)	Room	Room	30
4	Acid dip	HBF_4, 5-10%	Room	Room	5-10

(a) By volume, except where otherwise noted.

(b) Current density 1 to 3 A/dm^2 (10 to 30 A/ft^2), 3 to 4 V

Fig. 1 Surface preparation required for removal of buffing compounds and tarnish before plating of copper

alloys. If the buffing compound is hard and dry, an additional presoak in a solvent emulsion cleaner can be used.



Solution No.	Type of solution	Composition of solution[(a)]	Operating Temperature		Cycle time,s
			°C	°F	
1	Cathodic alkaline cleaner[(b)]	$Na_2CO_3 \cdot H_2O$, 40-50%; $Na_3PO_4 \cdot 12\ H_2O$, 25- 40%; NaOH, 10-25%; Surface active agent, 1%	60-71	140-160	60-180
2	Anodic cleaner[(b)]	Same as solution 1	60-71	140-160	5-10
3	Bright dip[(c)]	H_2SO_4, 65-75%; HNO_3, 20-35%; HCl, 1.1 g/L ($\frac{1}{6}$ oz/gal); H_2O, 5-10%	Cool	Cool	5-10

(a) By volume, except where noted.

(b) Current density, 1 to 3 A/dm^2 (10 to 30 A/ft^2), 3 to 4 V.

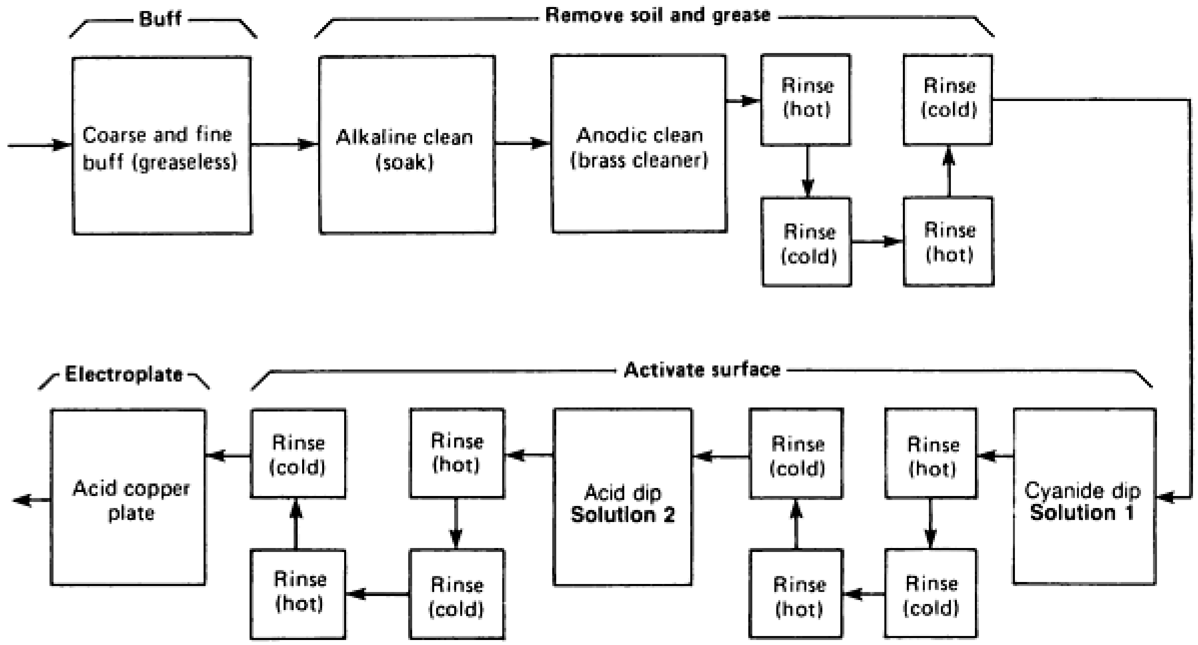
(c) Constant agitation of work

Fig. 2 Surface preparation required for the removal of buffing compounds and for bright dipping before plating of copper alloys

Oxides can be removed from cast or heat-treated copper alloys by either abrasive or chemical cleaning procedures. Castings always require abrasive cleaning; however, they do not necessarily require subsequent pickling or bright dipping for the removal of oxides. If acid treatment is required, thorough rinsing is mandatory to prevent spotting of the plating by entrapped acid. Stampings and drawn parts can be treated in the same manner as castings; however, it may be less expensive to pickle the parts before abrasive finishing if heavy oxides are present. Screw-machine parts made of leaded copper alloys usually require no treatment for oxide removal before plating, but abrasive cleaning can be used when required.

Beryllium Copper. Surface preparation procedures for beryllium copper are the same as for other copper alloys, unless the beryllium copper has been heat treated and still contains surface oxides resulting from that heat treatment. Such oxides on beryllium copper are more difficult to remove than normal oxides on other copper alloys. They can be best removed in strong, hot caustic solutions followed by a good bright dip. The procedure outlined in Fig. 2 should be sufficient if the bright dip cycle is increased to 10 to 15 s. The sulfuric-peroxide bright dips also work well on beryllium copper. The alkaline soak clean and the anodic alkaline clean may or may not be required, depending on the degree of surface contamination resulting from heat treatment. In rare cases, the plater is required to remove scale resulting from high-temperature (>400 °C, or 750 °F) heat treatments such as in solution annealing. The parts must be soaked in a 50% solution of sodium hydroxide at 130 °C (265 °F) for 1 or 2 min before acid pickling in a good bright dip.

Powder Metallurgy Parts. Technology has advanced to a level where parts sintered from metal powders are not as porous and can be easily electroplated. A sequence of operations for surface preparation of powder metallurgy (P/M) parts before electroplating is shown in Fig. 3. Because P/M parts are made from different alloys and because porosity varies, a suitable surface preparation and electroplating technique must be developed for each part.



Solution No.	Type of solution	Composition of solution	Operating temperature	Cycle time, s
1	Cyanide dip	NaCN, 7.5 g/L (1 oz/gal)	Room temperature	30-60
2	Acid dip	H_2SO_4, 3-5 vol%	Room temperature	5-10

Fig. 3 Surface preparation of brass powder metallurgy parts before plating

The methods applicable to porous cast parts can be used for low-porosity P/M parts with densities more than 95% of theoretical. P/M strip stock bonded to steel is an example of low-porosity material. The surface preparation and plating techniques vary for higher-porosity parts with densities 85 to 90% of theoretical.

During plating of P/M parts, the pores act as thermal pumps. Solutions are released from or absorbed by the pores, depending on whether the solution is hotter or colder than the part. Deep and interconnecting pores are likely to entrap cleaning or rinsing solutions, which are released slowly during plating. Porosity must be determined before cleaning, and suitable techniques must be used to prevent solution entrapment. Entrapped solutions may cause precipitation of metal compounds on the work surfaces during plating. The porous nature of P/M parts causes contamination and depletion of all solutions and necessitates that the solutions be closely controlled.

Spotty plating is caused by entrapped solutions that seep out of the pores and stain the plated surface as it dries. Spots may not develop for several days after plating or may appear to be insignificant immediately after plating and subsequently enlarge with time.

A continuous plated coating can seldom be attained on P/M parts unless the pores are closed. Methods for closing the pores include buffing, rolling, burnishing, heat treating, and impregnation. Buffing, rolling, or burnishing are used when appearance is important and dimensional tolerances are not critical. These techniques can be applied either before or after plating. Heat treating is one of the most satisfactory methods for closing pores when surface quality and size are more important than appearance. Occasionally, green compacts are electroplated and then sintered. Another technique is to sinter fully, then to plate and heat treat. This procedure requires washing and acid dipping the parts to neutralize alkalinity prior to heat treating.

Impregnation with copper, lead, tin, waxes, resins, or oils is another method for closing the pores of P/M parts before plating. Thermosetting polyester styrene and silicone resins are suitable impregnating materials. When the polyester-styrene resin is used, the parts are degreased, baked to remove moisture, then impregnated under vacuum and pressure. An emulsion cleaner can be used to remove excess resin from blind holes and threads prior to curing the resin at 120 to 150 °C (250 to 300 °F). Tumbling or polishing can be used to remove excess cured resin.

When silicone resin is used, the surfaces of the powder compact are coated with a thin water-repellent film. Then the compact is heated in air to 205 °C (400 °F), quenched in a solution of 4% silicone (type 200) and 96% perchloroethylene, and baked again for $\frac{1}{2}$ to 2 h. After being pickled in acid, the part can be plated in the conventional manner, preferably in an alkaline bath.

Before being impregnated with oil, the parts are heated in a vapor degreaser and, while hot, immersed in cold oil. After cooling in the oil, the parts are removed, drained of oil, and then rinsed in cold solvent. Parts impregnated with oil have been coated with copper by conventional electroplating processes with resultant satisfactory bonding of the coating.

Evaluation of Cleanness Prior to Plating. The degree of cleaning required for a copper alloy part depends on its intended end use. In some cases visual observation of the cleaned part is sufficient to determine if adequate cleaning has been accomplished. However, cleaning conducted prior to deposition processes must be very thorough, and methods of evaluating the surface cleanness are often required. For metal that has been degreased, this evaluation can be best achieved by spraying the part with water from an atomizer; areas that are clean show up as a continuous film, while areas that have been inadequately cleaned are covered with small water droplets.

Another technique for evaluating the cleanness of small parts involves suspending them in the mouth of a beaker containing a few mils of 10% ammonium sulfide. After an exposure time of 5 to 10 s, a uniform tarnish film will appear over clean areas. Nonuniformity in the color of the tarnish film indicates the presence of residual soils. With practice, the tarnishing test can provide a rapid assessment of the efficiency of a particular cleaning process. For safety reasons the test must be conducted in a fume hood.

It is often difficult to determine if residual oxides remain on a copper alloy surface following pickling operations, particularly if the oxides are of the refractory type. One evaluation method consists of first immersing the part in rosin

flux and then in 60-40 tin-lead solder held at 246 °C (475 °F) for 5 s. The resultant solder coating is compared to the solder coating on a part that is known to be clean. Areas still covered with oxide will appear as areas not wet by the solder.

Electroless Plating

Electroless plating involves the reduction of a metal salt to its metallic state by electrons supplied from the simultaneous oxidation of a reducing agent. The electroless plating solutions are compounded so that the concentration of the reducing salts, metal salts, buffering salts, and the pH controls the rate of reduction of the metal salt and of the oxidation of the reducing agent. If these reactions are not controlled, the metal deposit is reduced spontaneously to a fine powder. The metal to be plated acts as a catalyst and localizes the deposit of the plate to the part itself. Electroless plating completely plates uniform deposits to any thickness desired over intricately shaped parts or assemblies and into deep recesses and long tubular holes. Fine and close-fitting threads can be plated uniformly over the entire threaded area.

On copper-base materials, the process is limited to the plating of nickel, tin, gold, and silver deposits. Solutions for plating these deposits are affected adversely by contaminants, such as cyanides, lead, zinc, manganese, and cadmium. Tin may render the nickel plating solution inoperative; therefore, tin-containing copper alloys must be plated with copper or gold before a final nickel coating is applied.

Because copper is more noble than nickel, it will not act as a catalyst to start the deposition of nickel. This condition is alleviated by contacting the copper workpiece with an active metal such as iron or aluminum that causes the deposition of a thin nickel coating on the workpiece. The nickel coating is of sufficient thickness to continue the oxidation-reduction reaction for further nickel deposition after the activating metal is removed. Another procedure for starting the deposition of nickel is to make the part cathodic and apply a current briefly to the part as it is held in the electroless bath. Electroless nickel plating is particularly useful for coating deep recesses and holes that cannot be adequately electroplated. The article "Electroless Nickel Plating" in this Volume contains further information on the operating conditions of electroless nickel baths.

Electroless plating processes are used to plate copper with gold and silver for decorative purposes. Nickel, gold, and silver are frequently applied to copper electronic components to prevent tarnishing during subsequent processing and to aid in the soldering of semiconductors. Electroless tin plating has been used for copper tubes to prevent corrosion by carbonated waters.

Immersion Plating

Immersion plating, sometimes called galvanic plating, depends on the position that the base metal occupies in the electromotive series with respect to the metal to be deposited from solution. Plating occurs when the metal from a dissolved metal salt is displaced by a more active, less noble metal that is immersed in the solution. As the depositing metal is displaced from the bath, metal from the workpiece dissolves in the solution and becomes a contaminant in the bath. Depleted baths are never replenished, but are replaced with fresh solution.

When immersion plating copper-base materials, only those metals more noble than copper can be displaced from solution, thereby limiting this process to metals such as gold and silver. Immersion-plated deposits are thin, usually in the range of 0.050 to 0.50 μm (0.002 to 0.02 mil).

Compositions and operating temperatures of solutions for immersion plating of gold and silver are:

Gold plating	
Potassium gold cyanide	4 g/L ($\frac{1}{2}$ oz/gal)

Potassium or sodium cyanide	25 g/L ($3\frac{1}{2}$ oz/gal)
Sodium carbonate	30 g/L (4 oz/gal)
Temperature of solution	60 to 80 °C (140 to 180 °F)
Silver plating	
Silver cyanide	7.5 g/L (1 oz/gal)
Sodium or potassium	15 g/L (2 oz/gal)
Temperature of solution	18 to 38 °C (65 to 100 °F)

Electroplating

Metals such as gold, silver, rhodium, nickel, chromium, tin, and cadmium are electrodeposited on copper and copper alloys. Copper electroplating with these metals is used primarily for decorative purposes and for preventing tarnish or corrosion.

Chromium is occasionally plated directly onto copper and copper alloys as a low-cost decorative coating and color match. A plated nickel undercoat is applied when quality plating of chromium is required to produce color depth and resistance to corrosion, abrasion, and dezincification.

Decorative chromium deposits are characteristically thin and porous. Galvanic action between the chromium and base metal may occur during exposure to aggressive environments and result in accelerated corrosion. With copper alloys of high zinc content, dezincification and eventual lifting and flaking of the deposit may result. For added protection, chromium deposits plated directly on the base metal are coated with clear lacquers or with the more durable combination coatings of silicone and acrylic thermosetting organic resins.

Decorative chromium deposits are usually 0.25 to 0.50 μm (0.01 to 0.02 mil) thick. When chromium is deposited directly onto the base metal, the thickness of the deposit is seldom less than 38 μm (1.5 mils), and for many applications a minimum of 50 μm (2 mils) is specified. Additional information can be found in the article "Decorative Chromium Plating" in this Volume.

Hard chromium deposits are used primarily to improve wear resistance and friction characteristics. Because most of the copper-base materials are soft and ductile, the base metal lacks sufficient hardness to support thick deposits of hard chromium against heavy pressures without the risk of scoring or flaking. Hard chromium is electroplated from solutions under conditions similar to those used for decorative chromium plating; however, the deposits are much thicker, frequently dull in appearance, and generally deposited directly on the base metal. To conform to exact dimensional tolerances and to avoid buildup of deposit at corners, an excess of deposit is plated and the final dimension is attained by grinding or lapping. Further information can be found in the article "Industrial (Hard) Chromium Plating" in this Volume.

Cadmium. Copper-base materials are easily electroplated with cadmium from conventional plating baths. A typical bath has the following composition:

Cadmium oxide	22 to 33 g/L (3.0 to 4.5 oz/gal)
Sodium cyanide	85 to 110 g/L (11.5 to 15.0 oz/gal)
Sodium hydroxide	16 to 24 g/L (2.1 to 3.2 oz/gal)
Brightening agent	As required

Usually, applying an undercoat prior to the deposition of cadmium is unnecessary. Cadmium plating is used to minimize galvanic corrosion between copper-base materials and other cadmium-plated metals in the same assembly. Cadmium-plated copper parts are used in aircraft, marine, and military applications involving atmospheric exposure; however, the use of cadmium is being curtailed because of health and safety concerns associated with its use.

Gold is usually applied over an electroplated undercoating of nickel or silver, but may be electroplated directly on the copper alloy. In the electronics industry, nickel is plated to copper before gold plating. The nickel barrier stops migration of copper into the gold layer. The gold thickness is about 2.5 μm (0.1 mil). The nickel barrier is normally a minimum of 1.3 μm (0.05 mil) thick; however, exposure of the gold-plated part to elevated temperatures for extended periods of time may require a nickel barrier 127 μm (5 mils) thick. If silver is the barrier, government specifications for electronic applications usually require a minimum thickness of 5 μm (0.2 mil) of silver and 1.3 μm (0.05 mil) of gold.

When gold is plated directly on copper alloy, a deposit of 3 μm (0.1 mil) or more is needed because of rapid diffusion, especially at elevated temperatures. This rapid diffusion destroys the electrical and decorative properties of the deposit by interdiffusion between the coating and the base metal. Total coverage and freedom from porosity are necessary for corrosion protection.

For greatest adhesion, the part should be plated with a gold strike before the final deposit of gold. One satisfactory strike solution consists of potassium gold cyanide 0.8 g/L (0.1 troy oz/gal as gold) and potassium cyanide 45 g/L (6 oz/gal). To avoid tarnishing, the struck part should be transferred immediately to the plating solution with the current flowing as the work enters the solution. An alternate procedure is to rinse the struck work, then acid dip, rinse, and plate with a suitable current density.

Current density for racked parts varies from 0.2 to 1 A/dm^2 (2 to 10 A/ft^2), depending on the solution used. The rate of deposition depends on the solution and varies from 100 mg/A · min (0.3 A/dm^2, or 3 A/ft^2, for 14.4 min deposits 3 μm, or 0.1 mil, of gold) in most cyanide and neutral solutions to one-third of this rate in most acid solutions. For barrel plating, the limiting current density for all solutions is about one-;third of that used in rack plating.

Cyanide solutions are the most efficient and have the best throwing power, whereas deposits from acid and neutral solutions are less porous and are not stained by incompletely removed solution.

Patented solutions for plating gold contain 0.03 kg (1 troy oz) of gold per gallon, usually added as potassium gold cyanide, and proprietary brightening agents. Insoluble anodes are used with these solutions. The patent-free hot gold cyanide solution is extremely sensitive to impurities, and the deposits lack brightness. The solution is limited in application. Gold metal anodes are used with this solution.

The proprietary solutions are brightened or colored by codeposited base metals, especially silver, nickel, cobalt, and copper. These base metals may be classed as impurities for some applications. When gold deposits of less than 0.33 μm (0.013 mil) are used on a plated item, the deposit should be protected by lacquer or a chromate passivation.

Nickel is plated onto copper-base materials for decorative purposes and as an undercoating for increased corrosion resistance of nickel-chromium coating systems. Because nickel deposits have a yellow cast and tarnish easily, many nickel-plated parts are finished with electroplated chromium. Costume jewelry, lipstick cases, hardware for doors and windows, automotive hub caps, air valves, and plumbing fixtures are examples of copper-base parts regularly plated with nickel, either as a final coat or an undercoat.

Nickel electrodeposits from some solutions reproduce the irregularities in the base metal surface to a marked degree. The base metal must be polished and buffed before plating if a smooth uniform plated surface is required. Polishing and buffing are not required when nickel is to be plated on a reasonably smooth surface from solutions that produce a high degree of leveling of the deposit as it builds up in thickness. Deposits from these solutions are smooth and bright. Nickel plating with high leveling and brightness can provide an attractive mirrorlike finish. Proprietary leveler brighteners are added to the nickel bath to achieve high leveling with nickel deposits as thin as 7.6 to 10 μm (0.3 to 0.4 mil).

Numerous types of nickel electroplating solutions are available. The solutions differ in basic composition, preferred operating conditions, and quality of the deposit. These are described in the article "Nickel Plating" in this Volume.

Most decorative plating is done in solutions that yield bright or semibright deposits. Although dull nickel deposits may be buffed to a high luster, the cost of buffing limits dull nickel to nondecorative or functional uses.

Black nickel is a decorative finish only. It should be plated over a deposit or base metal that is corrosion resistant. Very thin deposits of black nickel are recommended because thick deposits lack the ductility and adhesiveness required to withstand shock.

Rhodium. An undercoat of nickel is used when copper alloys are to be plated with rhodium. For decorative purposes, the thickness of rhodium is usually about 0.25 μm (0.01 mil). Deposits of 25 μm (1 mil) or more are used for functional purposes, but these heavier deposits do not have the brightness or color characteristics of the decorative finishes. Rhodium plating solutions are of the sulfuric acid or phosphoric acid type. Formulas and operating conditions are given in the article "Platinum-Group Metals Plating" in this Volume.

Silver plating is used for decorative and functional purposes. Its useful characteristics for functional applications include:

- High surface conductivity for radio frequencies. A minimum of 3 μm (0.1 mil) of silver is required for these applications.
- Low resistance for electrical contacts. The thickness of silver used for electrical contacts ranges from very thin deposits, such as those produced by immersion coating to electroplates 13 μm (0.5 mil) thick.
- Antiseizing or antigalling properties for wear surfaces.

Silver can be deposited as a dull plate from cyanide solutions or as a bright plate from baths containing suitable brighteners. Details of electrolyte compositions and operating conditions are contained in the article "Silver Plating" in this Volume. Plating times for the deposition of 25 μm (1 mil) of silver, as a function of current density, are:

Current density		Plating time, min
A/dm^2	A/ft^2	
1	10	38
2	20	18
3	30	13
4	40	9

Pollution free, proprietary acid silver sulfate plating baths are now also available.

Tin. As a protective coating, tin is not necessarily anodic to copper alloys. A copper alloy may not always be fully protected against a corrosive environment at the expense of tin. Some corrosion products of tin are more noble than copper and can create the type of galvanic conditions that lead to pitting corrosion. Tin can be plated from alkaline stannate baths or from sulfate or fluoborate acid baths. For compositions and operating conditions of tin electrolytes, see the article "Tin Plating" in this Volume.

Tin-Copper Alloys. The 40 to 50% Sn alloy, speculum metal, has been used as a decorative coating because of its silverlike color. The bronze alloy coatings containing 10 to 20% Sn are producible to match the color of gold and have been used as decorative deposits for this reason. Information on plating bronze alloys is given in the article "Tin Alloy Plating" in this Volume.

Tin-lead alloys can be plated on copper alloys in almost any proportion from a fluoborate bath. An alloy of 7% Sn and 93% Pb has been used for corrosion resistance, especially to sulfuric and chromic acids. The 60% Sn, 40% Pb eutectic alloy has excellent solderability and good electrical properties and corrosion resistance. The eutectic alloy may be applied also by hot dipping, but control of thickness is as difficult as with hot dipping in pure tin.

Compositions of solutions for plating 7Sn-93Pb and 60Sn-40Pb (solder) are given in Table 14.

Table 14 Bath compositions and operating conditions for tin-lead plating

Conditions for operating include a cathode current density of 3 A/dm^2 (30 A/ft^2); anode to cathode ratio is 2 to 1; solution has maximum pH of 0.2 and is mildly agitated at a temperature of 16 to 38 °C (60 to 100 °F); air agitation cannot be used because it will oxidize the tin.

Constituent	Total tin		Stannous tin		Lead		Free fluoboric acid		Free boric acid		Peptone		Anode Composition
	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	g/L	oz/gal	
7Sn-93Pb	7.0	0.94	6.0	0.80	88.4	11.8	100.0	13.4	25	3.4	0.50	0.067	7Sn-93Pb

Chemical or electrolytic polishing imparts a smooth bright finish and removes burrs selectively from certain areas. Usually the same solution will accomplish both purposes, although variations in operating conditions may be desirable, depending on which feature is required.

For electropolishing, the parts are racked and made the anode in an acid solution. Direct current is applied and the process selectively removes more metal from the high points of the surface than from the low. This results in a high polish and the removal of burrs.

Chemical polishing imparts a finish similar to that obtained by electropolishing, but electropolished surfaces are usually smoother and brighter.

Electropolishing for 4 to 6 min will reduce the surface roughness to between one-third and one-half the original value. Electropolishing and chemical polishing will remove minor scratches and defects, as well as burrs.

Selection of these processes is influenced by the following considerations:

- For complex parts, electropolishing and chemical polishing are easier and less expensive than mechanical polishing.
- Copper-base materials that are polished either electrolytically or chemically do not require the use of buffing or polishing compounds. Thus, they do not encounter the difficulties associated with removal of

entrapped compounds and usually do not require any additional cleaning operations other than rinsing.
- Parts racked for electropolishing may be electroplated in the same racks, which results in considerable savings in handling costs.
- Electrolytically or chemically polished surfaces tarnish less readily than mechanically polished surfaces. Some chemical polishing baths can offer passivation and prevent copper from tarnishing during storage.
- Parts that might deform during mechanical polishing or tumbling will not be deformed by electrolytic or chemical polishing.
- Mechanical polishing may result in a deformed surface layer that differs from the base metal and does not accept plating uniformly. Electroplate on electropolished base metal has adhesion superior to that on mechanically finished surfaces

Parts that are electropolished include fishing lures, plumbing fixtures, furniture arms and legs, lamps and lighting fixtures, wire goods, brass appliance parts, jewelry, nameplates, and bezels. Copper-plated parts, such as automobile tail pipes, die castings that have not been buffed, and high-altitude oxygen bottles are electropolished effectively for an improved finish. The thickness of copper plate should be in excess of 20 μm (0.8 mil) before electropolishing. Most of the commercial solutions used for electropolishing copper alloys contain phosphoric acid with additional agents.

A sequence of operations for electropolishing consists of:

- Racking the parts
- Cleaning to remove oil, grease, dirt, and oxide
- Double rinsing in water at room temperature
- Electropolishing for 2 to 4 min at about 65 °C (150 °F), using a current density of 30 A/dm^2 (300 A/ft^2)
- Double rinsing in water at room temperature and drying

If the parts are to be electroplated after electropolishing, the drying operation in the above sequence is omitted and the process continues with anodic alkaline cleaning until the surface is light brown in color. Then the parts are rinsed in water at room temperature, dipped in 5% sulfuric acid solution, double rinsed in water at room temperature, immersed in the cyanide copper strike solution, and plated.

The quality of an electrolytically or chemically polished surface is affected by the following factors:

- *Composition of the material*. Most copper alloys are suitable except those containing appreciable amounts of lead, such as the free-machining alloys. Materials successfully treated include copper, beryllium copper, single-phase bronzes, and single-phase nonleaded brasses.
- *Condition of the initial surface*.
- *Grain size of the metal*. The smaller the grain size the better the finish. A grain size of 0.004 mm (0.0002 in.) yields excellent results; satisfactory results are produced with grain sizes up to about 0.01 mm (0.0004 in.).

Passivation

Passivation refers to the process of forming a protective film on metal. The blue-green patina of copper developed during atmospheric exposure of copper alloys is a protective coating that is aesthetically pleasing. The patina may be artificially produced or accelerated by a solution, developed by the Copper and Brass Research Association, having the formulation:

Ammonium sulfate	2.7 kg (6 lb)

Copper sulfate	85 g (3 oz)
Ammonia (technical grade, 0.90 sp gr)	39.6 cm^3 (1.34 fl oz)
Water	25 L (6.5 gal)
Total solution	27 L (7.3 gal)

A fine spray of the solution should be applied to a chemically clean surface. The film should be permitted to dry before the part is sprayed a second time. Five or six repetitions of the spraying and drying sequence are required. The color begins to develop in about 6 h and at first is somewhat bluer than natural patina. A more attractive color develops as the surface is exposed to natural weathering.

Small copper parts may be coated with an imitation patina by dipping them in or brushing them with the following solution:

Ingredient	**Parts by weight**
Copper	30
Nitric acid, concentrated	60
Acetic acid, 6%	600
Ammonium chloride	11
Ammonium hydroxide (technical grade, 0.90 sp gr)	20

When preparing the solution, copper is dissolved in the nitric acid, and as soon as the action ceases, the remaining three constituents are added. The solution is allowed to stand several days before use. Parts treated with this solution are coated with linseed oil.

Coloring

Copper-base materials may be surface treated to produce a variety of colors, ranging from dark reds to black. The final color depends on base metal composition, solution composition, immersion time, and operator skill. Coloring is primarily an art, and practical experience is necessary to develop the skill required to produce uniform finishes consistently. Copper alloys are colored chemically to enhance the appearance of a product, to provide an undercoating for subsequent organic finishes as with brass, and to reduce light reflection in optical systems. Chemical coloring produces a thin layer of a compound on the surface of the base metal. This layer retains some of the characteristics of the metal surface prior to coloring, such as smooth and lustrous or dull.

The procedures for artificial coloring of metals utilize many of the reactions that occur more slowly under natural conditions. Some colored films not found in nature can be produced artificially. Additional color combinations, such as

oxidized and highlighted finishes, can be produced by successive chemical and mechanical operations, to emphasize or to remove partially the chemically colored film.

Coloring copper alloys is essentially a process for coloring copper, because zinc and tin compounds are colorless. These constituents and their concentrations greatly affect many of the chemical reactions and color tones of the coatings formed. A copper content of less than 85% is required to produce a good blue-black finish on brass by an ammoniacal copper sulfate or ammoniacal copper carbonate blackening or blue dip solution. Other solutions are more suitable for coloring high-copper alloys.

After machining and mechanical surface preparation have been completed, the parts should be thoroughly cleaned to remove dirt, oil, grease, and oxide films. Cleaning is important for the development of a uniform film in chemical coloring. The cleaning and deoxidizing procedures should be selected so that the structure of the metal at the surface undergoes a minimum of undesirable change. Acid dipping or bright dipping using nitric-sulfuric acid solution may be necessary to remove oxides and to activate the surface for chemical coloring. A certain amount of trial and error is usually required to establish the most suitable techniques for surface preparation.

Coloring Solutions. Many types of chemical solutions are used for coloring copper alloys. The formulations and conditions commonly used in commercial applications to produce colors are given in Table 15.

Table 15 Solutions for coloring copper alloys

Desired color	Solution composition	Process conditions	Comments
Solutions for alloys containing $\geq$85% Cu			
Dark red	Molten potassium nitrate	Temperature, 650-700 °C (1200-1300 °F); immersion time, $\leq$20 s; hot water quench	Parts must be lacquered.
Black[a]	Solution A: liquid sulfur, 28 g (1 oz); sulfurated potash, 57 g (2 oz); ammonium hydroxide (sp gr 0.89), 7 g ($\frac{1}{4}$ oz); water, 4 L (1 gal)	Room temperature	Produces a dull black finish; a reddish bronze to dark brown finish can be obtained by dry scratch brushing with a fine wire or cloth wheel.
	Solution B: sulfurated potash, 1.9 g/L ($\frac{1}{4}$ oz/gal) of water	. . .	Solution strength should be adjusted to blacken the part in approximately 1 min; too rapid formation of coloring film can result in a nonadherent and brittle film.
	Solution C: potassium sulfide, 3.7-7.5 g/L ($\frac{1}{2}$-1 oz/gal) of water	Immersion time, $\leq$10 s	Parts must be lacquered.
Steel black	Arsenious oxide (white arsenic), 113 g (4 oz); hydrochloric acid (sp gr 1.16), 240 cm^3 (8 fl oz); water, 4 L (1 gal)	Temperature of solution, ~82 °C (180 °F)	Immerse parts in the solution until a uniform color is obtained; scratch brush while wet, then dry and lacquer.
Black	Sodium hydroxide, 45 g	Temperature, 82-99 °C (180-210 °F);	Adequate ventilation is required. After

anodizing	(16 oz); water, 4 L (1 gal)	current density, 0.2-1 A/dm^2 (2-10 A/ft^2); anode-to-cathode ratio, 1:1; voltage, 6 V; cathodes, steel, carbon, or graphite; anodizing time, 45 s to 3.75 min; tank material, steel	anodizing, the parts are washed in hot and cold water, rinsed in hot water, dried, buffed lightly with a soft cloth wheel, and lacquered, if desired.
Reddish bronze to dark brown (statuary bronze)	Sulfurated potash, 57 g (2 oz); sodium hydroxide, 85 g (3 oz); water, 4 L (1 gal)	Temperature, 77 °C (170 °F); immersion time depends on final color desired	Parts are usually scratch brushed with a fine wire wheel; lacquering is required.
Verde antique	Solution A: copper nitrate 113 g (4 oz); ammonium chloride, 113 g (40 oz); calcium chloride, 113 g (4 oz); water, 4 L (1 gal)	. . .	Verde antique finishes are also known as patina. They are stippled on brass or copper and dried. Parts made of copper or copper plated are usually treated in a sulfide solution to produce a black base color, which results in a dark background. The use of sodium salts in the verde antique solution results in a yellowish color, while ammonium salts impart a bluish cast. Stippling can be repeated, and when the antique green color appears, immersion in boiling water will produce several different color effects. Other color effects are obtained by using some dry colors such as light and dark chrome green, burnt and raw sienna, burnt and raw umber, ivory drop white, and drop black, or Indian red. After coloring, the surface should be lacquered or waxed. A semiglossy appearance of the lacquered surface can be produced by brushing with paraffin, beeswax, or carnuba wax on a goats-hair brush rotated at about 750 rev/min.
	Solution B: acetic acid, 2 L ($\frac{1}{2}$ gal); ammonium chloride, 570 g (20 oz); sodium chloride, 200 g (7 oz); cream of tartar, 200 g (7 oz); copper acetate, 200 g (7 oz); water, 2 L ($\frac{1}{2}$ gal)	. . .	
Light brown	Barium sulfide, 16 g ($\frac{1}{2}$ oz); ammonium carbonate, 7 g ($\frac{1}{4}$ oz); water, 4 L (1 gal)	Room temperature	. . .
Brown	Potassium chlorate, 155 g ($5\frac{1}{2}$ oz); nickel sulfate, 78 g ($2\frac{3}{4}$ oz); copper sulfate, 680 g (24 oz); water, 4 L (1 gal)	Temperature, 90-100 °C (195-212 °F)	. . .
Solutions for alloys containing <85% Cu			
Black	Solution A: copper sulfate, 85 g (3 oz); sodium thiosulfate, 170 g (6 oz); water, 11-19 L (3-5 gal)	Brass parts are placed in oblique tumbling barrel made of stainless steel. The parts are covered with water; the copper sulfate and sodium thiosulfate are dissolved in warm water and added to the contents of the barrel. The parts are tumbled for 15 to 30 min to obtain finish, the solution is drained from	Parts must be lacquered.

		barrel, and the parts are washed thoroughly in clean water. The parts are then removed from the barrel and dried in sawdust or air blasted.	
	Solution B: copper carbonate, 16 g ($\frac{1}{2}$ oz); ammonium hydroxide (sp gr 0.89), 113 g (4 oz); sodium carbonate, 7 g ($\frac{1}{4}$ oz); water, 4 L (1 gal)	Temperature, 88-93 °C (190-200 °F)	. . .
Statuary bronze	Copper carbonate, 16 g ($\frac{1}{2}$ oz); ammonium hydroxide (sp gr 0.89), 113 g (4 oz); sodium carbonate, 7 g ($\frac{1}{4}$ oz); water, 4 L (1 gal)	Temperature, 88-93 °C (190-200 °F). Immerse the parts in the hot solution for 10 s; rinse in cold water and dip in solution of dilute sulfuric acid; rinse in hot and then cold water; clean with soft cloth or sawdust.	Parts must be coated with clear lacquer.
Blue black	Copper carbonate, 0.45 kg (1 lb); ammonium hydroxide (sp gr 0.89), 1 L (1 qt); water, 3 L (3 qt)	Temperature, 54-79 °C (130-175 °F)	Excess copper carbonate should be present; proper color should be obtained in 1 min.
Brown	Part 1: copper sulfate, 113 g (4 oz); potassium chlorate, 227 g (8 oz); water, 4 L (1 gal). Part 2: liquid sulfur, 28 g (1 oz), or sulfurated potash, 57 g (2 oz); water, 4 L (1 gal)	Immerse parts in Part 1 for 1 min; without rinsing, immerse parts in Part 2 for a short time; rinse in cold water; repeat dipping operation in both solutions until desired color is obtained; rinse work in hot water; dry in hot sawdust or with an air blast; scratch brush with fine wire wheel and lacquer	. . .
Light brown (old English finish)	Part 1: liquid sulfur, 14 g ($\frac{1}{2}$ oz), or sulfurated potash, 28 g (1 oz); water, 4 L (1 gal). Part 2: copper sulfate, 57 g (2 oz); water, 4 L (1 gal)	Immerse parts in Part 1; without rinsing, immerse in Part 2; rinse in cold water; repeat dipping operations until light color is obtained. For uniform finish, scratch brush and repeat dipping operations until desired color is obtained; rinse parts in cold and hot water; dry in sawdust; scratch brush on a fine wire wheel; and lacquer.	. . .
Antique green on brass	Nickel ammonium sulfate, 227 g (8 oz); sodium thiosulfate, 227 g (8 oz); water, 4 L (1 gal)	Temperature, 71 °C (160 °F)	. . .
Hardware green on brass	Ferric nitrate, 28 g (1 oz); sodium thiosulfate, 170 g (6 oz); water, 4 L (1 gal)	Temperature, 71 °C (160 °F)	. . .

Brown on brass or copper	Potassium chlorate, 155 g ($5\frac{1}{2}$ oz); nickel sulfate, 78 g ($2\frac{3}{4}$ oz); copper sulfate, 680 g (24 oz); water, 4 L (1 gal)	Temperature, 91-100 °C (195-212 °F)	. . .
Light brown on brass or copper	Barium sulfide, 14 g ($\frac{1}{2}$ oz); ammonium carbonate, 7 g ($\frac{1}{4}$ oz); water, 4 L (1 gal)	. . .	Color is made more clear by wet scratch brushing and redipping.

(a) Alloys blackened by these solutions include silicon bronzes; beryllium coppers; bronzes containing up to 8% Sn; phosphor bronzes of all types; and brasses, leaded or unleaded, with zinc contents up to 35%. Several other proprietary processes are also available for producing a satisfactory black finish.

Post-Treatment. Many chemical films must be scratch brushed to remove excess or loose deposits. In addition, contrast in colors can be obtained by relieving by scratch brushing with a slurry of fine pumice, hand rubbing with an abrasive paste, mass finishing, or buffing to remove some or all of the colored film from the highlights. Clear lacquers are usually necessary for adequate life and service of chemical films used as outdoor decorative finishes. Finishes for exposure indoors are often used without additional protection to the conversion coating.

Organic Coatings

Information on the materials and methods commonly used for organic finishing of metal surfaces with clear or pigmented coatings is given in the article "Painting" in this Volume. Tarnishing or discoloration of copper alloys can be retarded or delayed indefinitely by the application of a lacquer. Lacquers should be selected and applied on the basis of the intended service environment of a given product. For exterior service, a dry film thickness of 38 to 50 μm (1.5 to 2 mils) is recommended. In less severe indoor service, a dry film thickness of about 13 to 18 μm (0.5 to 0.7 mil) performs satisfactorily.

Air-Drying and Thermosetting Lacquers. The performance of thermosetting or heat-cured lacquers is superior to that of air-drying lacquers. The use of the thermosetting types is preferred if ovens are available. Distinction should be made, however, between true thermosetting and forced drying. All lacquers can be force dried after a suitable air-flash period to facilitate handling, but thermosetting materials must be heated to an appropriate temperature, 120 to 205 °C (250 to 400 °F) or higher, for 5 to 60 min, to cross-link the polymers present in them and to develop their inherent characteristics.

The catalytic activity of copper is such that essentially complete curing of thermosetting lacquers is obtained at temperatures lower than those required with inert substrates. Consequently, many thermosetting lacquers discolor copper alloys severely when heated to temperatures recommended by their suppliers. Such discoloration can be minimized by curing at lower temperatures.

Resins are chosen on the basis of service requirements and include:

- Alkyds
- Acrylics
- Cellulosics, such as cellulose nitrates, ethyl cellulose, and cellulose acetate butyrates
- Epoxies
- Phenolics
- Polyesters

- Silicones
- Urea and melamine formaldehydes
- Vinyls
- Urethanes

An epoxy, cellulose nitrate, or alkyd resin provides satisfactory protection for an inexpensive container, such as a lipstick container. The use of a heat-resisting melamine provides satisfactory service at moderately elevated temperatures. Silicone formulated for high-temperature service provides the best heat resistance, but is a more costly material. If resistance to degradation by weather is important, high-quality acrylics provide the best results. General characteristics of these resins are given in the article "Painting" in this Volume.

Surface Engineering of Magnesium Alloys

Revised by James E. Hillis, Dow Chemical Company

Introduction

SURFACE TREATMENTS are applied to magnesium parts primarily to improve their appearance and corrosion resistance. Many factors may be involved in selecting a suitable surface treatment or finishing system, including surface conductivity, wear resistance, the service environment, alloy composition, and the presence (or absence) of dissimilar metals in the assembly.

Environmental exposures involving salt water or condensing moisture in the presence of chlorides, as well as other salts, have in the past proven very aggressive to magnesium alloys. The higher-purity alloys introduced in the mid-1980s, however, exhibit significantly reduced sensitivity to such environments. For example, die cast alloys AZ91D and AM60B, with controlled levels of iron, nickel, and copper contamination, have been used in increasing volumes in automotive applications as a result of their improved road salt corrosion durability, combined with their castability and light weight. In both painted and unpainted applications these alloys provide salt-water corrosion performance equal to or better than that of die cast aluminum and carbon steel. (See the article "Corrosion of Magnesium and Magnesium Alloys" in *Corrosion,* Volume 13 of *ASM Handbook,* and Ref 1, 2, 3, and 4.)

Figure 1 illustrates the contrast in performance of the old AZ91B die cast alloy versus the higher-purity AZ91D alloy, after 240 h of ASTM B 117 salt-spray testing. Figure 2 compares the performance of painted AZ91D and cold-rolled carbon steel after five years at a marine atmospheric exposure site on the Texas Gulf coast. The coating system in both cases consisted of an iron-phosphatizing pretreatment (without a chrome rinse) plus 12 to 20 μm (0.5 to 0.8 mil) each of cathodic epoxy and a spray acrylic top coat. Alloys AZ91E, WE54A, and WE43A are three sand cast alloys introduced since 1985 that offer similarly improved performance in gravity, or low-pressure cast applications (Ref 5, 6).

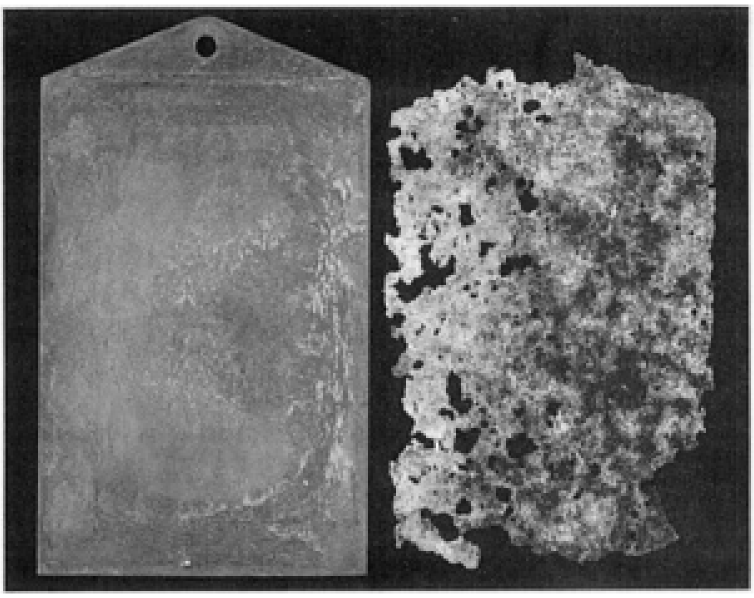


Fig. 1 Ten-day ASTM B 117 salt-spray corrosion performance of high-purity AZ91D (0.1 mm/yr, or 4 mils/yr, left) versus AZ91B (17 mm/yr, or 680 mils/yr, right). Source: Ref 3, 6

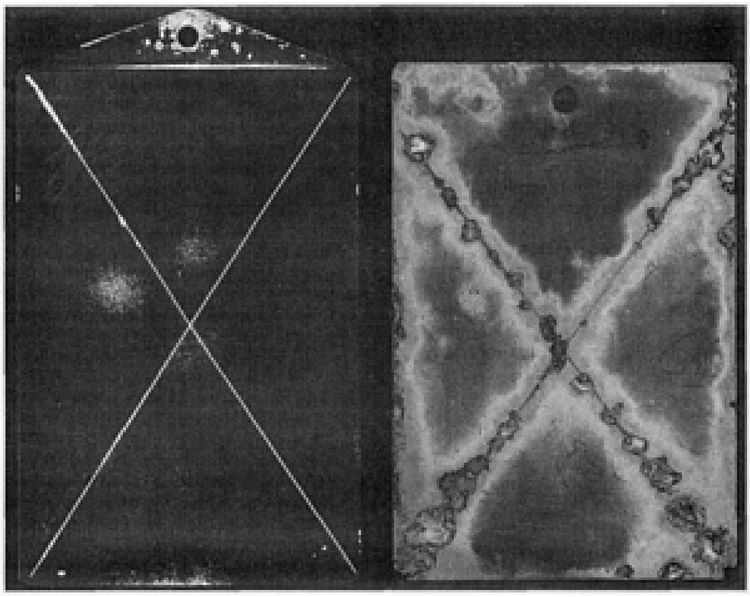


Fig. 2 Five-year Gulf Coast corrosion performance of coated AZ91D die cast magnesium (left) versus cold-rolled carbon steel (right). Both panels were cleaned, iron phosphatized, coated with 18 μm (0.7 mil) of baked cathodic epoxy primer and 12 to 20 μm (0.5 to 0.8 mil) of acrylic lacquer. The test was conducted at the ASTM Brazos River site near Freeport, TX using scribed panels per ASTM D 1654. Source: Ref 1

The following environments are listed in the order of increasing corrosiveness: oil immersion, indoor, rural, industrial, and marine. Magnesium alloys are afforded increasing protection in the following order: bare, pickled, chromate conversion coated, anodized, electroplated, and coated with organic finishes. Anodic coatings are porous and provide no corrosion protection unless sealed with a paint. Table 1 relates applications of various degrees of severity to finishing systems used. It should be noted that damaged paint films allow moisture to migrate through porous anodic coating, resulting in corrosion. Painting over the damage will seal in the moisture, creating further problems.

Table 1 Finishing systems applied to magnesium for various applications

Systems for specific parts	
Aircraft auxiliary component housings, sand cast	Sand blasted, sulfuric acid pickle, anodize or dichromate treatment (No. 7), epoxy sealed, baked epoxy primer, and top coat
Automotive engine brackets, die cast	Wet bowl abraded, no additional finishing
Automotive interior brackets, die cast	Chopped aluminum wire blast
Automotive valve/cam covers, die cast	Wet abraded, alkaline cleaned, iron phosphate treated, electrostatic powder coated (acrylic, polyester, or epoxy-polyester hybrid)
Chain saws, die cast	Wet barrel or bowl abraded, electrostatic powder coated (polyester or epoxy-polyester hybrid)
Computer disk drive component, extruded	Dichromate treatment No. 7 per Fig. 3; no additional finish
Dock boards, wrought	No finish applied
Electronic housing, die cast	Modified chrome pickle No. 20 per Fig. 4; sprayed acrylic, polyester, or urethane exterior coating
Foundry flasks	No finish applied
Line trimmer	Wet abraded, alkaline clean, phosphate treated, and powder coated
Lawnmower deck, die cast	Alkaline cleaned, phosphate pretreated, electrostatic powder coated (polyester)
Luggage frame, extruded	Acid pickled, phosphate treated, powder coated (polyester)
Missile exteriors, wrought	System A: dichromate, vinyl butyrate zinc chromate wash primer, baked phenolic epoxy varnish, 2 coats, enamel, 2 coats
	System B: chrome pickle or anodizing depending on alloy, phenolic epoxy paint, 2 coats
Satellites	System A: dichromate
	System B: anodize
	System C: zinc immersion coating, flash copper plate, 9.1 μm (0.36 mil), silver 0.0025 μm (0.0001 mil), gold, 0.0025 μm (0.0001 mil)
General systems--indoor exposures	

System A	Phosphate pretreat, epoxy, vinyl, epoxy hybrid urethane, polyester, or acrylic finish coat 8-20 μm (0.3-0.8 mil)
System B	Light to medium anodize or chromate pretreat, epoxy or epoxy hybrid, 8-20 μm (0.3-0.8 mil)
System C	Electroplate, 25 μm (1 mil)
Systems for marine or similarly corrosive exposures	
System A	High purity alloy; phosphate pretreat, epoxy, vinyl, epoxy-hybrid, urethane, or polyester coating 12-25 μm (0.5-1.0 mil)
System B	Standard alloy; chrome pickle or light anodize, vinyl wash primer, vinyl or epoxy chromate primer, 2 coats, baked enamel 1 or 2 coats
System C	Standard alloy; anodize, penetrating epoxy sealer, 2-3 coats, epoxy chromate primer, 2 coats, lacquer or synthetic enamel 2 or more coats

Because of its high position in the electromotive series, magnesium is more susceptible than other common metals to galvanic corrosion. However, galvanic corrosion is possible only if bare magnesium is in electrical contact with another bare metal and if the surface of the two metals is bridged by a conductive aqueous electrolyte. Because in many applications such conditions are difficult to avoid, galvanic corrosion is controlled through the use of compatible metals (e.g. aluminum alloys 5052 or 6061, or zinc, cadmium, or tin electroplated coatings on steel fasteners). With dissimilar metal components assembled to magnesium parts, paint, plastic tape, organic sealants, or compatible metal shims, such as 5000 or 6000 series aluminum, are used to prevent direct electrolyte bridging of the components at the interface. (See the article "Corrosion of Magnesium and Magnesium Alloys" in *Corrosion*, Volume 13 of *ASM Handbook*, and Ref 7 and 8.)

Proper and adequate cleaning is an important prerequisite to the successful application of finishing systems to magnesium alloy products. Failure to follow suitable cleaning procedures causes future problems of corrosion and product degradation. Mechanical and chemical cleaning methods are used singly or in combination, depending on the specific application and product involved. Cleaning processes of either type require suitable control to ensure repetitive reliability.

Acknowledgements

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References

1. J.E. Hillis and R.W. Murray, "Finishing Alternatives for High Purity Magnesium Alloys," Paper No. G-T87-003, Society of Die Casting Engineers 14th Int. Congress and Exposition (Toronto), 1987
2. R.W. Murray and J.E. Hillis, "Powder Coatings on High Purity Die Casting Magnesium for Appearance and Protection," Paper No. T91-012, North American Die Casting Association Congress and Exposition (Detroit), 1991
3. K.N. Reichek, K.J. Clark, and J.E. Hillis, "Controlling the Salt Water Corrosion Performance of Magnesium AZ91 Alloy," Paper No. 850417, Society of Automotive Engineers (Detroit), 1985
4. J.E. Hillis and K.N. Reichek, "High Purity Magnesium AM60 Alloy: The Critical Contaminant Limits and the Salt Water Corrosion Performance," Paper No. 860288, Int. Congress and Exposition of the Society of Automotive Engineers (Detroit), 1986

5. K.J. Clark, AZ91E Magnesium Sand Casting Alloy, The Standard for Excellent Corrosion Performance, *Proc. Int. Magnesium Assoc.* (Los Angeles), 1986
6. Standards B 93 and B 80, Aluminum and Magnesium Alloys, Vol 02.02, *Annual Book of ASTM Standards,* ASTM, 1993
7. D.L. Hawke, "Galvanic Corrosion of Magnesium, " Paper No. G-T87-004, Society of Die Casting Engineers 14th Int. Die Casting Congress and Exposition (Toronto), 1987
8. D.L. Hawke, J.E. Hillis, and W. Unsworth, "Preventive Practice for Controlling the Galvanic Corrosion of Magnesium Alloys," technical brochure, International Magnesium Association, McLean, VA, 1988

Mechanical Cleaning

Mechanical cleaning of magnesium alloy products is accomplished by grinding and rough polishing, dry or wet abrasive blast cleaning, wire brushing, and wet barrel or bowl abrading (vibratory finishing).

Grinding and Rough Polishing. Grinding with belts, wheels, and rotary files is used for cleaning sand castings. Belt grinding, however, usually is used as a finishing operation for the removal of flash and surface imperfections from die castings, or of die marks and scratches from significant surfaces of extrusions. No great danger of surface contamination exists, and no special abrasive or belt backings are necessary.

The possibility of fire resulting from the polishing of magnesium may be virtually eliminated by following the recommendations set forth by the producers of magnesium. These recommendations are summarized in the section "Health and Safety" in this article.

Dry Abrasive Blast Cleaning. Sand blasting is the method of dry abrasive blast cleaning most frequently used on magnesium alloys. Many foundries use flint silica sand with a fineness of 25 or 35 AFS. Occasionally, however, steel grit is used. Usually, castings are blasted immediately after shakeout to reveal any major surface defects. After gates, sprues, and risers are sawed off and other operations are performed to prepare the castings for shipment, a final abrasive blast with sand or steel grit is given just before pickling. Under conventional operating conditions, the two types of abrasives yield equally satisfactory results; but if excessive blast pressure is used, steel grit is more likely to cause surface corrosion, because of the embedding of steel particles in the magnesium surface.

Dry blasting with any abrasive is followed by acid pickling to remove the harmful effects of blasting. Table 2 describes two pickling baths, aqueous solutions of sulfuric acid and of nitric and sulfuric acids, frequently used for this purpose, and indicates conditions for their use.

Table 2 Acid pickling treatments for magnesium alloys

Treatment	Principal applications	Metal removed		Solution						
				Constituents	Amount		Operating temperature		Immersion time, min	Tank material or lining
		µm	mils		g/L	oz/gal	°C	°F		
For cast or wrought alloys										
Chromic acid	Remove oxide, flux, corrosion products	None		CrO_3	180	24	21-100[a]	70-212[a]	1-15	Stainless steel, 1100 aluminum, lead
Ferric nitrate[b]	Bright finish; maximum corrosion	8	0.3	CrO_3	180	24	16-38	60-100	$\frac{1}{4}$-3	Type 316 stainless steel,

nitrate[b]	resistance of bare metal; finishing of die castings			$Fe(NO_3)_3·9H_2$	40.0	5.3		100		vinyl, polyethylene
				O	3.5	0.47				
				NaF						
Hydrofluoric acid	Active surface for chemical treatment	3	0.1	50% HF	230	31	21-32	70-90	$\frac{1}{2}$-5	Type 316 stainless steel, lead, rubber
Nitric acid	Prepickle for ferric nitrate treatment[c]	13-25	0.5-1.0	70% HNO_3	50	6.7	21-32	70-90	$\frac{1}{5}$ - $\frac{1}{2}$	Stainless steel
For wrought alloys only										
Acetic-nitrate	Remove mill scale; improve corrosion resistance of bare metal	13-25	0.5-1.0	CH_3COOH	192	25.6	21-27	70-80	$\frac{1}{2}$-1	3003 aluminum, ceramic, lead
				$NaNO_3$	50.0	6.7				
Glycolic-nitrate	Remove mill scale or surface oxides; improve corrosion resistance[d]	12-25	0.5-1.0	70%	230	31	16-49	60-120	$\frac{1}{2}$-1	Rubber
				$CH_2OHCOOH$	40	5.3				
					40	5.3				
				70% HNO_3						
				$NaNO_3$						
Chromic-nitrate	Remove mill scale, burned-on graphite; preclean for welding	13	0.5	CrO_3	180	24	21-32	70-90	3	Stainless steel, lead, rubber, vinyl
				$NaNO_3$	30	4				
Chromic sulfuric	Preclean for spot welding	8	0.3	CrO_3	180	24	21-32	70-90	3	Stainless steel, 1100 aluminum, ceramic, rubber
				96% H_2SO_4	0.4	0.05				
For cast alloys only										
Nitric sulfuric	Remove effects of blasting from sand	50	2.0	70% HNO_3	77.0	10.3	21-32	70-90	$\frac{1}{6}$ - $\frac{1}{4}$	Ceramic, rubber, glass

sulfuric	castings			96% H_2SO_4	20	2.7			$\frac{1}{6}$ - $\frac{1}{4}$	glass
Phosphoric acid										
Step 1	Remove surface segregation from die castings	13-25	0.5-1.0	85% H_3PO_4	425-866	57-116	21-27	70-80	10-15 s	Fiber-reinforced plastic, polyvinyl chloride, polyethylene
Step 2[e]				NaOH	80-120	11-16	21-27	70-80	30 s	Carbon steel
Sulfuric acid	Remove effects of blasting from sand castings	50	2.0	96% H_2SO_4	30	4	21-32	70-90	$\frac{1}{6}$ - $\frac{1}{4}$	Ceramic, rubber, lead, glass

(a) For removal of flux, solution must be 88 - 100 °C (190 - 212 °F).

(b) For most uniform appearance, die castings must be mechanically finished before being pickled, because the ferric nitrate solution accentuates flow marks and segregation on die-cast surfaces.

(c) Use of nitric acid prepickle increases solution life and decreases treatment time in ferric nitrate pickling.

(d) Nonvolatile glycolic acid reduces costs compared to acetic acid.

(e) No rinsing between steps

Wet abrasive blast cleaning of magnesium alloys is used for final finishing before electroplating, producing a matte surface before chemical treatments, removing carbonaceous or heavy corrosion products, and removing residual paint after stripping operations. Equipment, abrasives, and process controls are the same as those used for many other materials (see the article "Mechanical Cleaning Systems" in this Volume). Remove any contamination by acid pickling, using the sulfuric or nitric-sulfuric baths described in Table 2.

Barrel or Bowl Abrading. Magnesium die cast components are often cleaned of charred and uncharred die lubricants and other surface contaminants using wet barrel, or vibratory bowl, abrading in combination with detergents and surface treatment formulations. The ceramic media employed in these operations serve to both clean and smooth parts. It is important that a good flow of solution is continuously applied to the media in order to keep contaminants from accumulating and recontaminating part surfaces. Abrading is used as both a stand-alone finishing operation with high-purity alloy parts (see the section "Mechanical Finishing," below) and as a pretreatment/cleaning operation prior to painting parts used in applications such as chain saws, lawn and garden equipment, and power hand tools.

Wire Brushing. Magnesium alloy sheet is wire brushed for in-process cleaning and for the removal of oxides before arc or resistance welding. The wire-brushing machine should be adjusted as to the amount of pressure exerted on the sheet. The machine should be designed so that it does not gouge the sheet. The final surface smoothness depends also on the coarseness and composition of the wire. Safety precautions should be observed when wire brushing magnesium as indicated in the section "Health and Safety" in this article.

Chemical Cleaning

Chemical methods for cleaning magnesium alloys are vapor degreasing, solvent cleaning, emulsion cleaning, alkaline cleaning, and acid pickling.

Solvent cleaning and vapor degreasing are used to remove oils, forming lubricants, waxes, quenching oils, corrosion-protective oils, polishing and buffing compounds, and other soluble soils and contaminants. Solid particles such as machining dust or chips are removed by the washing action of the solvent as it dissolves the oil or grease that holds the metal fines to the part. These processes must be used before painting, plating, and chemical treatments, as well as before and after machining and forming.

The same methods, equipment, and solvents are used for magnesium as for other metals (see the article "Solvent Cold Cleaning and Vapor Degreasing" in this Volume). Trichloroethylene and perchloroethylene are the solvents most often used. Methylene chloride is effective in removing the excess organic-resin impregnants from the surface of the castings without removing the compound from the pores in the metal.

Emulsion cleaning may be used for the removal of oils and buffing compounds (see the article "Emulsion Cleaning" in this Volume). The emulsion cleaner should be neutral or alkaline, with a pH of 7.0 or above, so as not to etch magnesium surfaces. Emulsion cleaners incorporating water with the solvent should be tested before use to avoid possible attack or pitting of the metal.

Alkaline cleaning is the most frequently used method of cleaning magnesium alloys preparatory to painting, chemical treatments, or plating. Alkaline cleaners are also used to remove chromate films from magnesium.

Most magnesium alloys are not attacked by common alkalis except pyrophosphates and some polyphosphates, and even these alkalis do not appreciably attack magnesium alloys above a pH of 12.0. Nearly any heavy-duty alkaline cleaner suitable for low-carbon steel performs satisfactorily on magnesium alloys. The pH of alkaline cleaners for magnesium alloys should be 11.0 or higher.

Soak cleaners are usually based on alkali hydroxides, carbonates, phosphates, and silicates, preferably in combinations of two or more, and also contain natural resinates or synthetic surfactants as emulsifying agents. Soak cleaners are used in concentrations of 30 to 75 g/L (4 to 10 oz/gal) and at 71 to 100 °C (160 to 212 °F). Alkaline cleaners used for spray cleaning cannot use a surface-active wetting agent, because the foaming problem would be too great. In this case, the mechanical force of the spray helps dislodge soils.

Cathodic cleaning uses the work as the cathode in the cleaning solution at approximately 6 V dc. Anodic cleaning is not recommended because of the formation of undesirable oxide or hydroxide films. Pitting of the surface of the magnesium may also result from prolonged anodic cleaning.

A simple aqueous bath for soak or electrolytic cleaning of magnesium alloys is made and used as follows:

Trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$), g/L (oz/gal)	30 (4)
Sodium carbonate ($Na_2CO_3 \cdot 10H_2O$), g/L (oz/gal)	30 (4)
Wetting agent, g/L (oz/gal)	0.7 (0.1)
Operating temperature, °C (°F)	82-100 (180-212)

Immersion time, min	3-10

Another formula for soak or electrolytic cleaning, which can be used before electroplating, consists of the following:

Sodium carbonate ($Na_2CO_3 \cdot 10H_2O$), g/L (oz/gal)	22.5 (3)
Sodium hydroxide (NaOH), g/L (oz/gal)	15 (2)
Wetting agent, g/L (oz/gal)	0.7 (0.1)
Operating temperature, °C (°F)	82-100 (180-212)
Immersion time, min	3-10

When either of these baths is used as an electrolytic cleaner, parts are made the cathode at a current density of 1 to 5 A/dm^2 (10 to 50 A/ft^2) at 6 V dc. Many proprietary compounds are better cleaners than the above formulas.

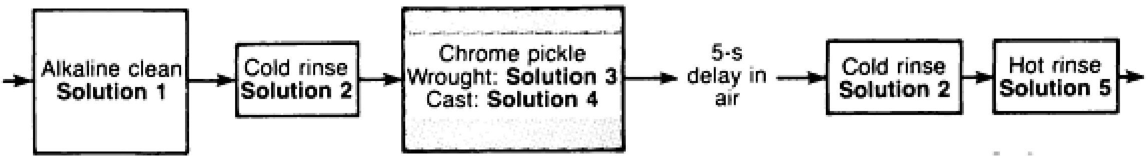
Hard-to-remove soils, such as graphitic lubricants used in the hot forming of magnesium alloy sheet products or in the fabrication of impact extrusions, can best be removed by soaking in the heavy-duty caustic cleaner:

Sodium hydroxide (NaOH), g/L (oz/gal)	98 (13)
Wetting agent, g/L (oz/gal)	0.7 (0.1)
Operating temperature, °C (°F)	87-100 (190-212)
Immersion time, min	10-20

A chromic acid pickle, as shown in Table 2, usually is used after cleaning in the above solution. Cleaners containing more than 2% NaOH attack ZK60A; therefore, the above solution should not be used on this alloy.

Acid pickling is required for removal of contamination that is tightly bound to the surface or insoluble in solvents or alkalis. These contaminants include natural oxide tarnish, embedded sand or iron, chromate coatings, welding residues, and burned-on lubricants.

In selecting an acid pickling treatment, consider the type of surface contamination to be removed, the type of magnesium alloy to be treated, and the dimensional loss allowable, as well as the desired surface appearance. Table 2 gives details of acid pickling treatments used for magnesium alloys. Confining these treatments to alloy types indicated avoids the formation of a powdery black smut on pickled surfaces.



Solution No.	Type of solution	Constituents	Amount, g/L (oz/gal)	Operating temperature, °C (°F)	Cycle time, min	Tank material
1	Alkaline cleaner	[a]	[a]	88-100 (190-212)	3-10	Low-carbon steel
2	Cold rinse	Water	. . .	Ambient	[b]	Low-carbon steel
3	Chrome pickle[c]	$Na_2Cr_2O_7 \cdot 2H_2O$ HNO_3 (sp gr 1.42) Water[d]	180 (24) 180 (24) bal	21-32 (70-90)	$\frac{1}{2}$-2[e]	[f]
4	Chrome pickle[g]	$Na_2Cr_2O_7 \cdot 2H_2O$ HNO_3 (sp gr 1.42) Na_2HF_2, KHF_2, or NH_4HF_2 Water[d]	180 (24) 120-180 (16-24) 15 (2.0) bal	21-32 (70-90) 49-60 (120-140)[h]	$\frac{1}{2}$-2[i]	Type 316 stainless steel[j]
6	Hot rinse	Water	. . .	71-82 (160-180)[k]	. . .	Low-carbon steel

(a) Type and strength of solution used governed by degree of surface contamination.

(b) Rinse thoroughly with adequate inflow of fresh water; agitate.

(c) For wrought materials, all alloys, not to be hot formed, and for wrought materials, all alloys, for which tolerances permit removal of approximately 15 μm (0.6 mil) of stock. When treatment is used on alloys M1A and ZK60A to provide paint base, use fresh solutions.

(d) Use water from steam condensate or water treated by ion exchange, when available, instead of well or hard tap water.

(e) For well-controlled bath, 1 min is standard.

(f) Tank material can be of stainless steel or low-carbon steel lined with glass, ceramic, synthetic rubber, or vinyl-based materials. Racks and baskets for use with Solution 3 may be stainless steel or Monel.

(g) For sand and permanent mold castings of all alloys for which tolerances permit stock removal of approximately 15 μm (0.6 mil); die castings, all alloys, of 3 to 8 μm (0.1 to 0.3 mil). Dip die castings for 15 to 30 s in water 71 to 82 °C (160 to 180 °F) before immersing in solution.

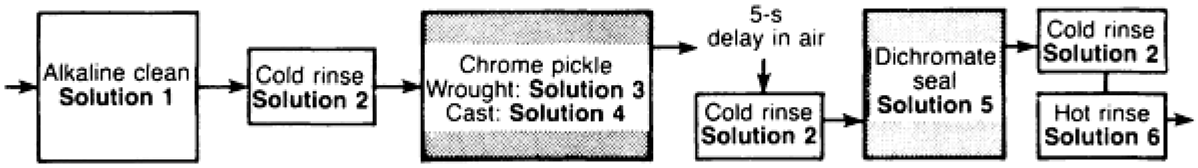
(h) For die castings.

(i) For well-controlled bath, 1 min is standard on all products except die castings. Immerse die castings only 10 s.

(j) Racks and baskets for use with Solution 4 can be type 316 stainless steel or phosphor bronze.

(k) Immerse long enough to heat parts sufficiently to facilitate rapid drying; keep rinse clean with inflowing fresh water.

Fig. 3 Chrome pickle treatment (chemical treatment No. 1; MIL-M-3171, type I). Applicable to all alloys and product forms. Used to provide a base for paint or short-time protection for shipment or storage



Solution No.	Type of solution	Constituents	Amount, g/L (oz/gal)	Operating temperature, °C (°F)	Cycle time, min	Tank material
1	Alkaline cleaner	[a]	[a]	88-100 (190-212)	3-10	Low-carbon steel
2	Cold rinse	Water	. . .	Ambient	[b]	Low-carbon steel
3	Chrome pickle[c]	$Na_2Cr_2O_7{\cdot}2H_2O$ HNO_3 (sp gr 1.42) Water[d]	180 (24) 180 (24) bal	21-32 (70-90)	$\frac{1}{2}$-2[e]	[f]
4	Chrome pickle[g]	$Na_2Cr_2O_7{\cdot}2H_2O$ HNO_3 (sp gr 1.42) $NaHF_2$, KHF_2, or NH_4HF_2 Water[d]	180 (24) 120-180 (16-24) 15 (2) bal	21-32 (70-90) 49-60 (120-140)[h]	$\frac{1}{2}$-2[i]	Type 316 stainless steel[j]
5	Dichromate seal	$Na_2Cr_2O_7{\cdot}2H_2O$ CaF_2 or MgF_2 Water[d]	120-180 (16-24) 2.47 (0.33) bal	99-100 (210-212) (boiling)	30	Low-carbon steel
6	Hot rinse	Water	. . .	71-82 (160-180)	[k]	Low-carbon steel

(a) Type and strength of solution used governed by degree of surface contamination.

(b) Rinse thoroughly with adequate inflow of fresh water; agitate.

(c) For wrought materials, all alloys, not to be hot formed, and for wrought materials, all alloys, for which tolerances permit removal of approximately 15 μm (0.6 mil) of stock. When treatment is used on alloys M1A and ZK60A to provide paint base, use fresh solutions.

(d) Use water from steam condensate or water treated by ion exchange, when available, instead of well or hard tap water.

(e) For well-controlled bath, 1 min is standard.

(f) Tank material can be of stainless steel or low-carbon steel lined with glass, ceramic, synthetic rubber, or vinyl-based materials. Racks and baskets for use with Solution 3 may be stainless steel or Monel.

(g) For sand and permanent mold castings of all alloys for which tolerances permit stock removal of approximately 15 μm (0.6 mil); die castings, all alloys, of 3 to 8 μm (0.1 to 0.3 mil). Dip die castings for 15 to 30 s in water 71 to 82 °C (160 to 180 °F) before immersing in solution.

(h) For die castings.

(i) For well-controlled bath, 1 min is standard on all products except die castings. Immerse die castings only 10 s.

(j) Racks and baskets for use with Solution 4 can be type 316 stainless steel or phosphor bronze.

(k) Immerse long enough to heat parts sufficiently to facilitate rapid drying; keep rinse clean with inflowing fresh water.

Fig. 4 Sealed chrome pickle treatment. Applicable to all alloys and product forms. Used as a substitute for dichromate coating or for more protection than is provided by the chrome pickle treatment

When a magnesium alloy product is used bare or with a clear finish, it is desirable to improve the corrosion resistance of the metal surface in addition to providing an attractive appearance. This can be accomplished by the use of ferric nitrate, acetic-nitrate, or phosphoric acid pickle (Table 2). The ferric nitrate pickle deposits an invisible chromium oxide film that passivates the surface and improves corrosion resistance. The acetic-nitrate and phosphoric acid pickles act as sequestering agents that effectively remove even invisible traces of other metals from the magnesium surface and thus prevent localized galvanic corrosion. Although all of these methods are effective in improving corrosion resistance, ferric nitrate and phosphoric acid pickles give best results.

Mechanical Finishing

Depending on required appearance, the most frequently used methods of mechanical finishing are barrel tumbling, polishing and buffing, vibratory finishing, fiber brushing, and shot blasting. Shot blasting with 0.10 to 0.25 mm (0.003 to 0.009 in.) glass spheres produces a satin finish. Plastic and chopped aluminum wire blasting media are also used. Sand or steel shot blasting should be excluded as means for producing a desired mechanical finish. If these media are used, heavy pickling (1 to 2 mils of metal removal) is required to restore corrosion resistance, and such pickling can seriously alter the mechanical finish produced. Surface contamination by plastic, chopped aluminum, or glass bead media is less damaging and the effects can be easily removed by subsequent mild etching treatments such as ferric nitrate pickling. Wet blasting

with glass beads or aluminum oxide is less contaminating than any dry blasting process. (See the article "Corrosion of Magnesium and Magnesium Alloys" in *Corrosion,* Volume 13 of *ASM Handbook,* and Ref 3, 5, and 9.)

Mass (Barrel) Finishing. The use of dry barrel finishing is usually limited to the production of a final finish on magnesium alloy parts that are small and relatively thin and for which metal removal must be held to a minimum. Wet barrel finishing is used for deburring, grinding, polishing, burnishing, and coloring. Procedures used in wet and dry barrel finishing are discussed in the article on mass finishing.

Vibratory finishing combines smoothing and brightening with cleaning to remove dirt, oxides, thin flash, and casting skin. Ceramic and other media are used depending on the surface condition of the part and the finish required. Acid additives etch magnesium surfaces and should never be used. Proper rinsing and drying are important.

Polishing and buffing are not used for final finishing, but for preparing magnesium alloy surfaces for other finishes, such as chemical treatments, anodizing, plating, or painting. As shown in Table 3, the procedures used to produce a highly polished or buffed surface on magnesium alloys are similar to those used for aluminum-base alloys. However, because most magnesium alloys are appreciably harder than aluminum alloys and tend to drag or tear to a lesser degree, it is unnecessary to use as much lubrication as is usually required with aluminum alloys. When polishing die castings, the metal removal is kept at a minimum to preserve the relatively thin nonporous outer layer of the casting.

Table 3 Procedures for polishing and buffing magnesium alloys

Operation	Abrasive grit size	Wheel				
		Type	Diam		Speed	
			mm	in.	m/s	sfm
Rough polishing[a]	60-100[b]	Canvas, felt, sheepskin	150-360	6-14	15.3-25.5	3000-5000
Medium polishing[c]	100-320[b]	Built-up cloth	150-360	6-14	20.4-30.6	4000-6000
Fine polishing	240-400	Cloth or sheepskin	250-360	10-14	22.9-38.2	4500-7500
Satin finishing[d]	50-320[e]	Full-disk buffs[f]	150-300	6-12	15.3-25.5	3000-5000
Buffing[g]	[h]	Cotton buffs	150-410	6-16	20.4-40.8	4000-8000

(a) For rough surfaces only, such as sand castings.

(b) Aluminum oxide or silicon carbide; grease stick may be used.

(c) For less severe surface condition and before buffing.

(d) For final finish or before plating.

(e) Greaseless compound.

(f) Loose or folded cotton cloth.

(g) A cutdown operation to produce a smooth finish with an intermediate degree of brightness.

(h) Tripoli or aluminum oxide buffing compound

Standard polishing wheels and abrasive belts are used to remove rough surfaces, parting lines, and other surface imperfections from magnesium alloy pieces. Aluminum oxide or silicon carbide abrasives are used, in grit sizes from 60 to 320, depending on the surface roughness and the final finish desired.

Particles of free iron or other heavy metals must not be used in abrasives for the polishing of magnesium alloys, because these metals, when embedded in the surface, can cause cell corrosion effects while parts are in storage or cause a pitting condition in pickling processes used before chemical treatments or electroplating.

Large castings require polishing of significant surfaces before buffing. Fine polishing belts are used on parts with little contour. Parts with more intricate contour are polished on setup wheels or on cloth wheels, using a greaseless compound. Grit sizes from 220 to 320 are most commonly used in polishing operations prior to buffing.

Satin finishing or flexible-wheel polishing is also used on magnesium alloys. This finish is produced by applying a greaseless compound to the surface of a clot wheel as it is slowly revolved. No lubricant is required.

Magnesium alloys can be buffed to a smooth, bright finish using aluminum oxide or tripoli compounds on a light-count sewed wheel. For color buffing, a dry lime compound may be used. Buffing compounds containing free iron or other heavy metal abrasives should not be used.

A ferric nitrate bright pickle, as shown in Table 2, is used on polished or buffed surfaces prior to the application of a clear organic coating. Using a ferric nitrate bright pickle produces a bright, passive surface that increases the adhesion and corrosion protection of the coating; it also serves to prevent blemishes such as spotting, blooming, and worm tracking in the coating after it has dried.

Precautions that must be exercised in the polishing and buffing of magnesium alloys are discussed in the section "Health and Safety" in this article.

References cited in this section

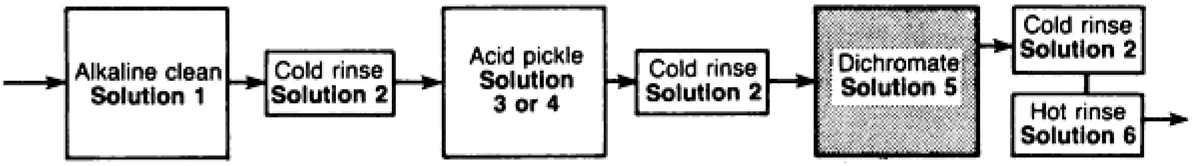
3. K.N. Reichek, K.J. Clark, and J.E. Hillis, "Controlling the Salt Water Corrosion Performance of Magnesium AZ91 Alloy," Paper No. 850417, Society of Automotive Engineers (Detroit), 1985
5. K.J. Clark, AZ91E Magnesium Sand Casting Alloy, The Standard for Excellent Corrosion Performance, *Proc. Int. Magnesium Assoc.* (Los Angeles), 1986
9. R.W. Murray and J.E. Hillis, "Magnesium Finishing: Chemical Treatment and Coating Practices," Technical Paper 900791, Society of Automotive Engineers Congress and Exposition (Detroit), 1990

Chemical Finishing Treatments

Chemical finishing treatments for magnesium alloys are used either to provide short-time protection against corrosion and abrasion during shipment and storage, or as pretreatments to additional finishing systems.

Figures 3, 4, 5, and 6 present flow charts of processing steps in four frequently used chemical treatments; tabular data accompanying each of these charts indicate operating conditions and applicability of the respective treatments. Note that the chrome pickle and sealed chrome pickle treatments cannot be used on close-tolerance machined parts unless tolerances will permit or allowances for metal removal have been made. The dichromate treatment (Fig. 5) involves no appreciable dimensional changes. Moreover, when a hydrofluoric-sulfuric acid pretreatment and brief exposure to the

chrome pickling solution are used, the modified chrome pickle treatment (Fig. 6) involves no appreciable dimensional changes.



Solution	Type of solution	Constituents	Amount, g/L (oz/gal)	Operating temperature, °C (°F)	Cycle time, min	Tank material
1	Alkaline cleaner	(a)	(a)	88-100 (190-212)	3-10	Low-carbon steel
2	Cold rinse	Water	. . .	Ambient	(b)	Low-carbon steel
3	Acid pickle(c)	60% HF water(d)	180 (24) bal	21-32 (70-90)	5(e)	Low-carbon steel(f)
4	Acid pickle(g)	$NaHF_2$, KHF_2, or water(d)	50 (6.7)	21-32 (70-90)	5	Low-carbon steel(f)
5	Dichromate	$Na_2Cr_2O_7 \cdot 2H_2O$ CaF_2 or MgF_2 water(d)	120-180 (16-24) 2.48 (0.33) bal	99-100 (210-212) (boiling)	30(h)	Low-carbon steel
6	Hot rinse	Water	. . .	71-82 (160-180)	(i)	Low-carbon steel

Note: Racks and baskets for use with all tank materials should be Monel, type 316 stainless steel, or phosphor bronze.

(a) Type and strength of solution used governed by degree of surface contamination.

(b) Rinse thoroughly with adequate inflow of fresh water; agitate.

(c) This bath may be used for all treatable alloys in all forms. This bath must be used for castings that have not been pickled after being sand blasted.

(d) Water from steam condensate or water treated by ion exchange should be used when available instead of well or hard tap water.

(e) For AZ31A and B, $\frac{1}{2}$ to 1 min.

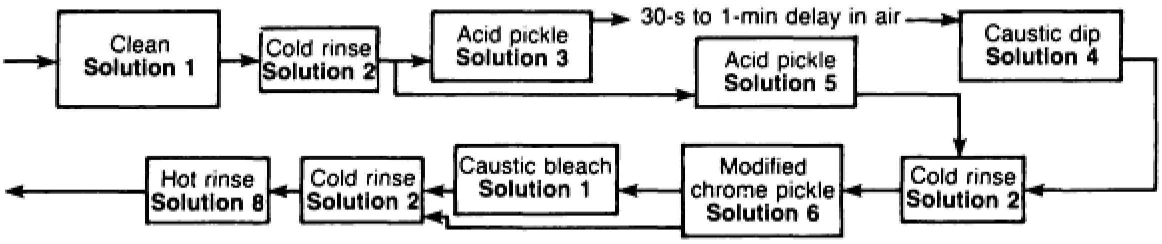
(f) Line tanks with lead or with natural or synthetic rubber.

(g) This pickle is preferred for AZ31B and C; an alternate pickle for wrought products and for castings that have been pickled after being sand blasted.

(h) For ZK60A. 15 min.

(i) Immerse long enough to heat parts sufficiently to facilitate rapid drying; keep rinse clean with inflowing fresh water.

Fig. 5 Dichromate treatment (chemical treatment No. 9; MIL-M-3171, Type III). Used for maximum corrosion protection and to provide a paint base. Results in no appreciable change in dimensions and can be used on finish-machined wrought and cast products of all alloys except EK30A, EK41A, HK31A, and M1A



Solution No.	Type of solution	Constituents	Amount, g/L (oz/gal)	Operating temperature, °C (°F)	Cycle time, min	Tank material
1	Cleaner[a]	$Na_4P_2O_7$ $Na_2B_4O_7 \cdot 10H_2O$ NaF Water[b]	30 (4) 68 (9) 8 (1) bal	77-82 (170-180)	2-5	Low-carbon steel
2	Cold rinse	Water	. . .	Ambient	[c]	Low-carbon steel
3	Acid pickle[d]	100% H_3PO_4 Water[b]	481-820 (65-110) bal	21-32 (70-90)	$\frac{1}{6}$ - $\frac{1}{4}$	Low-carbon steel[e]
4	Caustic dip	NaOH	50 (6.6)	21-82 (70-180)	$\frac{1}{2}$	Low-carbon steel

5	Acid pickle[f]	100% HF H_2SO_4 Water[b]	143-196 (20-25) 48 (6.4) bal	21-32 (70-90)	2-5	Low-carbon steel[e]
6	Modified chrome pickle[g]	$NaHF_2$ $NaCr_2O_7 \cdot 2H_2O$ $Al_2(SO_4) \cdot 14H_2O$ HNO_3 (sp gr 1.42) Water[b]	15 (2) 180 (24) 10 (1.3) 120 (16) bal	21-32 (70-90)	$\frac{1}{12}$-2	Type 316 stainless steel or low-carbon steel with vinyl
7	Caustic bleach[h]	NaOH, 5-10%	. . .	82-100 (180-212)[i]	$\frac{1}{2}$	Low-carbon steel
8	Hot rinse[j]	Water	. . .	71-82 (160-180)	[k]	Low-carbon steel

(a) Vapor degreasing, solvent washing, or conventional alkaline cleaning may be used instead of this special mild-etching cleaner. Metal removal in 5 min, 2.5 to 5.0 μm (0.1 to 0.2 mil).

(b) Use water from steam condensate or water treated by ion exchange, when available, instead of well or hard tap water.

(c) Rinse thoroughly with adequate inflow of fresh water; agitate.

(d) Acid pickle using this solution is preferred pretreatment if metal loss of 13 μm (0.5 mil) can be tolerated.

(e) Lined with rubber or vinyl.

(f) Alternative treatment; for use if metal loss of 13 μm (0.5 mil) is unacceptable.

(g) Metal removal rate, 1.2 μm (0.5 mil) per min.

(h) Optional; provides bright appearance.

(i) For castings; wrought products are best treated in a room-temperature solution.

(j) Oven drying, at temperatures not exceeding 150 °C (300 °F),may be substituted for hot water rinse.

(k) Immerse long enough to heat parts sufficiently to facilitate rapid drying; keep rinse clean.

Fig. 6 Modified chrome pickle treatment (chemical treatment No. 20). Used to provide a base for paint or for protection during shipment or storage. Provides a more uniform coating than chrome pickle treatment. Applicable to all alloys and product forms, particularly die castings, for which slight metal losses are acceptable

Traditionally chrome-free phosphates have not been recommended for use with magnesium components, however with the introduction of the new higher-purity die cast alloys (AZ91D, AM50A, AM60B, and AS41B; see Ref 10) a number of commercial phosphatizing treatments and simple phosphate formulations have been found to provide performance competitive with the best chromate-based surface treatments. These chrome-free treatments have been employed commercially with increasing frequency in finishing magnesium parts for a variety of markets including automotive, sporting goods, and power lawn equipment (Ref 1, 2, 9).

References cited in this section

1. J.E. Hillis and R.W. Murray, "Finishing Alternatives for High Purity Magnesium Alloys," Paper No. G-T87-003, Society of Die Casting Engineers 14th Int. Congress and Exposition (Toronto), 1987
2. R.W. Murray and J.E. Hillis, "Powder Coatings on High Purity Die Casting Magnesium for Appearance and Protection," Paper No. T91-012, North American Die Casting Association Congress and Exposition (Detroit), 1991
9. R.W. Murray and J.E. Hillis, "Magnesium Finishing: Chemical Treatment and Coating Practices," Technical Paper 900791, Society of Automotive Engineers Congress and Exposition (Detroit), 1990
10. Standards B93-94 and B94-94, Aluminum and Magnesium Alloys, Vol 02.02, *Annual Book of ASTM Standards*, ASTM, in press

Anodic Treatments

Of the many anodizing treatments developed for magnesium, only a few have achieved commercial significance. Chemical Treatment No. 9 (galvanic anodizing) is a low-voltage dc treatment that produces a thin black conversion coating, which is used mainly as a paint base. Chemical Treatment No. 17 and HAE treatment produce more substantial coatings (thicknesses of 5 to 30 μm) and are more widely used, primarily as bases for heavy-duty paint systems for rigorous service conditions, such as in military and aerospace applications. The heavier anodized coatings also provide significant resistance to abrasion. The Cr-22 treatment is a high-voltage process that is not currently used, but derivative proprietary processes are commercially available. Anodized coatings have varying degrees of porosity and must be sealed for use in severely corrosive salt environments. The coatings can be infused with various polymers to produce special properties such as lubricity.

Two proprietary chrome-free anodizing treatments have been introduced recently. Both have been demonstrated to provide excellent wear resistance, and when evaluated for a military application, one was found superior to both the HAE and No. 17 anodizing treatments in coated corrosion performance (Ref 11, 12, 13).

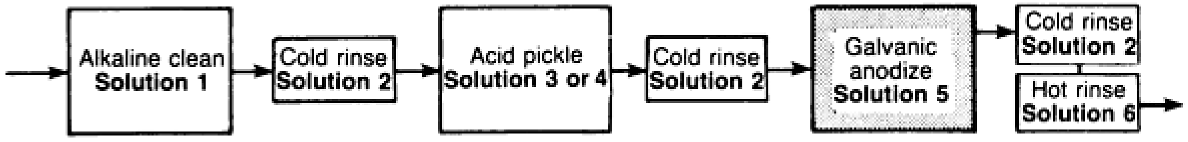
Surface Preparation. Before conversion coating, all surfaces must be scrupulously clean and free of contamination. Remove oil, grease, and other organic contaminants with suitable solvent cleaners, or with hot alkaline cleaning solutions such as those previously described in the section on chemical cleaning. Scales, oxides, burned-on drawing lubricants, and inorganic corrosion products should be removed in acid pickling solutions of prescribed composition and in accordance with the recommendations given in Table 2.

Parts that have been fabricated by stamping should be deburred to ensure that a coating is not applied to feathered edges that might break off and expose bare metal. Sharp edges and round corners should be made smooth before anodizing. Wherever close dimensional tolerances are entailed, adequate provision for buildup that results from coating should be made.

Chemical Treatment No. 9. A galvanic anodizing treatment in which a source of electric power is not required, Chemical Treatment No. 9 is applied to all forms and alloys of magnesium to produce a protective black coating with good paint-base characteristics. Parts with attachments of other metals may also be treated. Because this process does not result in appreciable dimensional change, the parts are machined to close tolerances before treatment.

Proper galvanic action requires the use of racks, made of stainless steel, Monel, or phosphor bronze. When the workpieces are immersed in the anodizing solution, they are made the anodes, and the tank, if made of low-carbon steel, acts as cathode. If the tank is equipped with a nonmetallic lining, separate steel cathodes must be used.

A processing diagram, together with details of solution compositions and operating conditions for Chemical Treatment No. 9, is presented in Fig. 7



Solution No.	Type of solution	Constituents	Amount, g/L (oz/gal)	Operating temperature, °C (°F)	Cycle time, min	Tank material
1	Alkaline cleaner	(a)	(a)	88-100 (190-212)	3-10	Low-carbon steel
2	Cold rinse	Water	. . .	Ambient	(b)	Low-carbon steel
3	Acid pickle(c)	60% HF Water(d)	180 (24) bal	21-32 (70-90)	5(e)	Low-carbon steel(f)
4	Acid pickle(g)	$NaHF_2$, KHF_2, or NH_4HF_2 Water(d)	50 (6.6) bal	21-32 (70-90)	5	Low-carbon steel(f)
5	Galvanic anodize(h)	$(NH_4)_2SO_4$ $Na_2Cr_2O_7 \cdot 2H_2O$ NH_4OH (sp gr 0.880) Water(d)	30 (4) 30 (4) 2.2 (0.3) bal	49-60 (120-140)	10-30(i)	(j)
6	Hot rinse	Water	. . .	71-82 (160-180)	(k)	Low-carbon steel

Note: Racks and baskets for use with all tank materials may be stainless steel, Monel, or phosphor bronze.

(a) Type and strength of solution governed by degree of surface contamination.

(b) Rinse thoroughly; agitate.

(c) May be used for all alloys in all forms; must be used for castings that have not been pickled after being sand blasted.

(d) Water from steam condensate or water treated by ion exchange should be used, when available, instead of well or hard tap water.

(e) For AZ31A and B, $\frac{1}{2}$ to 1 min.

(f) Lined with lead or with natural or synthetic rubber.

(g) An alternative pickle for wrought products and for castings that have been pickled after sand blasting; preferred for AZ31B and C.

(h) Current density should not exceed 1 A/dm^2 (10 A/ft^2); at least 753 A · min/m^2 (70 A · min/ft^2) is required for uniform coating.Maintain solution at pH 5.6 to 6.0 by adding solution containing 5% CrO_3 and concentrated H_2SO_4.

(i) Treat parts until a uniform black coating is obtained.

(j) If made of low-carbon steel, the tank acts as a cathode. If tank is made of or lined with nonmetallic material, use steel cathode plates.

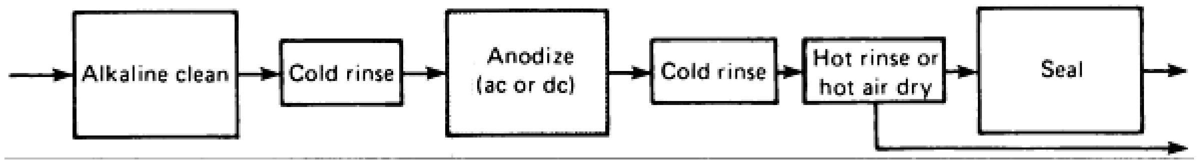
(k) Immerse long enough to sufficiently heat parts to facilitate rapid drying; keep rinse clean with adequate flow of fresh water.

Fig. 7 Chemical treatment No. 9 (MIL-M-3171A) galvanic anodizing

Chemical Treatment No. 17, which can be applied to all forms and alloys of magnesium, produces a two-phase, two-layer coating. A light green or greenish tan undercoating, about 5.0 μm (0.2 mil) thick, forms at lower voltages. This is covered by a much heavier, second-phase coating about 30.4 μm (1.2 mils) thick, vitreous, and dark green. The second-phase coating is relatively brittle and highly abrasion resistant. Formed at higher voltages, its corrosion resistance and paint-based properties are excellent. However, according to ASTM D 1732, the dark green, thick coating is preferable to the light green thin coating only when:

- Preliminary removal of surface contamination is not convenient.
- The highest degree of abrasion resistance is required from the coating.
- A dimensional increase of about 0.02 mm (0.001 in.) can be tolerated.
- The part is not to be subjected in service to severe impact, deformation, or flexing, which can cause spalling of the coating.

Details of solution compositions and operating conditions for this treatment are given in Fig. 8, which also shows a flow diagram of the processing steps.



Operating conditions	Alternating current treatment	Direct current treatment
For coatings of both colors and thicknesses		

Composition of aqueous anodizing solution[a]:		
NH_4HF_2, g/L (oz/gal)	240 (32)	360 (48)
$Na_2Cr_2O_7 \cdot 2H_2O$, g/L (oz/gal)	100 (13.3)	100 (13.3)
85% H_3PO_4, mL/L (fl oz/gal)	90 (12)	90 (12)
Operating temperature[b], °C (°F)	71-82 (160-180)	71-82 (160-180)
Current density, A/dm^2 (A/ft^2)	0.5-5 (5-50)	0.5-5 (5-50)
For light green coating, thin[c]		
Current consumption[d], $A \cdot min/m^2$ ($A \cdot min/ft^2$)	860-1075 (80-100)	540-645 (50-60)
Terminating voltage[d], V	75	75
Treatment time[d], min	4-5	$2\frac{1}{2}$-3
For dark green coating, thick[e]		
Current consumption[d], $A \cdot min/m^2$ ($A \cdot min/ft^2$)	4950 (460)	3230 (300)
Terminating voltage[d], V	100	100
Treatment time[d], min	23[f]	15[f]
Sealing post-treatment[g]		
Aqueous solution, sodium tetrasilicate ($Na_2Si_4O_9$), g/L (oz/gal)	53 (7)	
Temperature, °C (°F)	93-100 (200-212)	
Immersion time, min	15	

(a) Use water from steam condensate or water treated by ion exchange, when available, instead of well or hard tap water.

(b) Solution will not operate below 60 °C (140 °F). It may be operated up to the boiling point without adversely affecting results.

(c) Formed in first phase of treatment. Usual thickness, 5.0 μm (0.2 mil); range, 2.5 to 7.5 μm (0.1 to 0.3 mil).

(d) Terminating voltage and treatment time vary, but the number of ampere minutes per unit area remains constant for any one alloy.

(e) Formed in second phase of treatment. Usual thickness 30.4 μm (1.2 mils); range, 23 to 38.1 μm (0.9 to 1.5 mils).

(f) A denser coating is produced by maintaining the voltage, allowing the current to decrease for 20 min (ac) or 15 min (dc) after the indicated minimum amperage per square metre (foot) has been applied.

(g) Optional; to increase corrosion resistance, apply to parts not to receive organic finishes. Immerse in solution,rinse parts in cold, then in hot, water. Air dry.

Fig. 8 Chemical treatment No. 17 (MIL-M-45202) anodizing treatment. Conditions for cleaning and rinsing same as for galvanic anodizing treatment

Bath Preparation. Half the amount of water required should be heated to 71 °C (160 °F), then slowly add ammonium acid fluoride. Add other chemicals and the remainder of the water. The solution should be heated to 82 °C (180 °F), and stirred vigorously for 5 to 10 min. Reheating to 82 °C (180 °F) and stirring should be repeated each time the solution cools to room temperature.

Bath Replenishment. Rise of terminating voltage indicates depletion of bath. Usually, an adjustment in bath composition is required after about 0.5 m^2/L (20 ft^2/gal) of bath has been treated. The amounts of ingredients added are determined by standard methods of chemical analysis of the depleted solution.

Equipment. The anodizing tank and heating coils usually are made of low-carbon steel. However, tanks lined with synthetic rubber or a vinyl-based material may be used, provided the cathodes are of low-carbon steel and a sufficient distance is allowed between the work and the sides of the tank to prevent contact and burning.

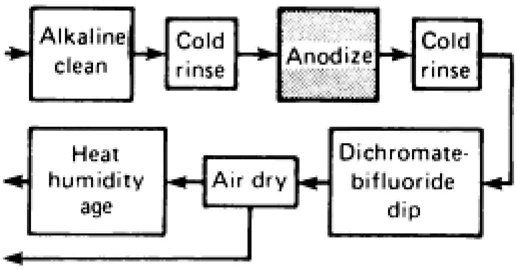
Most racks are made of magnesium alloys, and the coating formed on these racks during anodizing can be stripped in an aqueous solution containing 20% chromic acid. Aluminum alloys 5052, 5056, and 220 are also acceptable rack materials, but to avoid chemical attack, these alloys must not be immersed in the solution on open circuit.

Motor generators may be used to supply power for either alternating-current or direct-current installations. Rectifiers are suitable for supplying direct current only. A saturable reactor may be used to generate alternating current.

HAE treatment also produces a two-phase coating and is applied to all forms and alloys of magnesium, provided they contain no attachments or inserts of other metals. A light tan subcoating, about 5.0 μm (0.2 mil) thick, is produced at lower voltages. The thicker phase, formed at higher voltages, is normally dark brown in color and usually about 30 μm (1.2 mil) thick. Both phases have excellent paint-based characteristics.

The dark brown coating is hard and exhibits exceptionally good abrasion resistance, but it spalls under compressive deformation and can adversely affect the fatigue strength of a base metal less than about 2.5 mm (0.1 in.) thick. The subcoating has no effect on fatigue strength and does not spall.

Solution compositions and operating conditions for the HAE treatment are given in the table that accompanies the flow chart for the process in Fig. 9. The dichromate-bifluoride post-treatment that is part of the HAE treatment, as shown in Fig. 9, provides the coating with high resistance to corrosion.



Anodizing[(a)]	
Composition of solution, g/L (oz/gal):	
Potassium hydroxide (KOH)	165 (22)
Aluminum hydroxide ($Al(OH)_3$)	34 (4.5)[(b)]
Potassium fluoride (K_2F_2)	34 (4.5)
Trisodium phosphate (Na_3PO_4)	34 (4.5)
Potassium manganate (K_2MnO_4)[(c)]	19 (2.5)
Water	bal to 3.7 L (to 1 gal)
Operating temperature, °C (°F)	Room temperature to 25 (to 77)
Current density, A/dm^2 (A/ft^2)	1.5-2.5 (15-25)
Terminating voltage, V:	
First-phase coating	65-70
Second-phase coating	80-90
Treatment time[(d)], min:	
First-phase coating	7-10
Second-phase coating	60

Dichromate-bifluoride dip	
Composition of solution, g/L (oz/gal):	
Sodium dichromate, ($Na_2Cr_2O_7 \cdot 2H_2O$)	20 (2.7)
Ammonium bifluoride (NH_4HF_2)	100 (13.3)
Water	bal to 3.7 L (to 1 gal)
Operating temperature, °C (°F)	21-32 (70-90)
Immersion time, min	1
Heat-humidity aging[(e)]	
Temperature, °C (°F)	77-85 (170-185)
Relative humidity, %	~85
Time, h	7-15

(a) Acid pickling is not required before anodizing because of the chemical action of the anodizing bath on the alkaline-cleaned surface. Use alternating current for anodizing. Coatings are deposited in two phases: first a light tan coating 5.0 μm (0.2 mil) thick, then a dark brown coating usually 30.4 μm (1.2 mils) thick.

(b) For an exceptionally hard, abrasion resistant, dark brown coating, use 45 to 53 g/L (6 to 7 oz/gal) $Al(OH)_3$.

(c) An equal weight of potassium permanganate ($KMnO_4$) may be used instead of potassium manganate; dissolve the permanganate completely in water before adding to the solution; an additional 43 g (1.5 oz) of potassium hydroxide must also be added.

(d) Treatment time varies with current density. Increasing current density decreases treatment time; for uniform coating, 2 A/dm^2 (20 A/ft^2) is recommended.

(e) Improves corrosion resistance of coated parts

Fig. 9 HAE anodizing treatment (MIL-C-13335, amendment 1; MIL-M-45202). Conditions for cleaning and rinsing same as for galvanic anodizing treatment

Bath Preparation. As the first step in preparing the HAE solution, the anhydrous potassium fluoride and trisodium phosphate are dissolved in about half the amount of water required. To this is added an aqueous solution of potassium hydroxide in which aluminum hydroxide has been dissolved. It is difficult to dissolve commercially obtained aluminum

hydroxide in a potassium hydroxide solution at room temperature, but it can be dissolved by boiling it in the potassium hydroxide solution for 15 to 20 min.

Metallic aluminum may be dissolved in potassium hydroxide in place of aluminum hydroxide. The reaction, which should be performed under an exhaust hood or in a well-ventilated location, forms a clear liquid and black residue; only the clear liquid is added to the main solution.

Either potassium manganate or potassium permanganate, which is unstable in alkaline solutions and converts to the manganate, is added last. Conversion of the permanganate is evidenced by a color change from purple to green. Conversion can be accelerated by dissolving the permanganate in boiling water and then adding this solution to the bath, or by adding it to the potassium hydroxide solution and boiling. Finally, water is added to make the required volume of solution; continuous agitation is necessary to put all ingredients into solution.

Bath Replenishment. Expensive analyses are not required for maintaining the bath, because depletion of the manganese compound is indicated by a lightening of the characteristic dark brown color of the coating and serves as a bath control. It should be noted, however, that coatings of the lighter brown color have the same properties as those of dark brown color. To maintain the dark brown color of the coating, bath adjustments should be made after about 0.4 m^2/L (15 ft^2/gal) of bath has been treated.

To replenish, 3.7 to 7.5 g/L (0.5 to 1 oz/gal) of potassium manganate or permanganate is added while the bath is being constantly agitated. Additions of aluminum are made at 15 to 20% of the original quantities or aluminum hydroxide (11 g/L, or $1\frac{1}{2}$ oz/gal to solution) as previously described. The fluoride and phosphate ingredients deplete at a very slow rate and may be added at six-month intervals if the bath is used continually at the rate of 15 to 20% of original quantities.

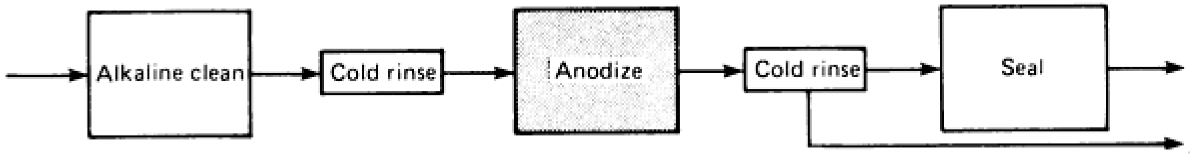
Post-Treatment. After anodizing, parts are rinsed thoroughly in water and immersed for 1 min in an aqueous solution containing 77 g (2.7 oz) of sodium dichromate and 377 g (13.3 oz) of ammonium bifluoride per 3.7 L (1 gal) of water. To dry parts, hot air may be used, without rinsing, and parts may be aged in an oven for 7 to 15 h. Aging at about 79 °C (175 °F) and about 85% relative humidity greatly improves the corrosion-protective quality of the coating. Heating of parts, particularly those with thick wall sections, should be done at low humidity until the surface is hot, after which aging is continued at higher humidity.

Equipment. The anodizing tank of double-welded construction and cooling plates or coils are made of black iron. Racks should be of magnesium alloy and should be protected by a suitable vinyl tape at solution level. Steel clamps can be used to clamp the racks to busbars. Galvanized iron, brass, bronze, tin, zinc, and rubber should not be used for equipment that comes in contact with the bath.

Alternating current at 60 Hz is supplied from a constant current regulator capable of delivering the required current over a range of 0 to 110 V.

The post-treatment dip tank must be lined with polyethylene or similar inert material. An oven or humidity cabinet, capable of maintaining temperatures to 86 °C (185 °F) and humidity to 85%, is used for aging.

Cr-22 Treatment. A flow chart of processing steps for the Cr-22 treatment is presented in Fig. 10, together with a table listing bath compositions and operating conditions. The green and black coatings obtainable by varying solution composition, operating temperature, and current density may be applied to all alloys, and although intended primarily as bases for organic finishes, these coatings provide excellent corrosion resistance to unpainted parts when sealed as described in Fig. 10. Inclusions or residual stresses in the magnesium surface occasionally result in the appearance of small nodules in the Cr-22 coating, but the presence of these nodules has no apparent effect on the corrosion protection provided by the coating. Heavier coatings produced by the Cr-22 treatment, like those produced by Chemical Treatment No. 17 and HAE treatments, spall under compressive deformation.



Operating conditions	Type of coating	
	Green[(a)]	**Black**[(b)]
Composition of anodizing solution:		
CrO_3, g/L (oz/gal)	25 (3.3)	50 (6.7)
50% HF (sp gr, 1.20), mL/L (fl oz/gal)	36 (4.7)	35 (4.7)
85% H_3PO_4 (sp gr, 1.70), mL/L (fl oz/gal)	50 (6.7)	50 (6.7)
NH_4OH (sp gr, 0.90), mL/L (fl oz/gal)	220 (29)	220 (28)
Water[(c)]	bal	bal
Operating temperature, °C (°F)	88-91 (190-195)[(d)]	85 (185)[(d)]
Current density	1.5 (15)[(e)]	2.5 (25)[(f)]
Terminating voltage, V		
For normal thickness	320	320
For heavy coatings	350-380	350-380
Treatment time, min	12-15	12-15
Sealing post-treatment[(g)]		
Solution, vol% sodium silicate (42° Bé)	10	
Temperature, °C (°F)	85-100 (185-212)	
Immersion time, min	2	

(a) Green coating, conforming to MIL-M-45202, type II, class B, ranges in thicknesses from 10 to 28 μm (0.4 to 1.1 mil); usual thickness, 20 μm (0.8 mil).

(b) Black coating, conforming to MIL-M-45202; type II, class C, ranges in thickness from 5 to 25 μm (0.2 to 1.0 mil); usual thickness, 13 μm (0.5 mil).

(c) Use water from steam condensate or water treated by ion exchange, when available, instead of well or hard tap water.

(d) Recommended; effective range, 74 to 93 °C (165 to 200 °F).

(e) Recommended; effective range, 1.0 to 3.0 A/dm^2 (10 to 30 A/ft^2).

(f) Recommended; effective range, 2.0 to 3.0 A/dm^2 (20 to 30 A/ft^2).

(g) Optional for both types; to increase corrosion resistance, apply to parts not to receive organic finishes

Fig. 10 Cr-22 (MIL-M-45202) anodizing treatment. Conditions for cleaning and rinsing same as for galvanic anodizing treatment

Bath Preparation. To half the required volume of water, the constituents of the bath are added in the order listed in Fig. 10, stirring continuously. When the chemicals are completely dissolved, water is added to bring the bath to the required volume, then sufficient ammonium hydroxide is added to raise the pH to 8.

Bath replenishment can be affected by adding the initial preparation chemicals in quantities determined by conventional chemical analyses for ammonia, phosphorus, fluorine, and hexavalent chromium. Replenishment after the anodizing of 0.6 m^2/L (30 ft^2/gal) of electrolyte, at 1.5 A/dm^2 (15 A/ft^2), has been found satisfactory. To minimize vapor losses at the high operating temperature of Cr-22 baths, polyethylene floats are used to cover bath surfaces.

Equipment. Tanks and heating coils should be made of low-carbon steel. Do not use copper, brass, or zinc for equipment that will come into contact with the bath. Racks should be made of magnesium alloys, and as in all anodizing treatments, electrical contact points should be clean and firm.

The power supply should be capable of delivering a current of 1.5 A/dm^2 (15 A/ft^2) of work area at a maximum of 350 V (60 cycles/s, alternating current).

Repair of Damaged Anodic Coatings. Touch-up procedures depend on the nature and extent of damage. Minor damage, scratches, or very small areas where magnesium metal is exposed can be treated as follows:

1. Clean damaged area with organic solvent.
2. Brush with chrome pickle solution (Fig. 3, solution 4); or with a solution containing 9.7 g/L (1.3 oz/gal) of chromic acid with water and 28 g (1 oz) of calcium sulfate, added in that order and stirred vigorously for 15 min.
3. Apply suitable primer and finish paint coat after thoroughly rinsing and drying.

Larger areas, several square inches, can be reanodized without removing the old coating, or the old coating can be stripped in a 20% solution of chromic acid and the entire part reanodized.

References cited in this section

11. D.E. Bartak, T.D. Schleisman, and E.R. Woolsey, "Electrodeposition and Characteristics of a Silicon Oxide Coating for Magnesium Alloys," Paper T91-041, North American Die Casting Association Congress and Exposition (Detroit), 1991
12. C. Jurey, Magoxid-Coat, A Hard Anodic Coating for Magnesium, *Proc. Int. Magnesium Association* (Washington, DC), 1993
13. J.H. Hawkins, Assessment of Protective Finishing Systems for Magnesium, *Proc. Int. Magnesium Association* (Washington, DC), 1993

Process Control of Chemical and Anodic Treatments

To achieve desired results with any acid pickle, chemical, or anodic treatment, proper control of temperature and concentration must be maintained. In these treatments, solution temperature governs the rate of metal removal or of film formation. Acid pickles and chemical treatments are conventionally formulated to be used at room temperature to avoid the expense of heating or cooling. Elevated temperatures are required only when chemical action is too slow at ambient temperature, as in alkaline cleaning, chromic acid pickling, and anodizing.

The rate of metal removal by acid pickling also increases with acid concentration. Solutions are usually formulated so that the pickling rate is fast enough to be economical, but not so fast that metal removal is difficult to control or that localized pitting results. As the bath is used, magnesium is dissolved and acid is consumed. Concentrated acid must be added periodically to replenish what is consumed and to maintain the solution within recommended composition limits. As the magnesium content of the solution increases, the pickling rate becomes slower, and eventually the rate becomes too slow, no matter how high the acid content. Chemical treatments cause staining when the magnesium content of solutions used is too high. These conditions can be avoided by discarding solution when its magnesium content reaches about 30 g/L (4 oz/gal).

When only one acid is present in a pickling solution, its concentration may be determined analytically by titration with standard sodium hydroxide solution. Magnesium content can be determined rapidly with atomic absorption spectroscopy or a flame photometer. Other components of the chemical baths can be determined by standard analytical procedures. In the absence of analytical facilities, it is necessary to fortify pickling solutions periodically to maintain the desired reaction rate; solutions for chemical treatment may be maintained by periodically replacing one-fourth of the volume with fresh solution.

Table 4 summarizes process control for various acid pickling, chemical, and anodic treatments and indicates the unfavorable effects that result when operating variables are above or below recommended ranges.

Table 4 Effects of lack of control of process variables in acid pickling, chemical, and anodic treatments

Treatment	Solution constituent or condition	Recommended range	Effect of operating out of recommended range	
			Too low	Too high
Acid pickling treatments				
Acetic-nitrate	Glacial acetic acid	115-300 g/L (15-40 oz/gal)	Slow rate	Uneconomical
	Sodium nitrate	30.0-75 g/L (4-10 oz/gal)	Smut	Slow rate
Chromic acid	Chromic acid	115-375 g/L (15-50 oz/gal)	Slow rate	Uneconomical

Chromic-sulfuric	Chromic acid	150.4-240.6 g/L (20-32 oz/gal)	Unknown[(a)]	Unknown[(a)]
	96% sulfuric acid	0.37-0.60 g/L (0.05-0.08 oz/gal)	Unknown[(a)]	Unknown[(a)]
	pH	0.4-1.0	Unknown[(a)]	Unknown[(a)]
Ferric nitrate[(b)]	Chromic acid	150.4-225 g/L (20-30 oz/gal)	Rapid rate; yellow stain	Slow rate
	Ferric nitrate	22.5-45.1 g/L (3-6 oz/gal)	Slow rate; rough or frosted	Rapid rate; yellow stain
	Sodium fluoride	2.2-6.7 g/L (0.3-0.9 oz/gal)	Slow rate; smut; rough or frosted appearance	Rapid rate; yellow or gray film
Glycolic-nitrate	70% glycolic acid	115-375 g/L (15-50 oz/gal)	Poor corrosion resistance	Uneconomical
	70% nitric acid	22.5-90.2 g/L (3-12 oz/gal)	Slow rate	Rapid rate
	Sodium nitrate	30.0-75.2 g/L (4-10 oz/gal)	Smut	Slow rate
Hydrofluoric acid	50% hydrofluoric acid	190-565 g/L (25-75 oz/gal)	Powdery dichromate treatment; incomplete MgF_2 film	Uneconomical
Nitric acid	70% nitric acid	30.0-75.2 g/L (4-10 oz/gal)	Slow rate	Rapid rate; rough surface
Nitric-sulfuric	70% nitric acid	30.0-90.2 g/L (4-12 oz/gal)	Smut	Rapid rate
	96% sulfuric acid	9.5-30.0 g/L (1.3-4 oz/gal)	Slow rate	Rapid rate
Phosphoric acid[(c)]	85% phosphoric acid	865-965 g/L (115-128 oz/gal)	Rapid rate	. . .
Sulfuric acid	96% sulfuric acid	15.0-45.1 g/L (2-6 oz/gal)	Slow rate	Rapid rate; rough surface
Chemical treatments				

Chrome pickle and sealed chrome pickle	Sodium dichromate	135.3-205 g/L (18-27 oz/gal)	Powdery coating	Shallow etch
	70% nitric acid	60.1-180.4 g/L (8-24 oz/gal)	Shallow etch	Powdery coating
	Temperature	21-49 °C (70-120 °F)	Shallow etch	Powdery coating
	Magnesium	30.0 g/L max (4 oz/gal max)	. . .	Shallow etch
	Prerinse delay in air	5 s max[d]	. . .	Powdery coating
Dichromate	Sodium dichromate	120-205 g/L (16-27 oz/gal)[e]	Nonuniform or no coating	Uneconomical
	Calcium fluoride		Powdery coating	No problem
	Free fluoride	0.2% max	. . .	No coating[f]
	pH[g]	4.1-5.5	Heavy or powdery coating	Nonuniform or no coating
	Temperature	93-100 °C (200-212 °F)	No coating	. . .
Modified chrome pickle[h]	Sodium acid fluoride	11.2-15.0 g/L (1.5-2 oz/gal)	Powdery smut	Powdery coating
	Sodium dichromate	135.3-205.0 g/L (18-27 oz/gal)	Pale color; too reactive	Slow rate
	Aluminum sulfate	7.5-11.2 g/L (1.0-1.5 oz/gal)[i]	Poor coating color on castings	Rapid rate; poor etch
	70% nitric acid	22.5-120.3 g/L (3-16 oz/gal)	Poor etch; slow rate	Pale color; poor etch
	Temperature	21-38 °C (70-100 °F)	Slow rate	Too reactive
Anodic treatments				
Chemical Treatment No. 9	Ammonium sulfate	16.5-24.0 g/L (2.2-3.2 oz/gal)[j]	Slow rate	Powdery coating
	Sodium dichromate	16.5-24.0 g/L (2.2-3.2	Thin coating	Slow rate

		oz/gal)[k]		
	pH[l]	5.6-6.0	Powdery coating	Slow rate
	Temperature	49-60 °C (120-140 °F)	Slow rate	Rapid rate
Chemical Treatment No. 17	Ammonium acid fluoride[m]	300.8-451.2 g/L[n] (40-60 oz/gal)	Local pitting	Insoluble
	Sodium dichromate[m]	53-120 g/L (7-16 oz/gal)	Thin coating	Uneconomical
	85% phosphoric acid[m]	53-105.2 g/L (7-14 oz/gal)	Soft coating	Uneconomical
	Chloride contamination	3% max	. . .	Soft coating
	Current density	0.5-5 A/dm^2 (5-50 A/ft^2)	Attack at liquid level	Pitting or burning
	Temperature	71-82 °C (160-180 °F)	No coating	No problem
HAE	Potassium hydroxide	105-190 g/L (14-25 oz/gal)	Pitting; burning; nonuniformity	Pitting; burning; roughness
	Potassium fluoride[o]	15.0-150.4 g/L (2-20 oz/gal)	Spottiness; nonuniformity	Uneconomical
	Trisodium phosphate[p]	15.0-225.6 g/L (2-30 oz/gal)	Light and dark areas	Uneconomical
	Aluminum hydroxide[p]	7.5-53 g/L (1-7 oz/gal)[q]	Coating hardness lowered	Hard, rough coating
	Potassium manganate	3.7-22.5 g/L (0.5-3 oz/gal)	Light brown coating	Dark brown, rough coating
	Current density	0.5-5 A/dm^2 (5-50 A/ft^2)	Slow rate	Nonuniformity in recesses[r]
	Temperature	25-38 °C (77-100 °F)[s]	. . .	Lower corrosion resistance
Cr-22	Chromic acid[t]	22.5-30.0 g/L (3-4 oz/gal)	Nonuniform or pale coating	Dark coating

	50% hydrofluoric acid[t]	30.0-53 g/L (4-7 oz/gal)	Low voltage, nonuniform coating	Pale coating
	85% phosphoric acid[t]	45.1-90.2 g/L (6-12 oz/gal)	Nonuniform coating	Uneconomical; rough coating
	pH[u]	6.0-6.5	. . .	Uneconomical
	Current density	1.0-3.0 A/dm^2 (10-30 A/ft^2)	Slow rate	Dark coating
	Temperature	74-93 °C (165-200 °F)	Slower corrosion resistance	. . .

(a) Effects of operation outside recommended ranges are not known. Depletion of solution is indicated by the formation of a brassy film and by a pH in excess of 1.0; at this point, add chromic and sulfuric acids, or discard solution.

(b) Discard solution when depleted or periodically add one fourth of volume of solution.

(c) Dragout loss prevents excessive salt buildup.

(d) Do not allow surface to dry out before rinsing.

(e) Limited solubility regulates fluoride.

(f) Add 0.2% calcium chromate if fluoride is too high.

(g) Correct pH with additions of sodium hydroxide or chromic acid.

(h) Fortify bath by additions of sodium dichromate to restore original concentration of 180.4 g/L (24 oz/gal) of nitric acid to maintain concentration of used bath at 60 g/L (8 oz/gal) and of 28 g (1 oz) of sodium acid fluoride for every 310 g (11 oz) of nitric acid added. Bath is considered depleted when concentration of nitric acid is below 22.5 g/L (3 oz/gal) and is indicated by poor color and nonuniformity of coating.

(i) For fresh bath; no additions required when fortifying.

(j) As H_2SO_4.

(k) As CrO_3.

(l) Control of pH achieved by additions of a solution containing, by weight, 5% CrO_3 and 5% H_2SO_4 (concentrated).

(m) Fortify after preparing 0.4 m^2/L (20 ft^2/gal) of solution.

(n) Local pitting begins at 1020 g (36 oz), particularly with thorium-containing alloys.

(o) Anhydrous.

(p) Fortify after treating 0.3 m^2/L (15 ft^2/gal) of solution to maintain dark brown color of coating.

(q) 2.2 to 15.0 g/L (0.3 to 2 oz/gal) as Al.

(r) Use 1.5 A/dm^2 (15 A/ft^2) for uniformity of coating in recesses.

(s) Ideal temperature, 27 °C (80 °F); 38 °C (100 °F) is satisfactory for alloys containing aluminum.

(t) Fortify after treating 0.7 m^2/L (36 ft^2/gal) to maintain deposition rate.

(u) Control of pH achieved by adding 28% solution of ammonium hydroxide

In-Process Corrosion. During periods of high humidity, magnesium parts in process often exhibit corrosion products, even though protected with a chrome pickle. This is especially true of sand castings. The corrosion products are readily removed by treating the parts in a boiling dichromate solution as shown in Fig. 5. The parts are then protected from further corrosion by slushing oil.

Difficulties with Chemical and Anodic Treatments

Difficulties experienced with chemical and anodic treatments result from the lack of control of processing variables. One difficulty common to all treatments, chemical or anodic, is nonuniformity of coating or actual failure to coat on certain areas of a part. This is most likely to occur on complex parts and is caused by the entrapment of air in pockets or blind holes. The remedy is to agitate parts when first placing them in the bath and to reposition them periodically to make sure the bath is brought into contact with all areas.

Other difficulties and their corrections vary for each chemical or anodic treatment. Tables 5, 6, and 7 describe the usual appearance of coatings produced by the chrome pickle, sealed chrome pickle, dichromate, Chemical Treatment No. 9, Chemical Treatment No. 17, and HAE treatments, and list common difficulties, as evidenced by deviations from usual coating appearance, together with causes of these difficulties and procedures to be followed for their correction.

Table 5 Causes and corrections of difficulties with coatings produced by the chrome pickle and sealed chrome pickle treatments

Normal appearance of coating, matte gray to yellow red iridescent

Difficulty	Cause	Corrective procedure
Pale color, shallow etch, slow reaction of solution with metal	Depletion of the chrome pickle bath. Paleness of color should not be confused with the lack of color from insufficient exposure to air during transfer to rinse	Revivify bath by additions of nitric acid and sodium dichromate to restore to proper operating level. Control bath by periodic chemical analysis of ingredients

Bright, brassy--smooth surface with occasional pits[a]	Excess of nitric acid in the bath	Adjust with additions of sodium dichromate to restore proper ratio of dichromate to acid
	Buildup of excessive amount of magnesium nitrate in the bath	Bath has been revivified too many times; discard and use fresh bath
Brown, nonadherent, powdery coatings	Work held in air too long before rinsing	Delay in air; 5 s max; surface should not dry before rinsing
	Ratio of acid to sodium dichromate concentration too high	Adjust concentrations to restore proper ratio
	Solution too hot because of small volume in relation to work	Cool solution or increase volume of solution used
	Metal not properly degreased	Use recommended cleaning method
	Oil film on solution	Prevent by using recommended cleaning procedures[b]
	Solution revivified too often	Discard; use fresh solution

Note: When viewed under magnification, coating exhibits a network of pebbled etching. The appearance of a properly applied chrome pickle coating is influenced to some degree by the age of the solution and by the composition and temper of the alloy treated.

(a) When examined under magnification.

(b) Correct by skimming off oil and adding small amount, 0.05%, of fluorinated-hydrocarbon wetting agent

Table 6 Causes and corrections of difficulties with dichromate coatings

Normal appearance varies from light to dark brown, depending on alloy composition

Difficulty	**Cause**	**Corrective procedure**
Abnormally heavy coatings	pH of dichromate bath too low, below 4.1	Raise pH by addition of NaOH
	Contact between work and tank	Insulate parts and rack from tank
Loose, powdery coatings	Acid fluoride or HF bath too dilute	Adjust fluoride content
	pH of dichromate bath <4.1	Raise pH by addition of NaOH
	Parts oxidized, corroded, or flux-contaminated	Chromic acid clean parts prior to dichromating

	Contact between work and tank	Insulate parts and rack from tank
Failure to coat, or nonuniform coatings	pH of dichromate bath >5.5	Lower pH by addition of CrO_3
	Dichromate concentration too low	Do not allow dichromate to fall below 120 g/L (16 oz/gal); maintain as high as economical
	Oily matter not removed; previous chrome pickle coating not completely removed	Careful rinsing after alkaline cleaning; use chromic acid pickle to supplement alkaline cleaning for complete removal of chrome pickle coating
	Part not fluoride treated	Give part acid fluoride or HF pickle before dichromating
	Part is made of EK30A, EK41A, HK31A, HM21A, HM31A, or M1A	Dichromate treatment does not coat these alloys; use another treatment
	Dichromate bath not kept boiling during treatment period	Solution should actually boil; minimum bath temperature, 93 °C (200 °F)
	High carryover of acid fluoride or HF into dichromate bath	Thoroughly rinse parts after acid fluoride or HF pickle
	Hydrofluoric acid dip too long	Use $\frac{1}{2}$ to 1 min for AZ31A and B; if 5 min dip is used, extend cold water rinse to 5.7 min
Pitting or other attack on aluminum inserts or attachments	Hydrofluoric acid dip reacts on aluminum	Use sodium, potassium, or ammonium acid fluoride solution in place of hydrofluoric acid dip

Table 7 Causes and corrections of difficulties with coatings produced by anodizing treatments

Difficulty	**Cause**	**Corrective procedure**
Chemical treatment No. 9[(a)]		
Grayish, nonuniform appearance	Insufficient or improper cleaning of work before treatment	Use proper methods for adequate cleaning
	Treating solutions depleted	Check pickling bath, HF or acid fluoride, for proper pH[(b)]
Failure to coat on certain alloys[(c)]	Lack of good external electrical contact of work with tank or cathode plates	Ensure good external electrical contact between work and cathode
	Work touching tank walls or bottom (or cathode plates)	Prevent work from contacting cathode in electrolyte

Chemical treatment No. 17[d]		
Deviation from characteristic appearance	Improper balance in content of bath ingredients[e]	Adjust bath ingredients to proper operating range; use chemical analysis to determine need
Spalling of dark green coating	Unusually thick coatings may spall when substrate is bent or otherwise deformed	Spalling can be minimized by sealing coating with an organic finish having low surface tension, low viscosity, and slow drying rate
HAE anodizing treatment[f]		
Significant color lightening	Depletion of the chemical ingredients of the bath[e]	Adjust aluminum and manganese contents to proper level[g]

(a) Usual appearance of thin coating; light tan; thick coating; dark brown.

(b) Galvanic anodizing bath is maintained at a pH of 5.6 to 6.0 with additions of a solution containing, by weight, 5% H_2SO_4 (concentrated).

(c) Especially alloys without aluminum content such as EK30A, EK41A, HK31A, HM21A, HM31A, and HZ32A.

(d) Usual appearance of a thin coating: light green; thick coating: dark green. A clear, colorless coating can also be deposited by Chemical treatment No. 17 by use of 40 V as terminal voltage.

(e) Solution unbalance may occur after treatment of as little as 0.4 m^2/L (20 ft^2/gal) of solution; however, when applying clear or thin coatings, 2 to 2.6 m^2/L (100 to 130 ft^2/gal) of solution usually can be treated before bath adjustment is indicated.

(f) Usual appearance of thin coating: light tan; thick coating: dark brown.

(g) Fluoride and phosphate become depleted at an extremely low rate and require adjustment only every few months in production.

For example, the adhesion of paint films applied to dichromated parts can be adversely affected by the presence of a dusty material on the parts after final rinsing and drying. Chemical analysis might indicate this material to be a sulfate precipitated from the domestic water that was being used to replace evaporation losses in the dichromating solution. The problem can be solved by recycling: storing the steam condensate obtained from heating the solution and installing an automatic level-control system to feed this condensate into the dichromating tank.

Although dichromating usually treats the metal satisfactorily, another example of special difficulties might involve a residue of dye-penetrant developer that can remain on the surfaces of castings and interfere with the adhesion of paint films. In this situation, vapor degreasing, either before or after the dichromating treatment, would only set the developer, rather than effect its removal. Thorough cleaning of parts to remove all developer residue immediately after penetrant inspection, and before vapor degreasing, can solve the problem. This cleaning would entail the use of an alkaline cleaner and, if necessary, scrubbing with a bristle brush.

Another example involves corrosion products that were observed surrounding stainless steel hardware that had been inserted into sand castings of alloy AZ91A before dichromating. The parts were free from corrosion immediately after application of the finish; corrosion occurred while parts were in storage.

The corrosion of the magnesium was found to be the result of a galvanic couple set up between the magnesium and stainless steel, caused by the entrapment of acid solution during dichromating. This condition was eliminated by applying the dichromate treatment to the castings before inserting the stainless steel parts, and by applying a coating of zinc chromate primer to the stainless steel parts just before inserting them into the castings.

Precision-machined parts that were given a chromic acid pickle might present another example of difficulty if the parts were found to have an etched surface. Analysis of the bath might indicate the presence of a high concentration of chloride and sulfate ions, 0.5 g/L (0.07 oz/gal), of Cl, as NaCl, and 1.7 g/L (0.2 oz/gal) of SO_4, as H_2SO_4,the source of which might be traced to the prepared water. Because chloride and sulfate ions cannot be readily removed, the bath would probably be discarded. To prevent further loss of parts, baths must be checked frequently and test panels treated for 15 to 30 s and examined; an evolution of gas during treatment and a dimensional change indicate that a bath is contaminated and must be discarded.

As another example, spacecraft parts were only given a Chemical Treatment No. 17 anodize for corrosion protection. Although this treatment was satisfactory during indoor in-plant processing, white corrosion appeared during stand-by in the salt air and fog atmosphere at the launch pad. This attractive anodic coating is porous and not corrosion-protective. Parts were sealed with a paint system to correct the problem.

Inspection Methods. Examine coatings on treated parts visually for complete and uniform coverage and for color peculiar to the type of treatment being checked. Buildup caused by the coating is determined most simply and reliably by measurement of the parts, before and after treatment, with a micrometer accurate to 2.5 μm (0.1 mil). If this is not possible, measure test panels that have been treated simultaneously with the parts before and after treatment.

Process test panels together with panels through all the steps of cleaning, pretreatment coating, and where applicable, post-treatment. Post-treatment should not consist of an additional film of coating, organic or inorganic, applied either by spraying or dipping. After processing for the time required to produce the coating, test panels should be subjected to the following tests:

- *Abrasion resistance:* The test panels should be rubbed by the tip of a 4.7 mm ($\frac{3}{16}$ in.) diam Pyrex rod, the end of which has been heated in a blast flame until it is fire polished and hemispherical. Press the rod against the coating and rub back and forth by hand with just enough pressure to abrade the surface of the rod. The coating should not break or show scratches that penetrate to the base metal.
- *Salt spray (fog) exposure:* The treated test panels, when exposed to salt spray in accordance with Federal Test Method 151 for a specified number of hours, rinsed in tap water, and air dried, should show an average of no more than eight corrosion spots, none larger than 0.8 mm ($\frac{1}{32}$ in.) in greatest dimension. Corrosion appearing at the electrical-contact area or at the edges of the test panels may be disregarded.

Plating

All commercial plating systems can be applied to magnesium alloys after proper preplating operations. However, zinc and nickel are the only metals that can be plated directly on magnesium. These deposits are not used commercially, but instead serve as undercoatings upon which other commonly plated metals are deposited. Standard practice for plating magnesium involves surface conditioning, zinc immersion plating (zincate solution), and a cyanide copper strike to a thickness of 8 μm (0.3 mil), followed by any standard plating process.

The preparation of magnesium for electroplating is similar in principle to that prescribed for many other metals. First, magnesium must be cleaned to remove all surface contaminants. Then, depending on the surface finish desired, it must be conditioned. This may be accomplished by one or more of the following finishing methods: glass or plastic bead blasting, pickling, barrel finishing, and polishing and buffing. Surface contaminants resulting from these treatments must be removed by additional cleaning. Depending on the type of soil, suitable cleaning methods include vapor degreasing, emulsion cleaning, alkaline soak cleaning, and water rinsing. Finally, the magnesium surface must be activated chemically before it can accept either of the recommended metal undercoatings.

Nickel Undercoating. The deposition of nickel on magnesium must be preceded by two acid etching treatments, one in a chromic-nitric acid solution and another in a solution of hydrofluoric acid. These pretreatments of magnesium, in combination with the deposition of a nickel undercoating, are generally referred to as the chemical-etching process.

Figure 11 illustrates the successive steps involved in alkaline cleaning, etching, and nickel plating. Operating conditions and pertinent data are given in the accompanying table. The nickel undercoating may be deposited from either an electrolytic, acid-fluoride, plating bath, or an electroless immersion bath as shown:

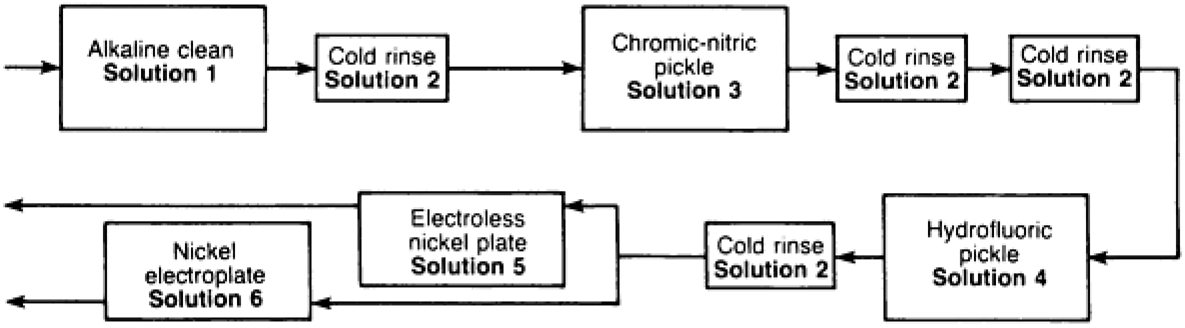
Constituent or condition	Value or range
Electroless nickel	
Basic nickel carbonate, g/L (oz/gal)	9.7 (1.3)
Hydrofluoric acid as 70% HF, mL/L (fl oz/gal)	6.4 (0.85)
Citric acid, mL/L (fl oz/gal)	5.2 (0.7)
Ammonium acid fluoride, g/L (oz/gal)	15 (2.0)
Sodium hypophosphite, g/L (oz/gal)	20.3 (2.7)
Ammonium hydroxide, mL/L (fl oz/gal)	30.4 (4.06)
Water	bal
pH (colorimetric)	4.5-6.8[a]
Operating temperature, °C (°F)	76-82 (170-180)
Agitation required	Mild mechanical
Rate of deposition (approx), μm/h (mil/h)	20 (0.8)
Nickel electroplate	
Basic nickel carbonate, g/L (oz/gal)	120 (16.0)
Hydrofluoric acid as 100% HF, mL/L (fl oz/gal)	43 (5.7)

Citric acid, g/L (oz/gal)	40.6 (5.4)
Wetting agent[b], g/L (oz/gal)	0.7 (0.1)[c]
Water	bal
pH (colorimetric)	3.0
Operating temperature, °C (°F)	48-60 (120-140)
Current density, A/dm^2 (A/ft^2)	3-10 (30-100)
Cathode-rod agitation, m/s (ft/min)	0.06-0.08 (12-16)

(a) Preferred, 6.5.

(b) Example, sodium lauryl sulfate.

(c) 1 g/L (0.134 oz/gal)



Solution No.	Type of solution	Composition	Amount	Operating temperature, °C (°F)	Cycle time, min	Tank material
1	Alkaline cleaner[a]	[b]	[b]	82-100 (180-212)	3-10	Low-carbon steel
2	Cold rinse	Water	. . .	Ambient	$\frac{1}{2}$-1	Low-carbon steel[e]

3	Chrome-nitric pickle[c]	CrO_3	125 mL/L (16 fl oz/gal)[d]	21-32 (70-90)	$\frac{1}{2}$-2	. . .
		70% HNO_3	110 mL/L (14 fl oz/gal)[d]			
4	Hydrofluoric pickle	70% HF	220 mL/L (28.2 fl oz/gal)[f]	21-32 (70-90)	10	Low-carbon steel[g]
5	Electroless nickel[h]	Basic nickel carbonate	9.7 g/L (1.3 oz/gal)	77-82 (170-180)	[i]	Low-carbon steel[j]
		Hydrofluoric acid (as 70% HF)	6.2 mL/L (0.8 fl oz/gal)			
		Citric acid	5.2 g/L (0.7 oz/gal)			
		Ammonium acid fluoride	15 g/L (2.0 oz/gal)			
		Sodium hypophosphite	20.3 g/L (2.7 oz/gal)			
		Ammonium hydroxide	30.4 mL/L (4.0 fl oz/gal)			
		Water	bal			
		pH (colorimetric)	4.5-6.8[k]			
6	Nickel electroplate[l]	Basic nickel carbonate	120 g/L (16.0 oz/gal)	49-60 (120-140)	[i]	Low-carbon steel[m]
		Hydrofluoric acid (as 100% HF)	43 mL/L (5.7 fl oz/gal)			
		Citric acid	40 g/L (5.4 oz/gal)			
		Wetting agent[n]	0.7 g/L (0.01 oz/gal)[o]			
		pH (colorimetric)	3.0			

(a) Alkaline cleaning may be preceded by vapor degreasing, emulsion cleaning, or mechanical cleaning.

(b) Type and strength of solution governed by degree of surface contamination.

(c) Solution must be ventilated.

(d) For aluminum-containing alloys. For alloys containing no aluminum, concentrations are 226 g (8 oz) CrO_3 and 326 g (11.5 oz) of 70% HNO_3 and water to make 3.8 L (1 gal).

(e) Stainless steel or low-carbon steel lined with polyethylene.

(f) For alloys containing more than 5% Al. For all other alloys, solution contains 195 g (6.9 oz) 70% HF and water to make 3.8 L (1 gal).

(g) Lined with polyethylene, synthetic rubber, or vinyl-based material.

(h) Agitation of work is recommended.

(i) Time determined by required thickness of nickel deposit.

(j) Lined with polyethylene, saran, or Lucite.

(k) Preferred, 6.5.

(l) Direct current required; agitation of cathode bar recommended.

(m) Lined with synthetic rubber or vinyl-based material.

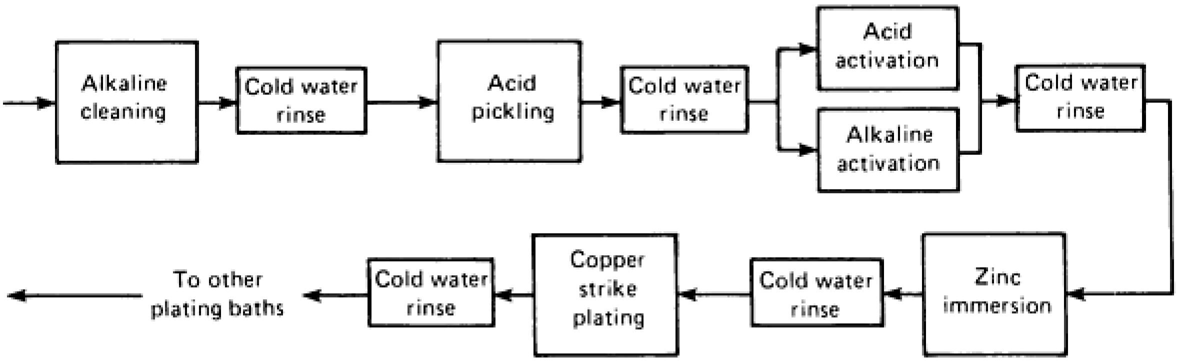
(n) Example, sodium lauryl sulfate.

(o) 1 g/L (0.13 oz/gal)

Fig. 11 Preparing magnesium alloys for nickel plating

To some extent, the two etching treatments undercut surface pits to provide mechanical anchorage for the plated deposits. After a nickel undercoating is applied to this roughened surface, the surface of the coating is not as bright or as smooth as that obtained with the zinc immersion process. However, in common with zinc coating, nickel coating can accept any of the standard electrodeposits, including cadmium, zinc, copper, brass, nickel, black nickel, chromium, gold, silver, and rhodium. Electroless deposits, such as gold or copper, also may be applied over the initial nickel plate.

Zinc Undercoating. After being alkaline cleaned, acid pickled, and surface-activated, magnesium can be prepared for plating by being immersed in a nonelectrolytic chemical bath that produces a thin deposit of zinc directly on the base metal. The basic steps, operating conditions, and tank materials required for the zinc immersion process are summarized in the flow chart and table of Fig. 12. After the immersion treatment, the very light zinc coating about 2.5 μm (0.1 mil) thick must be protected by a copper strike plate before any other standard electrodeposit may be applied. The following are the various steps that comprise the zinc immersion process, as well as the various solutions used.



Operation	Cycle time, min	Solution temperature		Tank material
		°C	°F	
Alkaline cleaning[(a)]	3-10	87-100	190-212	Low-carbon steel
Acid pickling	$\frac{1}{2}$-1	21-32	70-90	Ceramic or stainless steel[(b)]
Acid activation	1-5	21-32	70-90	Rubber, polyethylene, or vinyl plastisol
Alkaline activation	2-5	76	170	Stainless steel
Zinc immersion	1-3	79-85[(c)]	175-185[(c)]	Stainless steel
Copper strike plating[(d)]	6-10	65-71	150-160	Low-carbon steel; rubber
Cold water rinses	$\frac{1}{2}$-1	Ambient	Ambient	Low-carbon steel

(a) May be preceded by solvent cleaning, mechanical cleaning, or both.

(b) Mixtures containing fluorides require polyethylene, vinyl-based or synthetic rubber linings.

(c) Automatic temperature control preferred.

(d) Cathode agitation, constant filtration, and automatic temperature control preferred

Fig. 12 Preparing magnesium alloys for copper plating. See text for details of solution composition and other

operating conditions.

Alkaline cleaning, as used in the electroplating of magnesium, consists of soak cleaning or cathodic electrocleaning, or a combination of both. These processes are described in detail in the article on alkaline cleaning in this Volume. Strong caustic solutions are used to remove segregated metal, graphite, and other surface contaminants. The composition and operating conditions for one water solution of this type are:

Sodium hydroxide (NaOH), g/L (oz/gal)	120-720 (1-6)
Temperature, °C (°F)	99-170 (210-340)
Time, min	10-20

Follow this treatment by an acid dip to remove the heavy film of hydroxide.

Acid Pickling. Depending on magnesium alloy composition and product form, the following acid pickling solutions can be used prior to plating. All standard alloys and forms of magnesium can be pickled and chemically brightened by the use of the aqueous solution that follows:

Chromic trioxide (CrO_3), g/L (oz/gal)	180 (24.0)
Ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), g/L (oz/gal)	40 (5.3)
Potassium fluoride (KF), g/L (oz/gal)	3.5-7 (0.05-0.9)
Temperature, °C (°F)	Room temperature, 21-32 (70-90)
Time, min	$\frac{1}{4}$-2

All magnesium alloys and forms can be pickled under the following conditions:

Phosphoric acid, 85% H_3PO_4	No dilution
Temperature, °C (°F)	Room temperature, 21-32 (70-90)

Time, min	$\frac{1}{4}$-5

Sheet, extrusions, and forgings can be pickled in the following aqueous solution:

Glacial acetic acid (CH_3COOH), mL/L (fl oz/gal)	280 (37.4)
Sodium nitrate, g/L (oz/gal)	80 (10.7)
Temperature, °C (°F)	Room temperature, 21-32 (70-90)
Time, min	$\frac{1}{2}$-2

Where little or no dimensional change is permitted, parts may be pickled in an aqueous solution of chromic acid, 180 g/L (24.0 oz/gal) of chromic trioxide of water at any temperature from room to boiling temperatures. This dip removes graphite, oxides, and other soils without removing an appreciable amount of metal.

Surface Activation. To obtain an adherent and uniform coating of zinc on magnesium, the surface of the magnesium must be activated by immersion in a special acid or alkaline solution. The acid activating bath removes thin oxide or chromate films left by prior pickling or cleaning operations with a minimum of etching of the base metal. It also produces an equipotentialized surface on which the zinc immersion coating can deposit uniformly. The composition and operating characteristics of an aqueous acid activating solution in common use are:

Phosphoric acid, 85% H_3PO_4, mL/L (fl oz/gal)	200 (26.7)
Ammonium acid fluoride (NH_4HF_2), g/L (oz/gal)	100 (13.3)
Temperature, °C (°F)	Room temperature, 21-32 (70-90)
Time	25 s to 2 min

Operation of acid fluoride activating baths at appreciably below 21 °C (70 °F) may result in poor adhesion of the electroplated deposit.

An alkaline pyrophosphate activating solution also removes oxides and other films; by virtue of its alkalinity, it does not dissolve the metals employed for rack contacts. Thus, there is little or no danger that metals such as iron or copper can plate out by immersion at locations adjacent to rack contacts. This form of stray plating prevents the proper deposition of the subsequent zinc immersion coating. The composition and operating characteristics of the alkaline solution are:

Tetrasodium pyrophosphate ($Na_4P_2O_7$), g/L (oz/gal)	40 (5.3)
Sodium tetraborate ($Na_2B_4O_7$), g/L (oz/gal)	70 (9.3)
Sodium fluoride (NaF), g/L (oz/gal)	20 (2.7)
Temperature, °C (°F)	76 (170)
Time, min	2-5

The bath should not be operated much above 76 °C (170 °F), as the alkaline solution has a tendency to dry on the parts prior to rinsing. For this reason, the transfer from hot activator to water rinse should be as rapid as possible.

Zinc Immersion Coating. Standard zinc immersion baths (Table 8) are based on aqueous solutions of pyrophosphate, a zinc salt, a fluoride salt, and, if required, a small amount of carbonate for adjusting alkalinity to the proper range. The pyrophosphate dissolves oxide and hydroxide films to form water-soluble complexes. By effecting film removal under specific conditions of pH, temperature, and bath concentration, a thin, adherent coating of metallic zinc is deposited. Fluoride is added to control the rate of zinc deposition. To a considerable extent, the quality and adhesion of the zinc deposit depends on the rate of deposition; too rapid a rate usually produces less adherent coatings.

Table 8 Composition of zinc immersion bath

Activator	Constituent	Concentration			
		Nominal		Range	
		g/L	oz/gal	g/L	oz/gal
Acid	Oxalic acid $(CO_2H)_2$	5	0.7	2-10	0.3-1.3
Alkaline	Potassium pyrophosphate ($K_4P_2O_7$)	60	8	50-150	6.5-10.0
	Sodium carbonate (Na_2CO_3)	15	2	10-20	1.3-2.6

The most commonly used zinc immersion solution has composition and pH as follows:

Zinc sulfate monohydrate ($ZnSO_4 \cdot H_2O$), g/L (oz/gal)	30 (4.0)

Tetrasodium pyrophosphate ($Na_4P_2O_7$), g/L (oz/gal)	120 (16.0)
Sodium fluoride (NaF), g/L (oz/gal)	5 (0.7)
or	
Lithium fluoride (LiF), g/L (oz/gal)	3 (0.4)
Sodium carbonate (Na_2CO_3), g/L (oz/gal)	5 (0.7)
pH	10.0-10.6 (10.2-10.4 preferred)

Within limits, the bath constituents can vary from the above formula provided the ratio of pyrophosphate to zinc is kept to the proper range and fluoride concentration is maintained at the level indicated. Water for preparing the bath should be reasonably free from iron and other heavy-metal salts. Ordinary tap water may be used, but deionized water is preferred.

The bath is prepared by first dissolving the zinc sulfate monohydrate in water at room temperature. The solution is then heated to 60 to 82 °C (140 to 180 °F), and tetrasodium pyrophosphate is added slowly, while stirring. The white, fluffy precipitate (sodium zinc pyrophosphate) that first forms dissolves after further stirring for 5 to 10 min or longer, depending on the degree of agitation and temperature. Next, fluoride is added and then carbonate. The amount of carbonate added is the average required to produce the proper pH and should be determined by the actual pH of the solution. Sulfuric or phosphoric acid can be added to reduce pH, when necessary. The pH values given above are those determined by colorimetric methods; electrometric values, using a standard glass electrode, are 0.5 pH lower.

The bath is operated at 79 to 85 °C (175 to 185 °F). Mild agitation is used to prevent stratification, particularly when water is added to replace evaporation losses. Immersion time depends on alloy composition, bath temperature, surface preparation, and other variables; usually it ranges from 1 to 3 min, but it may be as long as 10 min for aluminum-containing alloys.

As indicated in Fig. 12, the tank should be made of stainless steel. Low-carbon steel, unless it is heavily nickel plated, will cause excessive iron contamination of the solution.

The zinc immersion bath has a fairly long life and can be maintained by analysis and regular additions. Eventually, it becomes contaminated with dissolved magnesium and other impurities and must be discarded.

Copper strike plating in a cyanide bath should follow immediately after the application of the zinc coating. The work should make electrical contact with the cathode bar before being immersed in the plating bath. If the work is to be subsequently plated in an alkaline bath or in a modified noncorrosive fluoride nickel bath, flash copper deposits of 3 μm (0.1 mil) or less are adequate. However, if an acid bath is to be used, copper deposits of 8 μm (0.3 mil) minimum are required to protect the base metal from chemical attack, and the work must be thoroughly neutralized and rinsed after the flash plating cycle.

In some applications, because of the complexity of the parts or porosity of the base metal, increasing the minimum thickness of the copper strike plate could be necessary. Castings, because of porosity, generally require a slightly higher minimum thickness of copper when the subsequent plating bath is to be an acid type.

A high current density 3 to 4 A/dm^2 (30 to 40 A/ft^2) is applied for $\frac{1}{2}$ to 1 min, and then reduced to 1.5 to 2.5 A/dm^2 (15 to 25 A/ft^2). Prolonged strike plating at high current density causes poor adhesion and blistering. Any other metal usually electrodeposited can be applied after flash copper plating is completed.

Zinc Undercoating for Die Castings. Whereas AZ91 with 9% Al is frequently used for die castings, any surface areas with aluminum-rich segregates are difficult to zincate. The best compromise for castability and plating characteristics is the AZ71 composition with a lower aluminum content of 7%. The section of this article on surface activation outlines normal practice of either an acid or alkaline activation after acid pickling and before zinc immersion plating (Fig. 12). Hot chamber magnesium die castings can be successfully plated using an acid activation followed by an alkaline activation. The patented process follows:

1. Acid activation, 0.3 to 1 min, 21 to 29 °C (70 to 85 °F)
2. Cold water rinse, minimum 1 min
3. Alkaline activation, 0.3 to 1 min, 60 to 65 °C (140 to 150 °F)
4. Cold water rinse
5. Zinc immersion bath, 60 to 65 °C (140 to 150 °F)

Acid copper is more efficient than semi-bright nickel for leveling and filling pits in the castings.

Uses of Plated Magnesium. Copper-nickel-chromium plating systems on magnesium satisfy decorative and protective requirements for interior and mild exterior environments. They have not found application for parts exposed to severe marine or salt splash conditions because of the accelerated galvanic corrosion that can occur wherever small areas of magnesium may be exposed by porosity or mechanical damage to the plating. Hard chromium plating provides excellent wear resistance and long working life for magnesium photoengraving plates. Electroless nickel plating on magnesium has found use in the computer and electronics industries for applications requiring corrosion and wear resistance, solderability, and stable electronic contacts; copper plus hot-flowed tin plating are also used. Gold over electroless nickel is used in space applications of magnesium.

Corrosion Resistance. Satisfactory corrosion resistance, especially in marine exposures or with salt-spray testing, is obtained only when the plated deposit is pore-free. Porosity in the base metal promotes porosity in the plated deposits; consequently, corrosion resistance of plated magnesium alloy parts having appreciable surface porosity is less than that of parts that have a minimum of surface porosity. This is evident from the results of salt-spray corrosion studies of plated wrought and sand cast alloys. Less total plate thickness is required to give comparable corrosion resistance over wrought alloys than over cast alloys. The results with wrought alloys are much more consistent over a number of tests than are those with cast alloys, undoubtedly because of the amount of variation in surface porosity or surface quality of the sand castings tested.

In general, on the same type of base metal, either wrought or cast, corrosion resistance is a function of total plate thickness. Service tests should be conducted to determine the best systems and plate thicknesses to give satisfactory corrosion resistance. Suggested minimum total plate thicknesses for decorative chromium plating and copper-nickel-chromium are shown in Table 9.

Table 9 Minimum total plate thicknesses for decorative chromium plating

Service environment	Wrought alloys		Cast alloys	
	μm	mils	μm	mils
Interior	13	0.5	19	0.75
Mild exterior	25	1.0	38	1.5
Average exterior	32	1.25	50	2.0

Severe exterior	38	1.5	64	2.5

Quality Control. The most widely used methods for determining the quality of plated deposits on magnesium alloys are adhesion, relative-humidity, and salt-spray tests. Relative-humidity and salt-spray tests are considered standard acceptance tests where corrosion resistance is required.

Adhesion tests are conducted by either baking the plated parts at 175 to 260 °C (350 to 500 °F) for 1 h followed by air cooling or immersing the plated parts in an oil bath at about 260 °C (500 °F) for a sufficient time for the parts to reach the temperature of the bath followed by quenching in a room-temperature kerosene bath, and then inspecting the parts for evidence of blistering. The absence of blistering of the plate generally indicates that proper adhesion of the plate has been obtained. These heat tests are simple, effective, and inexpensive nondestructive methods for determining adhesion and are particularly convenient where 100% testing of parts is required.

Stripping of Plated Deposits. Plated deposits can be satisfactorily stripped from magnesium alloys with little if any attack of the base metal.

Zinc immersion deposits can be stripped in a room-temperature bath containing 10 to 15 vol% of 70% hydrofluoric acid (HF). The standard acid activator as used prior to zinc immersion coating can also be used.

Chromium can be stripped by reverse current in a hot alkaline solution, such as one containing 60 to 75 g/L (8 to 10 oz/gal) of sodium hydroxide (NaOH), or combinations of sodium hydroxide and sodium carbonate, in water.

Copper can be stripped by immersion in hot alkaline polysulfide followed by a dip in cyanide, as in stripping copper from steel or die cast zinc.

Nickel can be stripped in a bath containing 15 to 25% HF and 2% sodium nitrate ($NaNO_3$), using 4 to 6 V. Work to be stripped is made anodic; cathodes can be carbon, lead, or magnesium.

Copper, nickel, tin, cadmium, and zinc can be stripped by immersion in the following solution, operated at room temperature: nitric acid (sp gr, 1.42), 1 part by volume; hydrofluoric acid, 70%, 2 parts; water, 2 parts. The tank for containing the solution should be made of polyethylene or some similar material.

Gold, silver, copper, and nickel can be stripped by immersion in proprietary alkaline chemical strippers containing cyanide. Add 15 g/L (2 oz/gal) of sodium hydroxide (NaOH) per gallon of prepared solution to aid in preventing possible etching of the magnesium base metal. Operating temperature of the bath may range from 21 to 60 °C (70 to 140 °F). Low-carbon steel tanks and heating coils are used.

Organic Finishing

Organic finishes are used on magnesium alloys to attain various effects in appearance and to provide durability. Organic finishing systems require careful adherence to manufacturers' recommendations on solvents, baking schedules, and compatibility of prime and finish coats to achieve desired film properties and adhesion.

A chemical conversion coating or anodizing treatment is required prior to application of organic coatings if the optimum in corrosion durability is desired. These treatments roughen and chemically modify the metal surface so that a good stable bond can be achieved with the paint coating applied. Surface treatments are not used for every application, however, as indicated in Table 1. Some commercial parts are coated with no more than mechanical cleaning. Oven drying should be used following spray or immersion surface treatment of castings to ensure that all moisture is driven from the porosity of the cast surfaces prior to applying bake-cured finishes. It has also been found that anodized components provide greatly improved corrosion durability, if the porosity, common to all, is sealed with a penetrating resin sealer prior to the application of primer and top coats (Ref 13).

Table 10 contains information on various appearance effects that are attainable with the mechanical or chemical pretreatment and organic finishing systems required for interior and exterior applications. Military finishing is controlled by specifications; Table 11 lists the various finishing steps involved and indicates the appropriate Government specifications.

Table 10 Organic finishing systems for magnesium alloys

Appearance effect	**Typical finishing system for**	
	Interior service[a]	**Exterior service**[b]
Bright metal	Buff + ferric nitrate bright pickle + clear epoxy or acrylic	Buff + ferric nitrate bright pickle + clear epoxy or acrylic
Satin finish	Wire brush + ferric nitrate bright pickle + clear epoxy or acrylic	Wire brush + ferric nitrate bright pickle + clear epoxy or acrylic
Tinted clear	Ferric nitrate bright pickle + tinted epoxy or acrylic	Not recommended
Dyed clear	Ferric nitrate bright pickle + clear epoxy or acrylic + dye dip	Not recommended
Metallic	Chrome pickle or dilute chromic acid + epoxy, acrylic, polyvinyl butyral or vinyl pigmented with metal powder or paste	Chrome pickle or dilute chromic acid + 1 coat polyvinyl butyral primer + epoxy or acrylic pigmented with metal powder[c]
Wrinkle	Chrome pickle or dilute chromic acid + standard wrinkle finish	Not generally used in outdoor service
High-gloss enameled	Chrome pickle or dilute chromic acid + epoxy, acrylic, polyurethane or alkyd enamel	Chrome pickle or dilute chromic acid + 1 coat polyvinyl butyral primer + acrylic, alkyd or polyurethane enamel
Leatherette (smooth or textured)	Chrome pickle or dilute chromic acid + vinyl cladding	Chrome pickle or dilute chromic acid + vinyl cladding
	Chrome pickle or dilute chromic acid + vinyl organosol	Chrome pickle or dilute chromic acid + polyvinyl butyral or vinyl primer + vinyl organosol

(a) Suggested minimum total film thickness, 25 μm (1 mil).

(b) Suggested minimum total film thickness, 50 μm (2 mils); marine environments may require total film thickness of 75 μm (3 mils).

(c) Or metal paste

Table 11 Military finishing systems for magnesium alloys

Operation	**Appearance**	**Applicable specifications**
Cleaning	. . .	MIL-M-3171
Chemical treatment	Varies with treatment	MIL-M-3171 or MIL-M-45202

Prime coat	Varies with protective pigment used	MIL-P-15930 or MIL-P-52192
Second coat	Matte	TT-E-529
	Semigloss	TT-E-485, TT-E-529, or MIL-L-52043
	Gloss	TT-E-489
Finish coat	Matte	TT-E-529, MIL-L-14486
	Semigloss	TT-E-485, TT-E-529, or MIL-L-52043
	Gloss	TT-E-489

Selection of Paint. Both air-drying and baking paints are currently in use. Baking paints are harder and more resistant to attack by solvents. Vinyl alkyds have been used for their resistance to alkali, acrylics for resistance to salt spray, alkyd enamels for exterior durability, and epoxies for good abrasion resistance. Vinyls can withstand temperatures up to about 150 °C (300 °F). Other finishes have increasing temperature resistance in this order: modified vinyls, epoxies, modified epoxies, epoxy-silicones, and silicones.

Primers for magnesium should be based on such alkali-resistant vehicles as polyvinyl butyral, acrylic, polyurethane, vinyl epoxy, and baked phenolic. Zinc chromate or titanium dioxide pigments are commonly used in these vehicles for corrosion inhibition. Finish coats are chosen to have:

- Compatibility with primer
- Adaptability to shop conditions and to finishing equipment available
- Ability to perform in service
- Economy consistent to compliance with service requirements

For a detailed discussion of types of paints and methods of application, see the article on painting in this Volume.

Examples of problems that might arise in productive painting of magnesium alloy products are given below, together with details of the methods used to solve them.

The first problem, masking multiple threaded inserts in castings before painting, was solved by this method:

1. A chemical-resistant finish was applied before drilling and tapping the castings for inserts.
2. Holes were then tapped and drilled.
3. Castings were reprocessed through the dichromate to treat threaded holes.
4. Inserts were set in zinc chromate sealer.

Another example involves bubbles and fisheyes appearing in the baked wrinkle-finish paint on dichromated magnesium alloy die castings. This condition was eliminated by lowering the paint-baking temperature from 150 °C (300 °F) to 120 °C (250 °F) and adding a baking cycle of 2 h at 175 °C (350 °F) after the dichromating treatment.

Die castings given a chrome pickle treatment followed by baked coats of primer and wrinkle-finish enamel present another example of problems that might arise. When the primer was applied and baked, small bubbles formed on the film surface; these would later break, leaving an unsightly ring on the surface and affecting uniformity and appearance of the

wrinkle finish. Preheating the castings to drive out entrapped air and painting them after they had cooled, greatly reduced the number of bubbles but did not completely eliminate their formation. Painting the castings while they were still hot from the preheating solved the problem.

Stripping of Paint. The ability of magnesium alloys to withstand strong alkalis lessens the problem of paint removal. After painted parts are soaked in a hot, 82 °C (180 °F), solution containing 360 g/L (3 lb/gal) of sodium hydroxide in water, most paints dissolve or lose adhesion to the extent that they can be removed by flushing with water, hand brushing, or other mechanical means. Paint strippers with a phenol or methylene chloride base may be used, but extended soaking of more than 24 h causes slight etching of the magnesium alloy, which is undesirable for close-tolerance machined areas.

Stripping vinyl-based enamels from dichromate-treated magnesium is more difficult. One method entails softening the coating and weakening the bond by soaking in methylene chloride for $\frac{1}{2}$ to 1 h, then resetting the paint by soaking in hot alkalis for 5 to 30 min. The loose paint is then brushed off, and any remaining paint is removed by wet blasting with 150-mesh aluminum oxide. This stripping operation should be followed as soon as possible by a dichromate treatment.

Chrome pickle and dichromate coatings can usually be removed in hot sodium hydroxide. Old chromate coatings are usually more difficult to remove and work to be stripped of them may require soaking in sodium hydroxide solution followed by immersion in a chromic acid pickling solution.

Special baked primers and other finishes that are difficult to remove in a sodium hydroxide solution may be stripped by being immersed for 5 min or longer in the following solution, at 82 to 100 ° C (180 to 212 °F):

Sodium hydroxide, vol%	10-20
Diethylene glycol, vol% or ethylene glycol, vol%	10 20
Water	bal

Coatings that are difficult to remove by the methods described above can be effectively stripped by mild abrasive blasting using plastic media. Plastic media blasting is widely used for stripping of aircraft and aerospace components with little or no damage to the substrate.

Reference cited in this section

13. J.H. Hawkins, Assessment of Protective Finishing Systems for Magnesium, *Proc. Int. Magnesium Association* (Washington, DC), 1993

Health and Safety

Magnesium and magnesium oxide dusts are considered nontoxic. The usual precautions taken to prevent gross inhalation of dirt, dust, and other foreign matter are required. No unusual health hazard has been found associated with the handling, mechanical finishing, or pickling of magnesium alloys, including those containing thorium or beryllium.

Some of the chemical baths used contain chromate or fluorides. Because of the toxic nature of these materials, adequate ventilation is required when baths containing chromate or fluorides are used.

Although bulk magnesium is difficult to ignite unless temperatures are near the melting point, finer particles, such as chips, sawings, and especially sanding dust, are more easily ignited. Proper handling of these materials is required to prevent ignition.

Polishing and Buffing. Special precautions must be followed in the polishing and buffing of magnesium alloys. Magnesium dust or powder must not be allowed to accumulate because it will create extreme fire and explosion hazards. The fire hazards produced in buffing are somewhat less than those produced in polishing. Belt polishing is potentially more dangerous than wheel polishing because the resulting dust is more difficult to collect.

Under no circumstances should steel be polished in the same setup that is used for polishing magnesium, because the polishing of steel causes sparks that can ignite magnesium dust. Because of strong oxidizing properties, heavy chromate coatings also cause sparking when magnesium alloy parts to which they have been applied are being polished.

A system considered safe for the collection of magnesium grinding and polishing dust is one in which the dust is precipitated by a heavy spray of water or low-viscosity mineral oil to form a sludge with a great excess of liquid. The equipment must be designed so that the sludge does not accumulate and dry out and thus become flammable. Inspect the dust-collecting system periodically to ensure that the dust is kept moist.

The best collectors for grinding or polishing stands are small units that serve one or two stands and have the power supply for the grinder or polisher, water circulation, and air blower interconnected so that the grinder or polisher cannot operate unless the collector system is operating. Connect the grinding or polishing machine to the collector by short, straight ducts. Do not allow dry dust to accumulate in the ducts. Clean all polishing machines each day, dust collector and suction pipes at least once a week.

Hydrogen is formed in the reaction of magnesium with water. Ventilate sludge pits adequately to prevent the accumulation of hydrogen. The sludge that collects under the hood frequently must be removed and spread out in thin layers on a noncombustible surface in a safe, isolated area. The sludge may be burned in small quantities. Sludge from dust collectors may be rendered noncombustible by reacting it with a 5% solution of ferrous chloride ($FeCl_2 \cdot 2H_2O$) in an open container placed outdoors.

Central collecting systems in which the dust is passed through long dry ducts, or conventional dust collectors using dry filters, are definitely not recommended, because accident records have indicated dry systems of these types to be extremely dangerous.

Wire Brushing. The dust generated during wire brushing also must be trapped in a water-wash dust collector to minimize fire hazards and prevent the formation of explosive concentrations. This same method of collection has proved suitable for removing the dust during the wire brushing of sheet containing thorium (HK31A and HM21A) and preventing contamination of the air and work area with low-level radioactive dust.

Surface Engineering of Titanium and Titanium Alloys

A. Bloyce, P.H. Morton, and T. Bell, University of Birmingham, U.K.

Introduction

TITANIUM AND ITS ALLOYS are characterized by low density relative to other structural metals and alloys, excellent corrosion resistance, and high specific proof strengths. Since titanium first became available in the mid-twentieth century, its major area of application has been in the aerospace industry, which makes up about 80% of its usage. Its level of use in chemical and petrochemical applications is also significant, and the combination of chemical and specific mechanical properties make titanium alloys ideal candidates for prosthetics in joint replacements. The desire to reduce moving mass in machinery is increasing interest in its use outside of these sectors (e.g., for use in general engineering applications, where titanium-base material is often a direct replacement for ferrous materials).

The first part of this article is concerned with cleaning and finishing operations that are used throughout titanium-related industry and are widely applied to semifabricated products (see Ref 1 and *Materials Properties Handbook: Titanium Alloys*, ASM International, 1994). The second part of the article describes surface engineering processes and their

application to titanium-base materials, which are, in the main, applied to near-finished components. These processes are used either to improve the wear resistance of the titanium-base material or to improve its oxidation resistance:

- The poor wear resistance of titanium (Ref 2) is caused by its low c/a ratio as a hexagonal close-packed metal. The slip systems produce relatively low shear strengths and a high coefficient of friction. Lower tensile strengths allow relatively easy material transfer to conterfaces in adhesive wear. Low hardness allows damage by abrasive and related wear mechanisms.
- The oxidation (Ref 3) and general corrosion resistance of titanium and its alloys are excellent at relatively low temperatures, but for conventional alloys, at around 430 °C (800 °F) and above, depending on exposure time, oxygen is taken up by the substrate, which causes embrittlement. Titanium γ-aluminide alloys have useful mechanical properties up to ~900 °C (1650 °F), but their oxidation resistance is satisfactory to only ~815 °C (1500 °F).

Some of the processes described in this article, such as electroplating and thermal spraying, are widely used; others, such as ion implantation, are starting to find industrial applications; still other processes are as yet used only for prototyping or producing relatively small numbers of products, such as for use in racing cars.

The dominant engineering characteristics of the metal and its alloys are their ability to form a tenacious surface oxide film in air that dissolves in the titanium and the fact that titanium reacts with all but the most stable materials at some temperature.

Acknowledgements

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References

1. *Surface Cleaning, Finishing, and Coating,* Vol 5, 9th ed., *Metals Handbook,* American Society for Metals, 1982, p 650-668
2. K.E. Budinski, Tribological Properties of Titanium Alloys, *Wear,* Vol 151, 1991, p 203-217
3. G. Bertrand et al., Oxidation of Titanium, *Oxid. Met.,* Vol 21 (No. 1/2), 1983, p 1-19

Cleaning and Finishing

Cleaning and finishing processes for titanium and its alloys are similar to those for other metals. Proper selection of processes, methods, and cleaning solutions are of major importance to procure maximum use of the finished metal and to maintain safe procedure during the working of titanium materials.

Generally, a heavy oxide layer resulting from hot working of the metal is removed by grit blasting or other mechanical means, or by salt bath descaling. After removal of the scale, further mechanical or chemical treatment is applied to remove the hardened, oxygen-rich metallic case beneath the scale in order to avoid cracking during subsequent working operations. Heavy grease, oil, and black lubricant coatings resulting from cold working are removed by alkaline or caustic soaking, followed by acid pickling. To remove soil or light oil from a metal, cleaning by detergents, solvent washing, or vapor degreasing is generally applied.

Cleaning and Descaling Problems

The metallurgical and chemical properties of titanium create a number of very special cleaning problems:

- Affinity of titanium to common gases
- Galvanic effects caused by discontinuities in scaled surfaces
- Metallurgical restrictions on the temperature of the descaling media

- Variety of scales encountered in titanium descaling
- Protective coatings used in titanium manufacturing

Gas Absorption. The property that causes the most difficulty is the capacity of titanium to absorb common gases, including oxygen, hydrogen, and nitrogen, all of which tend to embrittle the product. Because tightly packed hot-rolling scale acts as partial protection against additional gas absorption, some mills perform two or three heat treatments over the scale. Each additional heat treatment toughens the scale and compounds descaling difficulties. An additional problem is that heat-treating furnace atmospheres are maintained on the oxidizing side to prevent hydrogen pickup. A layer of oxygen-rich metal (Fig. 1) develops beneath the resulting scale formation, varying in thickness from 0.05 to 0.07 mm (0.002 to 0.003 in.) in the heat-treated condition to 0.15 to 0.20 mm (0.006 to 0.008 in.) in the hot-rolled condition. This brittle surface is usually removed by acid or electrolytic chemical pickling.

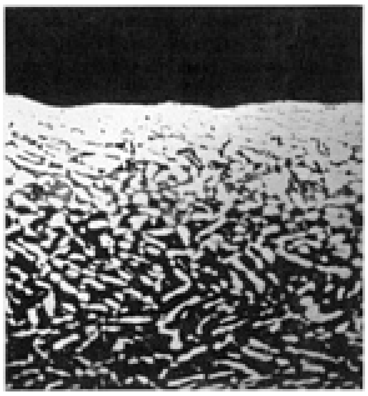


Fig. 1 Ti-6Al-4V alpha case. 250×

Galvanic effects and discontinuities in the surface scale are encountered in all types of metal descaling, but they appear to be more pronounced in titanium. Although the exact cause of small pits or cells formed in descaled material is debatable, possibilities include alloy or nonmetallic segregations, scale porosity, and surface contamination. A more severe galvanic attack problem is created by patch scale conditions on titanium surfaces when areas of heavy scale flake away from an apparently uniform surface. The same problem has been observed with superimposed oxides, even though the surface layer may be quite thin and powder-like. Surface contamination with oil, grease, or fingerprints can also create a patch scale condition. All of these factors promote severe localized attack when areas of the substrate metal are exposed selectively during descaling. Some producers have considered reoxidation of the product during processing as a possible solution.

Metallurgical Restrictions on Descaling. Solution-treated, age-hardenable titanium alloys are sensitive to time-temperature reactions and the temperatures of descaling media. The metastable or high-beta alloys, which are solution treated and aged at temperatures ranging from 370 to 540 °C (700 to 1000 °F) for $\frac{1}{2}$ h or more, may undergo a subsequent aging effect and cause a change in mechanical properties. This is particularly true in thin-gage sheet materials and may cause property changes of as much as 70 MPa (10 ksi) in tensile strength. These alloys normally should not be allowed to exceed 260 °C (500 °F).

Variety of Scale. Another factor that contributes appreciably to titanium descaling problems is the wide variety of scale encountered, including scale formed by annealing, forging, solution treating, stress relieving, extruding, rolling, aging, hot forming, or a combination of several of these operations. With processing temperatures ranging from 425 to 1150 °C (800 to 2100 °F), the scale spectrum for titanium is far broader than for most other difficult-to-descale materials.

Protective coatings are often used in titanium manufacturing operations. These coatings, which are an asset and a necessity in manufacturing operations, become a liability and a contaminant in cleaning operations. They are soluble and removable if the proper techniques are used. Protective coatings are applied to titanium surfaces during manufacturing operations to:

- Lubricate and aid in metal flow, good die contouring, and forming operations
- Act as barrier films, reducing gas contamination during high-temperature forming and heat-treating cycles
- Reduce surface flaws caused by nicking and scratching during manufacturing operations

The gas protective films are usually applied directly to the titanium surface. They are silicate-based materials that deposit uniform fusible films through solvent evaporation. These films form glassy barriers at treatment temperatures up to 815 °C (1500 °F) and are quite effective in reducing oxygen, hydrogen, and nitrogen contamination. Above 815 °C (1500 °F), most of these films are less effective, because speroidizing creates voids in the film. Lubricant films or abrasion-protective films are applied over a silica-based coating. This process has the advantage of providing double protection against scratching and scoring. During hot forming operations and metal surface stretching, some voiding and penetration occurs, creating a titanium oxide on the surface. The contaminant then consists of organic bond or residues, graphite, molybdenum disulfide, silicates, and titanium oxides.

Removal of Scale

Scale is removed from titanium products by several mechanical methods. Abrasive methods, such as grinding and grit blasting, are preferred for removing heavy scale from large sections. Centerless grinding is used for finishing round bars, and wide-belt grinding is used for finishing sheet and strip. Grinding is usually most efficient when it is performed at low wheel and belt speeds.

Most alloy sheet materials with a high aluminum content, such as Ti-5Al-2.5Sn, are ground to eliminate pits and a rippled condition that develops in hot rolling as a result of discontinuous slip during plastic deformation. Grinding is frequently used to eliminate surface defects before cold rolling. Originally, strip was ground on standard strip grinders, using various oil lubricants; however, oils contributed to fire hazard and several grinding machines were partially or wholly destroyed when the oil ignited. When titanium was ground with aluminum oxide belts, a water lubricant was less effective than air. The water reacted with the aluminum oxide to form a weak hydroxide that proved ineffective as a grinding lubricant.

Belt Grinding. Dry belt grinding is dangerous because fine titanium powder can explode or ignite. Dry belt grinding is also uneconomical because of poor belt life. When stock is removed during dry grinding, small globules of molten metal and oxide roll along the sheet, causing a type of pitting by burning that is not removed by the grinding. Weld grit scratches and embedded grit result when titanium welds to the dry grit.

A 5% aqueous solution of potassium orthophosphate, K_3PO_4, is widely used as a grinding lubricant. It is applied as a flood at both the entrance and exit sides of the contact line. Water-soluble oils, particularly highly chlorinated and sulfochlorinated oils, have also been successful as lubricants. These compounds should be used with care because of the possibility of chloride residues remaining as an integral part of the surface. Both types of lubricants improve grinding efficiency when the belts are coated with aluminum oxide or silicon carbide.

Flooding the work with lubricant is recommended; however, machines built for flooding are equipped with a recirculating and filtering system and waterproof cloth belts, and they are expensive. An alternative is to spray a water-soluble wax fog through atomizing nozzles on the line of contact at both the entrance and exit sides of the belt. The solution should not be sprayed through an ejector that mixes it with air and increases the fire hazard; instead, it should be sprayed as an atomized liquid. Application of the spray can be controlled to volatilize the lubricant during grinding. This eliminates the need for waterproof belts. Care must be exercised to avoid a buildup of titanium chips that may cause a fire. Chips that would wash away in a flood are not removed by the spray.

Titanium should be ground at belt speeds not exceeding rates of 8 m/s (25 ft/s). Using a 5% solution of potassium orthophosphate as a lubricant, maximum efficiency is achieved at about 6 m/s (18 ft/s). Both billy roll and flat table

grinding machines have been successful in grinding titanium. Sheet grinding machines, equipped with feed rolls, sometimes leave a ground line on the sheet where the feed rolls, on the exit side of the machine, and interrupt uniform travel when they grip the sheet. A high degree of grinding uniformity is obtained on machines equipped with a flat table and vacuum chuck. On these machines, the table holding the sheet usually oscillates. Traveling-head machines are available also.

The belt grinding sequence is usually begun with an 80-grit belt when it is necessary to remove more than 0.07 mm (0.003 in.) of stock from the surface of the sheet. Descaling and pickling the sheet before grinding prolongs belt life. Following the initial grit, each successive grit must remove enough stock to eliminate the scratches caused by the previous grit. The alpha alloys, such as Ti-5Al-2.5Sn, are less sensitive to surface condition than the alpha-beta alloys, such as Ti-6Al-4V. Surface pits on Ti-6Al-4V sheet, caused by weld grit scratches, seriously detract from bend ductility. A flow chart for the belt grinding of Ti-6Al-4V sheet is shown in Fig. 2.

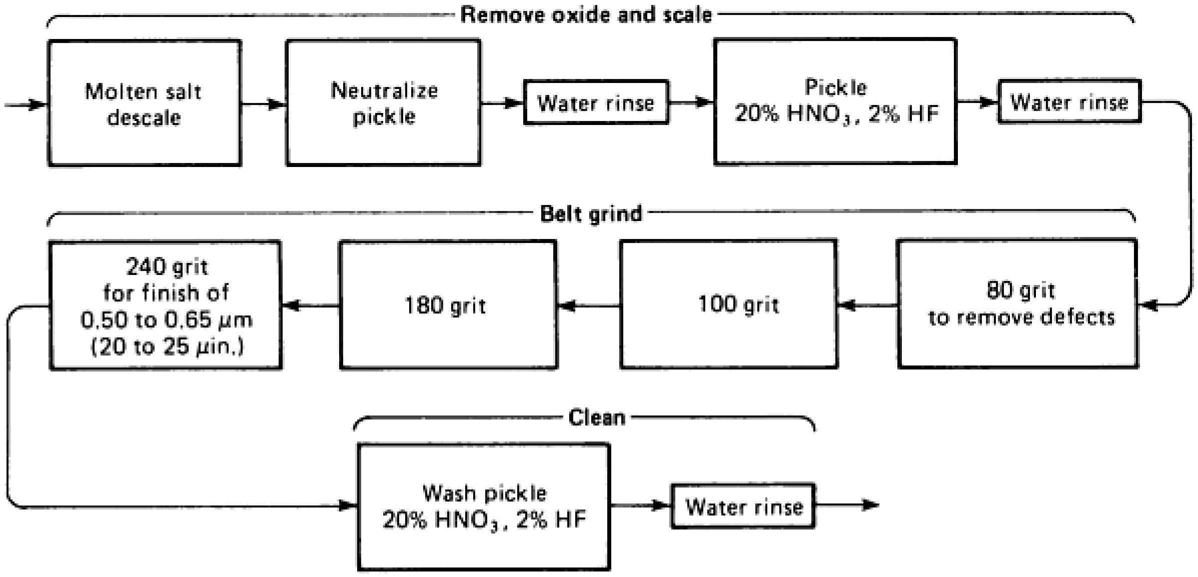


Fig. 2 Cleaning and belt grinding sequences for Ti-6Al-4V sheet

Abrasive blast cleaning techniques, either wet or dry, are convenient for removing scale from a variety of titanium products, ranging from massive ingots to small parts. Because it can be used at lower velocities and is less likely to be embedded in the surface, alumina sand is preferred to silica sand.

Sheet thicknesses to about 0.50 mm (0.020 in.) can be descaled without distortion if fine sand and low velocities are used. Mill scale on titanium products can be removed with coarse high-carbon steel shot or grit, whereas finished compressor blades can be cleaned with zircon sand of 150- to 200-grit. The type of product to be cleaned, the cleaning rate, and the cost of the abrasive must be balanced in the selection of a specific blast cleaning method.

Mineral abrasive particles, such as silica, zircon, or alumina sands, are used more commonly than metal abrasives for blasting finished or semifinished products. Although these abrasives are more expensive, they produce the finer finish that is required in final processing or service. Adequate safety precautions must be observed to avoid inhalation of fine sand particles. Air-circulating and dust-collecting systems must be cleaned frequently and equipped to cope with the fire hazard associated with titanium dust.

A fine dust remains on the titanium from the blasting operation, particularly when mineral abrasives have been used. This is not considered detrimental, although a washing or pickling cycle following the blast is desirable if the part is to be welded subsequently. The following describes a wet blasting procedure and a dry blasting procedure used for descaling titanium parts:

- *Wet blasting:* Parts are wet blast cleaned, using a slurry that consists of 400-grit aluminum oxide (40 vol%) and water. Air pressure of 655 kPa (95 psi) is used to pump the slurry in a steady stream with a

pressure of about 34 kPa (5 psi). The descaling rate, normally about 50 min/m^2 (5 min/ft^2), depends on the complexity of the part. Distortion and the need for planishing are held to a minimum by placing the blast nozzle approximately 50 mm (2 in.) from the workpiece and by using a 60° angle of impingement.

- *Dry blasting:* Rocket motor case assemblies are dry blasted after final stress relieving at 480 to 540 °C (895 to 1005 °F). Blasting is accomplished with 100- to 150-grit zircon sand at an air pressure of 275 kPa (40 psi). Each assembly is rotated at 2.5 rpm and is passed at a speed of 65 mm/min (2.5 in./min) between two diametrically opposed fixed-position blasting nozzles. The nozzles blast the inside and outside surfaces simultaneously at the same wall location. To prevent distortion, each nozzle is placed at the same distance, 300 mm (12 in.), from the metal surface.

Molten salt descaling baths are primarily used for descaling, bar, sheet products, and tubing. With the most effective barrier films available today, some gas penetration of titanium surfaces can be expected at the elevated temperatures required for working and heat treatment. The alpha case or oxygen-enriched layer resulting from this gas reaction is extremely hard and brittle and must be removed. Bar products used for machining finished parts must have this hard scale and oxide removed because they are very abrasive and cause rapid tool wear. These scales must be removed before welding or forming, or poor and small welds will be made and forming (hot or cold) will be virtually impossible without surface rupture or failure of parts. Removal presents no serious problems, because chemical milling techniques have been perfected by the aircraft industry to effect weight savings. In the case of titanium, the purpose is to improve the structural soundness of metal, and the solvent materials applied are of a different chemical composition.

One specific problem encountered in alpha case removal is that the titanium oxide formed is substantially more insoluble in the nitric hydrofluoric etchant than the base metal. Residues of oxide on the surface develop areas resembling craters on the finished product. Figure 3 illustrates the effect of surface condition on etched metal surfaces.

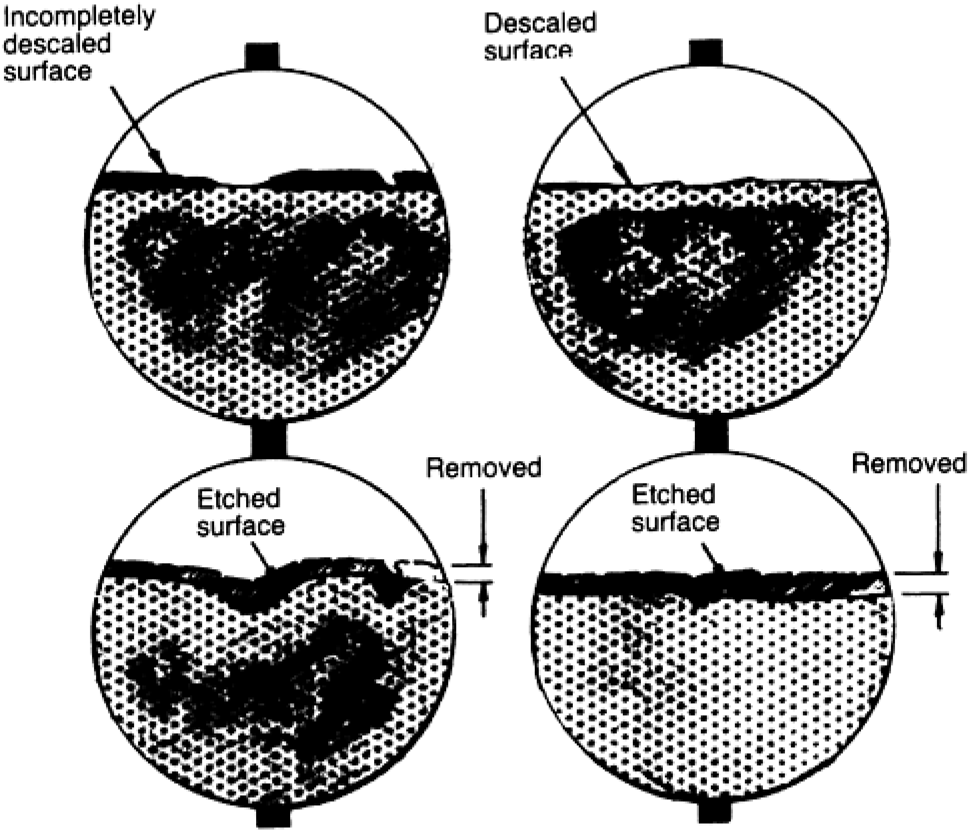


Fig. 3 Effect of surface condition on etched metal surface

Where alpha case removal is required, salt bath cleaning is specified, because proper cycling practically guarantees a chemically clean surface. Conditioning salt baths fall into two basic categories: high-temperature salt baths and low-temperature salt baths.

High-temperature salt baths may vary in chemical reaction and effectiveness, depending on composition. All types operate at a range of 370 to 480 °C (700 to 895 °F). The temperature range is sufficiently high to produce the most rapid reaction possible for soil and oxide films. High-temperature oxidizing salt baths are also capable of reacting chemically with organic films to destroy them. These baths are also excellent solvents for silicate barrier films. They do require special fixturing to reduce the strong galvanic effects present at these temperatures, and for this reason, they are used in cleaning primary forming operation products, such as forgings, extrusions, rolled plate, and sheet. The major advantage of high-temperature oxidizing or reducing salt baths for titanium descaling is their great speed in removing extremely tenacious scale. Although reducing baths have the inherent disadvantage of promoting hydrogen absorption, this can be overcome or minimized by chemical additions. Vacuum degassing is another solution.

A primary producer of titanium sheet uses an oxidizing salt bath for removing the hot-work scale in the following sequence of operations:

1. Immerse in oxidizing salt for 5 to 20 min at 400 to 480 °C (750 to 895 °F).
2. Quench with water 1 min.
3. Immerse in sulfuric acid, 10 to 40 vol%, for 2 to 5 min at 50 to 60 °C (120 to 140 °F).
4. Rinse with water 1 min.
5. Recycle if necessary.
6. Pickle in nitric-hydrofluoric acid solution, time and concentration as required.

The same producer also uses a sodium hydride reducing salt bath for descaling high-beta or metastable beta alloys. A typical cycle using this type of salt is:

1. Immerse in reducing salt for 1 to 3 min at 370 °C (700 °F).
2. Quench in water 1 min.
3. Immerse in sulfuric acid (10 to 40 vol%) for 2 to 5 min at 50 to 60 °C (120 to 140 °F).
4. Rinse in water.
5. Pickle in nitric-hydrofluoric acid solution, time and concentration as required.
6. Vacuum degas or decontaminate titanium beta alloys that absorb hydrogen in reducing baths.

These baths are used by one major aerospace contractor for cleaning titanium blades for jet engines. The blade materials are Ti-6Al-4V and Ti-8Al-1Mo-1V. The descaling cycles for removing oxides and proprietary glass-like compounds from these blades are:

1. Immerse in oxidizing salt for 15 min at 455 °C (850 °F).
2. Rinse in cold water.
3. Pickle in solution of 35% nitric acid and 3.5% hydrofluoric acid for 1 min max at 20 °C (70 °F).
4. Rinse in hot water.

Low-Temperature Baths. The temperature range used for cleaning fabricated parts is 200 to 220 °C (390 to 430 °F). Descaling systems based on salts in this temperature range eliminate some of the possible problems associated with higher-temperature baths, including:

- Age hardening
- Dissimilar metal reactions
- Chemical attack
- Metal distortion

- Hydrogen embrittlement

Salts in this range have a very limited composition because of the effect of various compounds on the melting point. Although they contain oxidizing agents, the effect of these materials is not as aggressive as it is in the high-temperature fused salts. Consequently, organic materials are not destroyed, but are saponified and absorbed. Silicate barrier films and molybdenum disulfide are soluble in these low-temperature salts. The temperature range permits cycling between salt and acid to reduce cleaning times and costs. Examples of salt bath and acid cycle times are given in Table 1.

Table 1 Low-temperature salt bath and acid bath conditions for cleaning titanium alloys

Sample composition	Scale formation temperature		Salt bath immersion time[(a)], min	Acid cleaning bath time[(b)], min	Acid cleaning bath time[(c)], s
	°C	°F			
Ti-6Al-4V	650	1200	2	2	30
Ti-8Al-1Mo-1V	650	1200	2	2	30
Ti-8Al-1Mo-1V	820	1510	5	2	30
Ti-6Al-4V[(d)]	820	1510	5	5	30
Ti-6Al-4V[(e)]	950	1745	5	5	60
Ti-8Al-1Mo-1V[(f)]	950	1745	5	5	60

(a) Salt bath temperature 205 °C (400 °F).

(b) Bath composition, 30% sulfuric acid.

(c) Bath composition, 30% nitric acid, 3% hydrofluoric acid.

(d) Sample recycled in salt bath for 5 min, in sulfuric acid bath for 5 min, in nitric acid-hydrofluoric acid bath for 30 s.

(e) Sample recycled in salt bath for 5 min, in sulfuric acid bath for 5 min, in nitric acid-hydrofluoric acid bath for 60 s.

(f) Sample recycled in salt bath for 5 min, in sulfuric acid bath for 5 min, in nitric acid-hydrofluoric acid bath for 60 s

Aqueous caustic descaling baths have been developed to remove light scale and tarnish from titanium alloys. Aqueous caustic solutions containing 40 to 50% sodium hydroxide have been used successfully to descale many titanium

alloys. One bath containing 40 to 43% sodium hydroxide operates at a temperature near its boiling point (125 °C, or 260 °F). Descaling normally requires from 5 to 30 min. Immersion time is not critical because little weight loss is encountered after the first 5 min. Caustic descaling conditions the scale so that it is removed readily during subsequent acid pickling.

A more effective aqueous solution contains either copper sulfate or sodium sulfate in addition to sodium hydroxide. This bath operates at lower temperature (105 °C, or 220 °F). A composition of this solution by weight is: 50% sodium hydroxide, 10% copper sulfate pentahydrate ($CuSO_45H_2O$), and 40% water. Using immersion times of 10 to 20 min, this bath has proved effective in descaling Ti-6Al-4V and Ti-2.5Al-16V alloys.

Pickling Procedures following Descaling

All advantages gained through proper conditioning and handling of titanium parts during cleaning can be lost if the composition of the final pickling acid is not controlled. Cold spent acid solutions increase appreciably the time required for pickling and the possible quality problems experienced with hydrogen pickup. Highly concentrated hot acids can be overly aggressive, resulting in surface finish problems such as a rough and pitted surface caused by preferential acid attack. Sulfuric acid, 35 vol% at 65 °C (150 °F), is recommended for pickling immediately following salt bath conditioning and rinsing to remove molten salt and residual softened scales. An acid of this formula has very little effect on titanium metal. Metal salts in the original and additional acid solutions further minimize these base metal attacks. Table 2 gives conditions for corrosion of titanium in various sulfuric acid pickle baths.

Table 2 Corrosion of titanium in sulfuric acid pickle baths

A nitric-hydrofluoric acid solution, which is the final stage brightening in most alloy cleaning lines, should be maintained at a minimum ratio of 15 parts nitric acid to 1 part hydrofluoric acid to reduce hydrogen pickup effects. The concentration of hydrofluoric acid may vary from 1 to 5%, or even higher as long as the ratio is not exceeded. The activity of these pickle solutions is affected by titanium content, and the acids are frequently discarded at a level of 26 g/L (3 oz/gal). The solution used for final brightening can be used for the required alpha case removal also, with careful watch of titanium content.

Sulfuric acid concentration, %	Acid addition	Bath temperature		Corrosion rate	
		°C	°F	μm/yr	mils/yr
30	0.5% copper sulfate	38	100	100	4.0
30	1% copper sulfate	38	100	20	0.8
30	10% copper sulfate	38	100	400	16.0
30	0.25% copper sulfate	95	205	76	3.0
10	2% ferrous sulfate	Boiling point	Boiling point	125	5.0
17	7-8% ferrous sulfate	60	140	125	5.0

Removal of Tarnish Films

Tarnish films are thin oxide films that form on titanium in air temperatures between 315 and 650 °C (600 and 1200 °F). After exposure at 315 °C (600 °F), the film is barely perceptible, but with increasing temperature and time at temperature, it becomes thicker and darker. The film acquires a distinct straw yellow color at about 370 °C (700 °F) and a blue color at 480 °C (900 °F). At about 650 °C (1200 °F), it assumes the dull gray appearance of a light scale. Alloying elements and surface contaminants also influence the color and characteristics.

Tarnish films are readily removed by abrasive methods, and all but the heaviest films can be removed by acid pickling. Prolonged exposures at temperatures above about 595 °C (1105 °F), in combination with surface contaminants, result in heavier surface films that are not removed satisfactorily by acid pickling and so require descaling treatments.

Acid pickling removes a light amount of metal, usually a few microns. It is used to remove smeared metal, which could affect penetrant inspection. Titanium and titanium alloys can be satisfactorily pickled by the following procedure:

1. Clean thoroughly in alkaline solution to remove all shop soils, soap drawing compounds, and identification inks. If coated with heavy oil, grease, or other petroleum-based compounds, parts may be degreased in trichloroethylene before alkaline cleaning. Degreasing will not be harmful to the part in subsequent processing.
2. Rinse thoroughly in clean running water after alkaline immersion cleaning.
3. Pickle for 1 to 5 min in an aqueous nitric-hydrofluoric acid solution containing 15 to 40% nitric acid and 1.0 to 2.0% hydrofluoric acid by weight, and operated at a temperature of 24 to 60 °C (75 to 140 °F). The preferred acid content of the pickling solution, particularly for alpha-beta and beta alloys, is usually near the middle of the above ranges. A solution of 33.2% nitric acid and 1.6% hydrofluoric acid has been found effective. When the buildup of titanium in the solution reaches 12 g/L (2 oz/gal), discard the solution.
4. Rinse the parts thoroughly in clean water.
5. High-pressure spray wash thoroughly with clean water at 55 ± 6 °C (130 ± 10 °F).
6. Rinse in hot water to aid in drying. Allow to dry.

To avoid excessive stock removal, the recommended immersion times for pickling solutions should not be exceeded. It is equally important to maintain the composition and operating temperature of the bath within the limits prescribed to prevent an excessive amount of hydrogen pickup. Gage loss from all acid pickling after descaling is estimated to be less than 0.025 mm/min (0.001 in./min), depending on the combination of variables used.

Hydrogen contamination is estimated to be 0 to 15 ppm per 0.025 mm (0.001 in.) of metal removed, depending on alloy composition and gage material pickled. Table 3 gives data on hydrogen pickup for an alpha, an alpha-beta, and a beta alloy pickled in a 15% nitric acid, 1% hydrofluoric acid bath at 49 to 60 °C (120 to 140 °F). Hydrogen contamination can be held to a minimum by maintaining an acid ratio of 10 to 1 or greater of nitric acid to hydrofluoric acid. Hydrogen diffuses more rapidly into the beta phase. Alpha-beta alloys that have α+ β microstructures, which have been heat treated to complete equilibrium, pick up less hydrogen than microstructures of transformed beta and/or simple mill-annealed structures.

Table 3 Effect of titanium alloy composition on hydrogen pickup in acid pickling

Pickling bath is an aqueous solution containing 15% nitric acid and 1% hydrofluoric acid by weight; operating temperature is 49 to 60 °C (120 to 140 °F).

Alloy	**Thickness**		**Hydrogen pickup (gage removed), ppm/0.0250 mm (ppm/0.001 in.)**
	mm	**in.**	
Alpha alloy			
Ti-5Al-2.5Sn	0.50	0.020	0-4
Ti-5Al-2.5Sn	1.00	0.040	0-3
Alpha-beta alloy			

Ti-6Al-4V	0.50	0.020	4-7
Ti-6Al-4V	1.00	0.040	3-5
Beta alloy			
Ti-13V-11Cr-3Al	0.50	0.020	10-15
Ti-13V-11Cr-3Al	1.00	0.040	5-8

Mass Finishing (Barrel Finishing). Oxide films formed by heating to temperatures as high as 650 °C (1200 °F) for 30 min have been effectively removed from Ti-8Mn alloy parts by wet mass finishing. At barrel speeds of 43,000 to 51,000 mm/min (1700 to 2000 in./min), parts have been cleaned satisfactorily in about 1 h. Complete barrel loading procedures for three barrels, ranging from 0.02 to 0.25 m^3 (0.75 to 8.85 ft^3) capacity, are given in Table 4.

Table 4 Mass finishing conditions for titanium parts

Barrel size						Speed, rev/min	Part load		Medium[(a)]		Water		Abrasive compound[(b)]		Alkaline cleaner[(c)]	
Capacity		Diameter		Width												
m^3	ft^3	mm	in.	mm	in.		kg	lb	kg	lb	L	qt	kg	lb	kg	lb
0.02	0.75	381	15	178	7	36	1-2	3-4	18	40	1.2	1.25	0.2	0.5	0.2	0.5
0.07	2.33	559	22	240	10	28	4-5	8-12	54	120	4	4	0.7	1.5	0.34	0.75
0.25	8.85	813	32	457	18	20	14-18	30-40	209	460	14	15	2.3	5	0.5	1

(a) Aluminum oxide nuggets 6.4 to 38 mm (0.25 to 1.5 in.) or preformed vitrified chips 4.8 by 9.5 to 7.9 by 28.6 mm ($\frac{3}{16}$ by $\frac{3}{8}$ to $\frac{5}{16}$ by $1\frac{1}{8}$ in.).

(b) Dry, mildly alkaline compound.

(c) Mild cleaner with high soap content

In mass finishing of titanium parts, the ratio of medium to parts should be between 10 and 15 to 1, depending on the size of the parts. Proportionately more medium is required as part size increases. Water is used to cover parts and medium. Surface finish is improved when more water is added, but cycle time required to obtain a given finish is increased. The rate of descaling increases directly with barrel speed but is limited by the fragility of the parts being processed. Parts are randomly loaded in the barrel and rotated at relatively low barrel speeds to minimize distortion and nicking. Conditions for mass finishing of titanium parts are also given in Table 4.

Aluminum oxide media are the most satisfactory. They do not contaminate the work and have a long useful life. For oxide removal, small well-worn media produce the highest finish. To avoid possible metallic contamination, the medium used for titanium should not be used in processing other metals. Strong acid-forming compounds should be avoided, principally because they are corrosive and contribute to hydrogen embrittlement. Because of the fire hazard created by fine, dry titanium particles, dry mass finishing of titanium parts is not recommended.

Polishing and Buffing

The polishing and buffing of titanium is accomplished with the same equipment used for other metals. Polishing is frequently done wet, using mineral oil lubricants and coolants. Silicon carbide abrasive cloth belts have been effective. It is common to polish in two or more steps, using a coarser grit initially, such as 60 or 80, to remove gross surface roughness, followed by polishing with 120- or 150-grit to provide a smooth finish. Titanium tends to wear the sharp edges of the abrasive particles and load the belts more rapidly than steel. Frequent belt changes are required for effective cutting. A good flow of coolant improves polishing and extends the life of the abrasives.

Dry polishing is more appropriate than wet for some applications. For these operations, belts or cloth wheels with silicon carbide abrasive may be used. Soaps and proprietary compounds may be applied to the belts to improve polishing and to extend belt life. Abrasive belt materials that incorporate solid stearate lubricants offer improved results for dry polishing operations.

Fine polishing of titanium articles for extremely smooth finishes requires several progressive polishing steps with finer abrasives until pumice or rough types of abrasive are applied. With the softer grades of titanium, such as unalloyed material, fine polishing requires more time and care to prevent scratching. The harder alloy grades can be polished more readily to a surface of high reflectivity. If a matte finish is desired, wet blasting with a fine slurry may be used after initial polishing.

Titanium alloys can be buffed safely. The purpose of buffing is to improve the surface appearance of the metal and produce a smooth tight surface. Buffing is used as a final finishing operation and is particularly adaptable to finishing a localized area of a part. Parts such as joint prostheses, pacemakers, and heart valves require a highly buffed tight surface to prevent entrapment of particles. Close-fitting parts for equipment, such as guidance systems and electronics applications, require highly polished surfaces obtained by buffing. In addition, sheet sizes too large to be processed by other abrasive finishing methods, such as mass finishing or wet blasting, can be economically processed by buffing.

The principal limitations of buffing are distortion, caused by the inducement of localized stress; surface burning, resulting from prolonged dwell of the buff; an inability to process inner or restricted surfaces; and the feathering of holes and edges. Proper care of the buffing wheel is essential. Buffing with insufficient compound or a loaded wheel produces burning or distortion of the part. After buffing, no further cleaning of parts is required except degreasing to remove the buffing compound.

Wire Brushing

Wire brushing of titanium alloys is not recommended when other finishing methods, such as buffing, can accomplish the objective. In one case, wire brushing resulted in serious defects. A stiff-bristled wire brush removed surface scratches and oxide films, but the surface was pitted by the wire tips. To avoid pitting, softer wire bristles were tried, and the surface of the titanium acquired a burnished appearance. When the surface layers were cold worked, the grinding scratches, instead of being removed, were filled with smeared metal. Wire brushing with a silicon carbide abrasive grease has been used successfully to remove burrs, break sharp edges from edge radii, and blend chamfers.

Removal of Grease and Other Soils

Removal of grease, oil, and other shop soils from titanium parts is normally accomplished with the same type of equipment and the same cleaning procedures used for stainless steel and high-temperature alloy components.

Vapor degreasing normally employs either trichloroethylene or perchloroethylene. Under certain conditions, these solvents are known to be a cause of stress-corrosion cracking in titanium alloys. Methylethyl ketone is used as a cleaner in situations where chlorinated solutions are not desired. All titanium parts should be acid pickled after vapor degreasing.

Other cleaning methods use chemicals that, if they are left to dry on the part, may have a harmful effect on the properties of titanium. Among these are soda ash, borates, silicates, and wetting agents commonly used in alkaline cleaners; kerosine and other hydrocarbon solvents used in emulsion cleaners; and mineral spirits employed in hand wiping operations. Residues of all these cleaning agents must be completely removed by thorough rinsing. To ensure that a surface that is free of contaminants, rinsing is frequently followed by acid pickling.

Surface Modification

Ion Implantation

The ion implantation process involves the acceleration of ions to a sufficiently high velocity so that they are able to penetrate the surface of the substrate material being implanted. The mean depth of penetration depends on the energy, the atomic number, the atomic masses of the implanted and the target species, and the angle of incidence. A 1 mA beam takes approximately 16 s to achieve a dose of 1×10^{17} ions over 1 cm^2, assuming perfect implantation. Industrial implanters are typically designed to accelerate the ions to energies of between 50 and 200 keV, resulting in implant layer thicknesses of up to several hundred nanometers. High ion current densities, 30 to 40 $\mu A/cm^{-2}$, reduce the time necessary to reach a required dose, but they significantly increase the workpiece temperature, which is also dependent on the thermal mass of the substrate, which may in turn be influenced by appropriate heat sinking.

Wear resistance of titanium and titanium alloys may be improved by ion implantation. This is the most commercially used aspect of the technology applied to titanium substrates. The most commonly implanted species are nitrogen and carbon, which may be noted from a review of the ion implantation of Ti-6Al-4V (Ref 4). This improvement in wear behavior is effected by the increase in surface hardness that is achieved by ion implantation offsetting a change in wear mechanism from mild oxidative to severe adhesive wear. The surface oxide layer formed on titanium and conventional titanium alloy substrates provides a useful low-friction surface, but when this oxide is removed, rapid adhesive wear occurs against many counterface materials. An increase in near-surface hardness allows the material to resist plastic deformation at higher stresses and hence support the oxide at higher stresses. A threefold increase in microhardness at loads of 1 to 2 g can be achieved in these alloys (Ref 5).

There are three mechanisms from which hardening of ion implanted titanium arises: ion-induced damage, solid solution hardening, and precipitation hardening. Ion-induced damage arises from the creation of a dense network of dislocations similar to that achieved during cold working or in shot peening: improvements in fatigue properties may be achieved through appropriate ion implantation. The strain fields associated with the dense dislocation network require that a higher-energy barrier be overcome to enable the atomic motion required for plastic deformation.

Solid solution hardening may be achieved by either substitutional or interstitial alloying elements. The strain field associated with an "impurity" atom increases the load required to permit dislocation movement.

Precipitation hardening is effected by dislocations being pinned by coherent or incoherent precipitates. For the maximum precipitation hardening effect, a fine distribution of coherent precipitates is required. For very low ion doses, $\sim 10^{15}$ to 10^{16} ions/cm^2, damage-induced hardening effects dominate; for intermediate doses, $\sim 10^{16}$ to 10^{17} ions/cm^2, solid solution hardening becomes dominant; for high doses, $>10^{17}$ ions/cm^2, precipitation hardening dominates. The boundaries obviously depend on the physical properties of the implanting and implanted species and the relevant phase equilibria.

The hardening effect achieved in implantation of nitrogen into Ti-6Al-4V is shown in Fig. 4, the maximum hardness increase being in excess of 170% at a depth of 50 nm below the surface. In this case, the microstructure of nitrogen-implanted Ti-6Al-4V consisted of a fine dispersion of TiN precipitates in a deformed nitrogen-rich matrix. This resulted in a hardening of the surface region and the presence of surface compressive residual stresses. A dose of 1×10^{17} atoms N/cm^2 improved the wear resistance, but no TiN precipitation was observed. The survival of the implanted layer was extended by increasing the ion dose to 4×10^{17} atoms N/cm^2, where the hardness increase levels off. The slower oxidative wear mode was obtained against both ruby and steel in ball-against-disc wear tests.

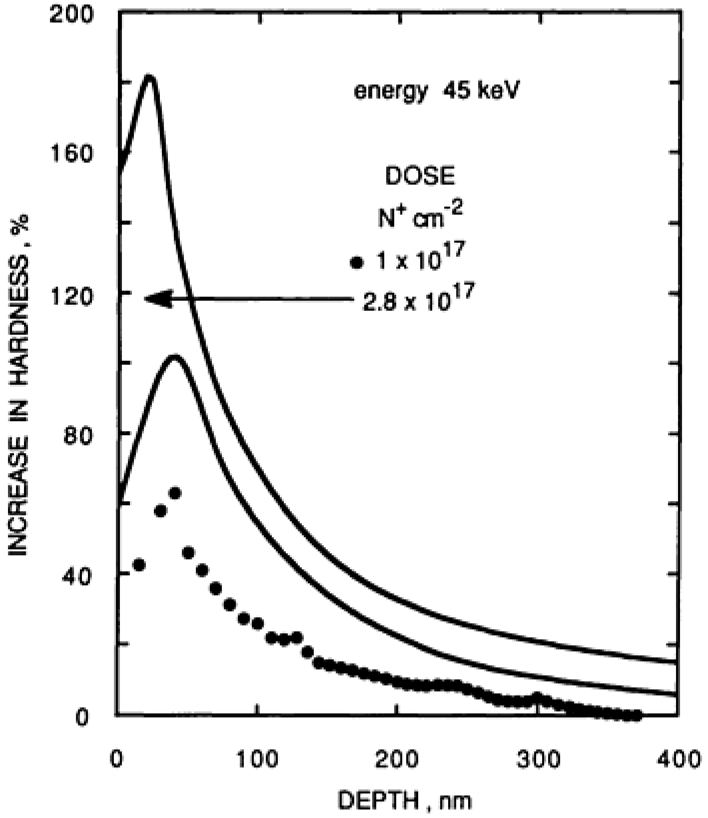


Fig. 4 Percentage increase in hardness with depth into material for N^+ implanted Ti-6Al-4V. Source: Ref 6

In addition to the simple hardening mechanism, ion implantation is thought to supply a reservoir of nitrogen to the oxide layer when it is removed, with the result that the reformed surface layer is possibly an oxynitride. Low wear rates have been maintained to depths two to three times the depth of the implanted layer, which can be explained in terms of physical displacement due to plowing during the wear process. The relative effects on hardness of nitrogen- and carbon-implanted Ti-6Al-4V are shown in Fig. 5. The very low solubility of carbon in α-Ti as compared to that of nitrogen in α-Ti limits the contribution of solid solution strengthening to the hardnesses measured.

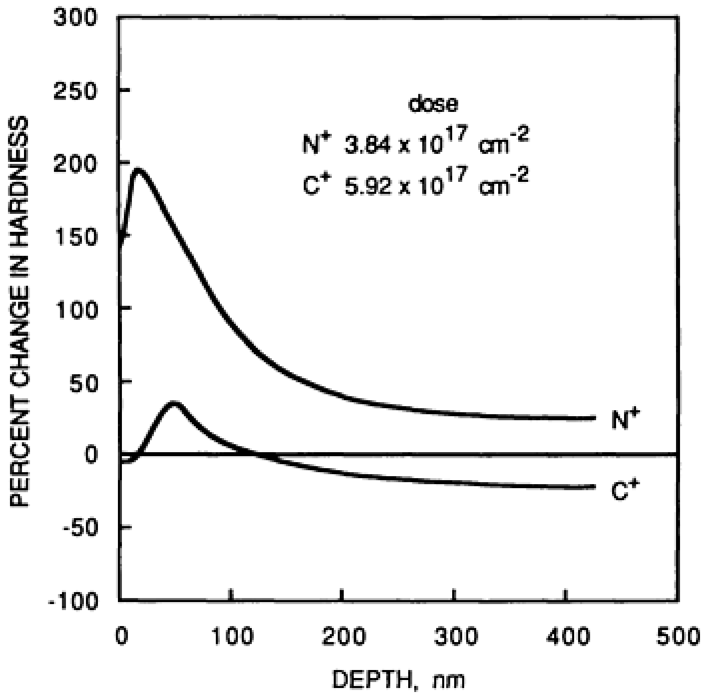


Fig. 5 Percentage change in hardness with depth for N^+ and C^+ implanted Ti-6Al-4V. Source: Ref 7

An example of the application of an ion-implanted titanium alloy is in total joint replacement, where the excellent biocompatibility combined with its specific mechanical properties make the use of Ti-6Al-4V desirable. The combination of this alloy and ultrahigh-molecular-weight polyethylene is unsatisfactory because of unacceptably high levels of wear in the joint. Ion implantation can improve this situation. In α+ β alloys such as Ti-6Al-4V, a hard α-case is produced at the surface because of the high levels of the α-stabilizing element, nitrogen, present. Although significant improvements in wear resistance for ion-implanted femoral heads have been noted in many investigations, wear does occur through a combination of oxidative wear, caused by the loss of the passivating oxide debris. The use of the process in the treatment of biomaterials has reached some degree of commercial maturity (Ref 5). Alloys used in hip, knee, and small quantities of wrist, shoulder, finger, and toe joint replacements are routinely ion implanted. Ion implantation of titanium and titanium alloys for improvements in wear is best summarized by noting that the very small depth to which hardening of the substrate alloy occurs allows these significant improvements to be effective only in moderately mild regimes of wear.

Other areas of application (Ref 5) are found in gas turbines, where discs and blades are implanted. Fretting wear is the problem, which can be significantly reduced by ion implantation. The best results using this process are obtained when one surface is treated with carbon and the other surface is implanted with a different species, such as nitrogen. Titanium gears for a variety of low-load aircraft applications are used because of weight savings, and problems of scuffing can be reduced by nitrogen implantation. Titanium components for use in hydraulic systems are often used because of the corrosion-resistant nature of the metal and its alloys. Ion implantation has been used to reduce galling against both steel and other titanium alloy counterface materials. Titanium ball valves articulating against PEEK valve seats suffer unacceptably high rates of wear, producing leaks after as few as ten open/close cycles. Ion-implanted balls withstand 100 operations with no sign of abrasion.

High cycle fatigue may be influenced by ion implantation with both nitrogen and carbon. Increases in fatigue strength have been measured in rotating beam fatigue tests (Ref 8). The endurance limits have been increased for both implanted species, the largest increase being 20% achieved with carbon implantation. The improvements are attributed to the creation of residual compressive stresses at the surface of the Ti-6Al-4V substrate, though the reasons for the greater improvement achieved with carbon implantation over that achieved with nitrogen implantation are not clear.

Corrosion behavior of titanium and titanium alloys can be modified by appropriate surface alloying using ion implantation. Implantation of molybdenum, tantalum, and molybdenum and tantalum together produces beneficial effects on passivation curves in a sulfuric acid solution (Ref 9). Other implanted species that produce beneficial effects include

platinum and palladium. Palladium implantation also improves the resistance of titanium to crevice corrosion and hot chloride solutions (Ref 10).

Oxidation resistance of ion-implanted titanium alloys has been researched using a variety of alloying elements. Oxidation for 50 min in dry oxygen at 600 °C has been reduced by implantation to a level of $\sim 2 \cdot 10^{16}$ ions/cm^2 of species that have either oxides with high negative free energy of formation or large ionic radii for smaller heats of formation (Ref 11). Particularly beneficial effects were obtained from implanting barium, rubidium, cesium, strontium, calcium, ytterbium, and europium. The reduction in oxidation was thought to be caused by implanted impurities obstructing short-circuit diffusion paths or forming Ti + M (implant) mixed oxides. $BaTiO_3$ has been found after barium implantation and oxidation, which improved the fretting fatigue behavior of both titanium and Ti-6Al-4V. Implantation of various elements, including rubidium, cesium, strontium, and calcium, affected the oxidation resistance of titanium (Ref 12). This has been explained in terms of changes in oxidation rate laws, limited solubilities of the implanted elements in the titanium, and the tendency to form ternary oxides with titanium. Implantation of elements in excess of their equilibrium solubility may be necessary for a significant effect on oxidation behavior. Europium, which is one of the less soluble elements in titanium, was shown to produce significant inhibition to oxidation at 600 °C, where the presence of ternary oxides was a prerequisite for a strong inhibitive effect.

Laser and Electron Beam Treatment

Energy beam surface treatment for materials encompasses a wide range of processes, ranging from laser ablation at very high power densities to the transformation hardening of steels and the annealing of metals and alloys at relatively low power densities. The only processes applied to titanium and titanium alloys to any significant extent are surface melting, surface cladding, and surface alloying techniques. These processes all involve the use of the energy beam to melt a surface layer in order to produce a conduction-limited melt profile, as opposed to melting in the "keyhole" regime, which is necessary for deep penetration welding. A conduction-limited melt profile may be close to hemispherical if the beam is a focused spot or something similar, or it may be flat-bottomed if some form of beam scanning across the direction of beam-workpiece relative movement is employed. This molten region may vary in size from <1 μm, where gas alloying is used to mark surfaces, up to >400 μm, where hard surface layers are created for load-bearing, wear-resistant applications. The maximum melt depth is dependent on the absorbed power of the beam by the workpiece, the traverse speed, and the maximum temperature reached in the melt pool before unacceptable surface disruption occurs.

Surface melting using energy beams can homogenize a surface by melting all the microstructural components of the workpiece and allowing the relatively rapid resolidification of the melted region, distributing the phases on a much refined scale, or allowing the phases to solidify as new, metastable phases. In the extreme case, surface melting can be used as a rapid solidification tool by employing very high power densities and very rapid traverse speeds, thus relying on the efficient heat extraction from the melted region by the unheated bulk of the workpiece. In simple terms, the cooling rate, dT/dt, through the solidification range is equal to the product of the temperature gradient, dT/dx, in the melt and the solidification rate, dx/dt, which is the speed of the solidifying interface where T is temperature, t is time, and x is distance. The temperature gradient is related to the power density and the solidification rate is related to the traverse speed or pulse length.

Energy beam surface melting has been carried out using electron beams of powers similar to those commonly used for welding and a variety of lasers, the most useful of which is the carbon dioxide laser, which has output powers ranging from 500 W to multikilowatts. The depth of melting employed is normally between 0.1 and 1 mm, and the beams are usually moved across the workpiece surface at speeds between 5 and 100 mm/s. These parameters result in cooling rates through the solidification range of most alloys, between 10^2 and 10^6 K/s, with the heat being conducted away into the bulk of the workpiece. Mass transport in these melts results from thermal gradients and surface tension gradients.

No significant changes in the overall mechanical properties occur with either commercially pure titanium or Ti-6Al-4V after laser surface melting. For example, columnar beta grains formed upon solidification of Ti-6Al-4V transform to martensite on further cooling (Ref 13). Surface melting has been used to rapidly solidify dispersion-strengthened titanium alloys. For example, titanium plus erbium has been melted with the objective of improving the high-temperature strength of titanium alloys by forming thermally stable dispersoids (Ref 14). Supersaturated solutions containing erbium and oxygen were produced by laser surface melting of experimental alloys, which, after subsequent heat treatment, formed fine dispersions of rare earth oxides, partially coherent with the titanium matrix. Alloys with an excess of oxygen relative to the erbium content for the formation of Er_2O_3 were found to be the most resistant to coarsening of the precipitate.

Energy beam surface alloying is achieved by changing the chemical composition of the substrate material during surface melting. Of the many possible alloying additions, nitrogen is the most widely researched. The object of the

process is to harden the surface of the titanium alloy to a depth of 0.1 to 0.5 mm in order to improve its wear resistance. It is usually carried out using a CO_2 laser and incorporates a gas jet blowing nitrogen or nitrogen and argon at the melt pool. By controlling the amount of nitrogen takeup by the melt pool, a range of solidification structures can be obtained that are usually described as predominantly TiN dendrites, nitrogen-rich α-Ti dendrites, or nitrogen-rich basket-weave. In fact, the microstructure most commonly contains TiN dendrites surrounded by nitrogen-rich α-Ti as a result of nonequilibrium solidification through the peritectic of the titanium-nitrogen phase equilibrium system. There is also a series of continuous layers across the surface of the laser-alloyed track that are responsible for the gold color of the surface after the process. The degree of alloying has a direct influence on the hardness of the alloyed volume, which can be simply controlled by changing the interaction time of the nitrogen with the melt pool (i.e., by altering the traverse speed) (Fig. 6) or changing the nitriding potential of the alloying gas (i.e., by diluting the nitrogen with an inert gas such as argon) (Fig. 7).

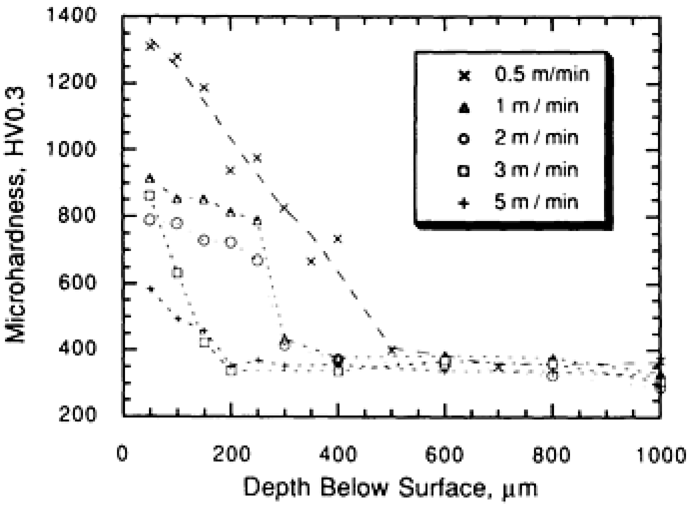


Fig. 6 Influence of feed rate on hardness profile for laser gas nitrided Ti-6Al-4V, 6.6 × 10^4 W/cm^{-2}, 40:60 N2:Ar, 75% track overlap. Source: Ref 15

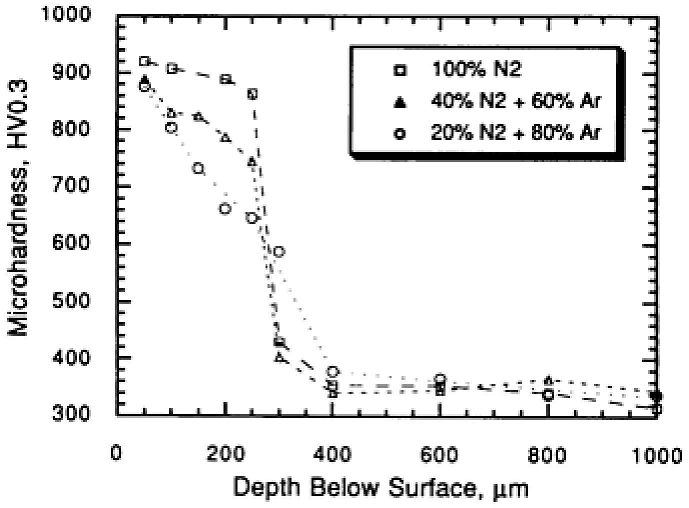


Fig. 7 Influence of gas mixture on hardness profile for laser gas nitrided Ti-6Al-4V, 6.6 × 10^4 W/cm^{-2}, 1 m/min^{-1}, 75% track overlap. Source: Ref 15

The major concerns of this process, and of other energy beam melting processes of all materials, are to avoid cracking, porosity formation, and unacceptably rough surfaces. Cracking is the major problem associated with laser-gas-nitrided titanium; it results from thermal stresses acting on the hard, relatively brittle phases arising from the process. The problem is ameliorated by using a mixture of argon and nitrogen in the treatment gas to produce an alloyed region of less than

maximum possible hardness (<650 HV) and by preheating the substrate. With typical processing parameters, if the preheating temperature exceeds 300 °C (570 °F), cracking can be completely eliminated (Ref 15, 16).

Laser gas nitriding has also been used on a much finer scale to produce marking on the surface of, for example, watch cases. Nitrogen is used to produce a gold color, and oxygen may be used to produce a gray color. Carbon dioxide or neodymium yttrium-aluminum-garnet lasers may be used for this process, where melts as shallow as 1 μm are created.

Other systems that have been investigated include carbon and boron alloying. These substances are usually added to titanium alloys by using preplaced graphite or boron powder, although laser gas carburizing of titanium alloys may be achieved using a carbon-bearing gas in a manner similar to that for laser gas nitriding. These two systems produce similar microstructures, which is a reflection of the similarity between the Ti-C and Ti-B equilibrium systems at the relevant compositions. At low alloying additions, a divorced eutectic solidification is predominant where Ti + TiC and Ti + TiB solidify in each system, respectively. At higher interstitial contents, primary TiC and TiB (Ti_2B) solidify as large dendrites, together with the eutectic solidification microstructure. The hardnesses measured in the alloyed regions have been found to be a reflection of the volume fraction of the compounds solidified, because negligible amounts of carbon and boron can be in solution in α- or β-Ti. Laser gas carburizing using methane diluted 1 to 4 with argon produces a maximum hardness of 650 HV for 100 μm, decreasing to the substrate value at a depth of 300 μm below the surface (Ref 17).

More recently, combinations of alloying elements have been used to produce hardness increases and wear performance improvements. The most successful of these is the simultaneous addition of carbon and silicon in the form of silicon carbide (Ref 16). Surface hardnesses of 650 to 750 HV without any cracking are achieved using electron beam surface alloying of a powder slurry of SiC powder and a polyvinyl alcohol binder. The microstructure comprises TiC dendrites surrounded by α-Ti dendrites, which contain some silicon and very fine precipitation of Ti_5Si_3, and a eutectic of α-Ti + Ti_5Si_3. The overall silicon content of the melt was ~6 wt% Si. The advantage of this system is that the α-Ti component of the microstructure is relatively tough compared to that solidified after laser gas nitriding. A typical hardness profile obtained from this process is shown in Fig. 8. Wear performance similar to that of hardened and tempered low-alloy steels, and superior to that of laser nitrided and untreated Ti-6Al-4V, has been measured in unlubricated sliding-rolling wear tests (30% sliding) at contact stresses of up to 750 MPa (applied load 120 kg/F) (Fig. 9).

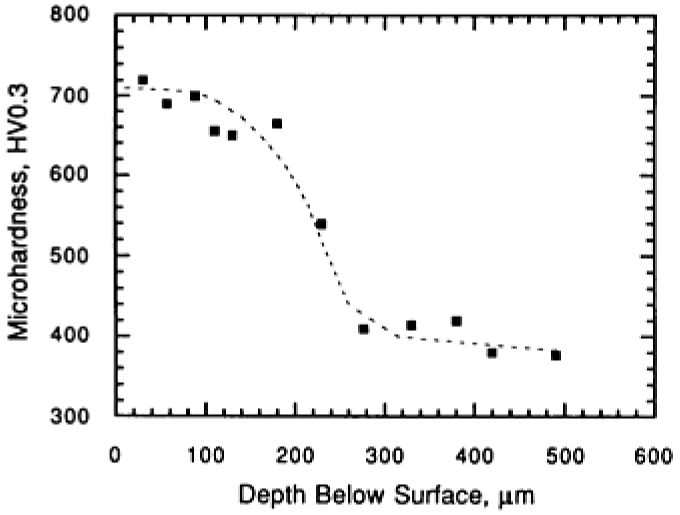


Fig. 8 Hardness profile from electron beam SiC alloyed Ti-6Al-4V after surface grinding to remove rippling. Source: Ref 16

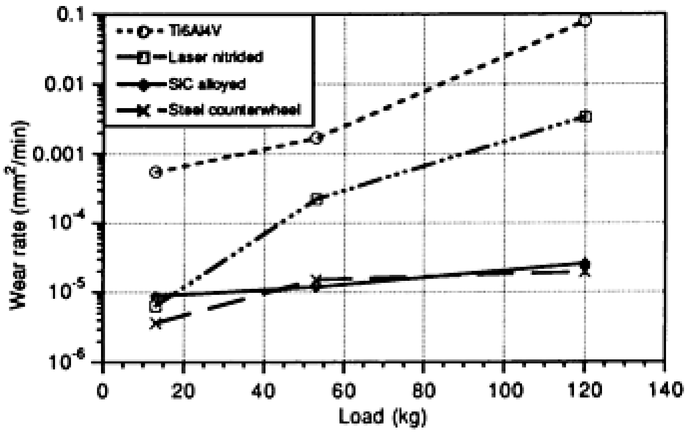


Fig. 9 Wear rates from Amsler sliding-rolling wear tests for high-energy-beam beam surface alloyed Ti-6Al-4V. Source: Ref 16

Other elements that have been electron beam surface alloyed into the surface region of titanium alloys include nickel, chromium, silicon, aluminum, and silicon and aluminum. Surface alloys containing silicon and aluminum (Ref 18) have been subjected to high-temperature oxidation tests, between 750 and 910 °C (1380 and 1670 °F) in air. Beneficial effects of the alloying were measured regarding both oxidation kinetics and the adherence of oxide scale.

Laser particle injection is an energy beam treatment that retains some solid phase during the thermal excursion. It involves the injection of hard particles into a shallow laser melt track. In a Ti-6Al-4V matrix, TiC particles ranging in size from +325-230 to +140-70 mesh have been injected (Ref 19). Partial dissolution of the carbides occurs, but they remain substantially in a particulate form, effectively creating a particulate-reinforced metal matrix composite. Maximum volume fractions of 0.6 included carbide have been created. Improvements in performance by a factor of four, independent of carbide volume fraction for $V_f > 25\%$, were measured for TiC-injected Ti-6Al-4V over untreated materials using dry sand/rubber wheel abrasive wear tests (Ref 20).

Laser cladding involves the addition of a sacrificial layer on the surface of the substrate material, ideally with minimum dilution of the cladding by the substrate but with good adhesion of the clad. A prerequisite for good bonding of the clad to the substrate is similar coefficients of thermal expansion. For erosion resistance in gas turbines, TiC in a β-Ti alloy matrix has been clad on a Ti-6Al-4V substrate, as has TiC in a maraging steel matrix for particularly arduous service (Ref 21).

References cited in this section

4. J.E. Elder, R. Thamburaj, and P.C. Patnaik, Optimizing Ion Implantation Conditions for Improving Wear, Fatigue and Fretting Fatigue of Ti6Al4V, *Surface Eng.,* Vol 5 (No. 1), 1989, p 55-78
5. P. Sioshansi, Improving the Properties of Titanium Alloys by Ion Implantation, *J. Metals,* March 1990, p 30-31
6. R. Hutchings and W.C. Oliver, A Study of the Improved Wear Performance of Nitrogen Implanted Ti6Al4V, *Wear,* Vol 92, 1983, p 143-153
7. W.C. Oliver, R. Hutchings, J.B. Pethica, E.L. Paradis, and A.J. Shuskis, in *Ion Implantation and Ion Beam Processing of Materials,* G.K. Hubler et al., Ed., MRS Symposia Proceedings, North-Holland, 1984, Vol 27, p 705-710
8. R.G. Vardiman and R.A. Kant, The Improvement in Fatigue Life in Ti6Al4V by Ion Implantation, *J. Appl. Phys.,* Vol 53 (No. 1), 1982, p 690-694
9. Y. Sugizaki, T. Yasunaga, and H. Satoh, Electrochemical Behaviour of Titanium Implanted with Molybdenum and Tantalum Ions, *Titanium '92,* F.H. Froes and I. Caplan, Ed., Minerals, Metals and Materials Society, 1993, p 2103-2109

10. P. Munn and G.K. Wolf, The Effect of Palladium Implantation on the Crevice Corrosion of Titanium, *Mat. Sci. Eng.,* Vol 68, 1985, p 303-310
11. J.D. Benjamin and G. Dearnaley, Further Investigations of the Effects of Ion Implantation on the Thermal Oxidation of Titanium, *Inst. Phys. Conf. Ser.,* Vol 28, 1976, p 141-146
12. A. Galerie, High Temperature Oxidation of Ion Implanted Metals, *Ion Implantation into Metals, Proceedings 3rd International Conference on Modification of Surface Properties by Ion Implantation,* V. Ashworth, W.A. Grant, and R.P.M. Procter, UIST 1981, Pergamon, 1982, p 190-200
13. W.A. Baeslack III, S. Krishnamurthy, and F.H. Froes, Solidification Characteristics of Laser Surface Melts in Advanced Titanium Alloys, *Rapid Solidification Technology,* F.H. Froes, and D. Eylon, Ed., TMS-AIME Annual Meeting (New Orleans), 1986, p 97-110
14. D.G. Konitzer, B.C. Muddle, R. Kircheim, and H.L. Fraser, The Production of Rare Earth Oxides in Ti Alloys Using Rapid Solidification, *Rapidly Quenched Metals,* S. Steeb and H. Warlimont, Ed., Elsevier, 1985, p 953-956
15. P.H. Morton, T. Bell, A. Weisheit, B.L. Mordike, and K. Sagoo, Laser Gas Nitriding of Titanium and Titanium Alloys, *Surface Modification Technologies V, Proceedings of the 5th International Conference,* T.S. Sudarshan and J.F. Braza, Ed., Institute of Materials, 1992, p 593-609
16. Wolfson Institute for Surface Engineering, University of Birmingham, "Surface Engineering of Titanium Components," Final Report, BRITE/EURAM Contract RI. 1B.0151C(H), Feb 1991
17. S.Z. Lee and H.W. Bergmann, Laser Surface Alloying of Titanium and Titanium Alloys, *Proc. Sixth World Conference on Titanium,* P. Lacombe, R. Tricot, and G. Beranger, Societe Francaise de Metallurgie, Cannes, June 1988, p 1811-1816
18. A. Galerie, A. Fasasi, M. Pons, and M. Caillet, Improved High Temperature Oxidation Resistance of Ti6Al4V by Superficial Laser Alloying, *Surface Modification Technologies V,* T.S. Sudarshan and J.F. Braza, Ed., Institute of Materials, 1992, p 401-412
19. J.D. Ayers, T.R. Tucker, and R.J. Schaefer, Wear Resisting Surfaces by Carbide Particle Injection, *Rapid Solidification Processing, Principles and Technologies II,* R. Mehrabian, B.H. Kear, and M. Cohen, Ed., Claitors Publishing Division, p 212-220
20. K.P. Cooper and J.D. Ayers, Laser Melt-Particle Injection Processing, *Surface Eng.,* Vol 1 (No. 4), 1985, p 263-272
21. M. Vilnat, Traitment de Durface: Le Laser S' Affirme, *Technologies,* March 1993, p 36-44 (in French)

Diffusion Treatments

Diffusion treatments, as the name suggests, require sufficient time at temperature to allow significant atomic mobility to occur. Because the process temperature usually affects the bulk of the component to be treated, the effects of the thermal cycle on the bulk properties of the material must be considered. If, for example, wrought Ti-6Al-4V bar has been annealed at 700 °C (1300 °F), it is highly likely that a thermal excursion to 800 °C (1470 °F) for 20 h will affect its mechanical properties to a significant degree. For this reason, it is desirable that a diffusion treatment be carried out at as low a temperature as possible if it is the final heat-treatment step for a material and if the workpiece is temperature sensitive.

Nonmetallic Elements

Oxidizing of titanium and titanium alloys can be using to improve their tribological properties. Oxygen in solution in α-Ti produces significant strengthening of the material (Fig. 10).

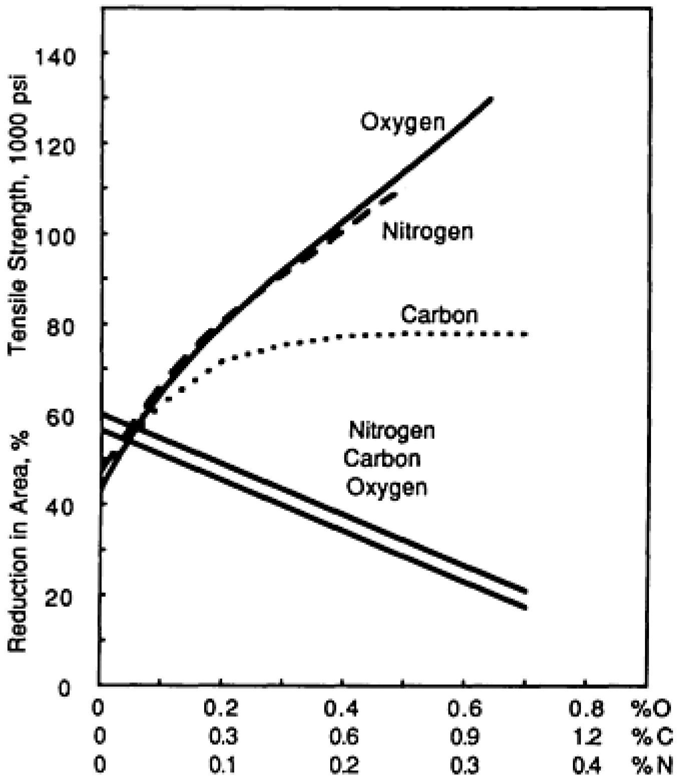


Fig. 10 Effect of interstitial alloying elements on strength and reduction in area of iodide titanium. Source: Ref 22

Over the past 40 years, a great deal of work has been devoted to the study of the oxidation of titanium and its alloys, as described above in this article. By contrast, little attention has been paid to deliberate oxidation as a tribological surface treatment of titanium alloys. Investigations are scattered over many journals over a long period of time. One observed that when chemically pure titanium was heated in the range 850 to 1000 °C (1560 to 1830 °F) in air at a pressure between 10^{-3} and 10^{-2}mm Hg, the surface was effectively hardened (Ref 23). The process was commonly disregarded, however, because at a temperature high enough to achieve an appreciable hardening effect, a considerable amount of scale is also formed (Ref 24). Fatigue strength is also reduced. It was subsequently shown that the friction coefficient of commercial titanium markedly decreases when titanium is heated in air at 350 °C for 17 h (Ref 25) and that the coefficient of friction of the oxidized surface of titanium remains low after removal of the brittle compound layers (Ref 26). These early results led to a number of more detailed studies concerning the oxidizing treatment of titanium for improvements in wear behavior.

In view of the difficulties associated with the severe scaling of titanium alloys when heated in air, controlled oxidizing in molten salts has been attempted. When titanium specimens are heated in lithium carbonate salt baths at temperatures between 600 and 900 °C (1110 and 1650 °F) for 2 to 4 h, satisfactory layers are formed. The technique has been used for production batches of titanium pistons (Ref 27).

The Tifran process has been used to treat Ti-6Al-4V, and in one set of tests, even in the absence of lubricant, seizure was eliminated. Decreases in the wear rate and improvements in the behavior of the lubricating film were observed. The technique is based on diffusion in the gaseous phase, resulting in formation of a layer on the surface of the alloy, which has a titanium oxide base. The effect of Tifran treatment on the wear life and efficiency of annealed Ti-6Al-4V gears has been studied by vacuum testing. Compared with other surface treatments, Tifran-treated gears exhibit the best wear resistance and the lowest power losses (Ref 28).

Oxygen diffusion hardening (ODH) of Ti-6Al-7Nb alloys results in a surface with a gradation in hardness from the surface to a depth of 50 μm. The maximum hardness is 900 HV, compared with 360 HV for the untreated alloy. The corrosion resistance of the ODH-treated titanium alloy is equal to that of commercially pure titanium and untreated Ti-6Al-7Nb alloy (Ref 29).

A wear-resistant surface treatment, based on oxidizing of titanium alloys in air, is used to protect valve spring retainers made of Ti-22V-4Al β-Ti alloy (Ref 30). Better wear resistance was afforded to the component with the oxidation process treatment than with either ion nitriding or gas carburizing. The brittle oxide layer formed on the surface was removed before use. The wear resistance of oxidized (at 850 °C, or 1560 °F, for 30 min) valve spring retainers was better than that of steel retainers, and after shot peening, the fatigue strength of oxygen-surface-hardened Ti-22V-6Al exceeds that of the as-received alloy.

Nitriding of titanium and titanium alloys has been investigated for many years and is used effectively on a small scale for protection against wear. The wear resistance is imparted by a very favorable phase equilibrium relationship between the elements. Nitrogen has a high solid solubility in α-Ti, and the strength increase effected by the interstitial nitrogen is significant, as shown in Fig. 10. Reference to a titanium-nitrogen equilibrium phase diagram shows that above 12.7 wt% N, the compound Ti_2N is formed at temperatures below 1100 °C (2010 °F); it has a tetragonal crystal structure and a hardness of ~1500 HV. At higher nitrogen contents, over a wide range of compositions, TiN with an NaCl-type crystal structure and a hardness of ~3000 HV is formed. Nitriding produces a thin compound layer of TiN at the surface, above a thicker compound layer of Ti_2N, which is above a diffusion zone of nitrogen-strengthened titanium. The surface differs from that achieved through oxidizing in that a useful, hard compound layer structure is created at the surface.

Nitriding cannot be achieved in air because of the tendency of titanium to form TiO_2 in preference to either of the nitrides, but it can be achieved in a nitrogen gas atmosphere. At 1 atm in nitrogen or ammonia, no technologically useful surface is created below 800 °C (1470 °F). However, treatment in ammonia at higher pressures, for example 1.2 MPa, yields thicker compound layers and diffusion zones. In order to remove the hydrogen from parts treated in ammonia, a tempering treatment at a temperature between 300 and 400 °C (570 and 750 °F) at a pressure of 10^{-2} mbar is included in this process. Components treated by this process include surgical instruments, watch cases, racing engine and racing car components, and precision machine parts. The high pressure used in the process allows treatment of narrow, deep, blind holes and intricate details such as fine threads (Ref 31).

It follows that nitriding of titanium alloys may be carried out in hot isostatic pressing equipment, where pressures of up to 100 MPa have been used (Ref 32).

An alternative medium for the introduction of nitrogen and its subsequent diffusion into the surface of titanium and titanium alloys is a plasma. Plasma, ion, or glow discharge nitriding has long been applied to ferrous alloys, but the direct current plasma process is equally applicable to titanium-base materials. Nitrogen, nitrogen-hydrogen, nitrogen-argon, or cracked ammonia may be used as the treatment gas. Nitriding may be achieved at temperatures down to 300 °C (570 °F), but the value of processing at these temperatures is doubtful because of the very thin (1 μm) hardened region produced. More usually, processing is carried out at temperatures in the range of 700 to 900 °C (1300 to 1650 °F). The plasma process uses and exhausts smaller volumes of gas than any gaseous treatment. However, experience is needed to monitor and control the temperature throughout the workpiece. Because all the heat input comes from the plasma, sections of component with significantly different surface area-to-volume ratios may differ in temperature. The thicknesses of compound layers found adjacent to corners also differ from layers on continuous surfaces of workpieces. This effect is attributed to variations in the sputtering rates at these different points. Successfully plasma-nitrided components include racing car steering racks, gears, and ball valves. Components are ready for use directly after treatment and have the characteristic gold color of TiN (Ref 16).

Significant improvements in wear resistance are gained after nitriding titanium-base materials, the sources of the benefits being twofold; the hard surface compound layers of TiN and Ti_2N and the support given by the nitrogen-strengthened diffusion zone beneath them. A typical hardness profile from plasma nitrided Ti-Al-4V is shown in Fig. 11, in which the dashed line represents the hardnesses of the thin TiN and Ti_2N compound layers. The processing conditions used were 850 °C (1560 °F) for 20 h in ammonia. A loss of about 10% of fatigue strength is associated with nitriding, but this can be mitigated against by appropriate design of a component.

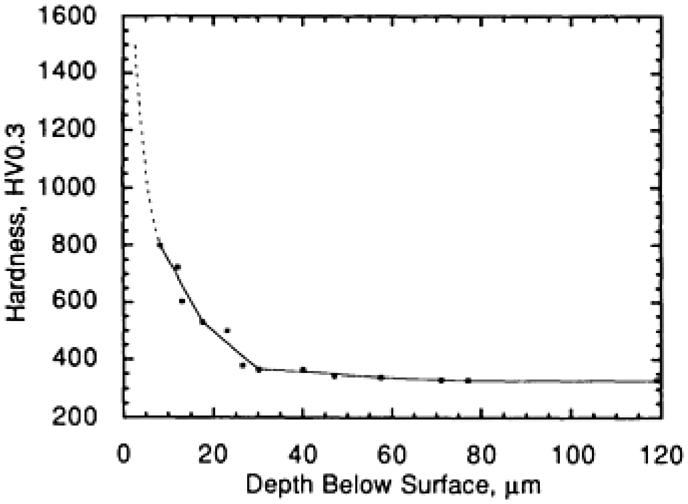


Fig. 11 Hardness profile (Vickers, 0.3 kg load) from plasma-nitrided Ti-6Al-4V. Source: Ref 16

A number of salt bath treatments have been developed for titanium, the oldest of which is probably the Tiduran process (Ref 33). In this process, the titanium component is immersed in a cyanide-based salt bath at 800 °C (1470 °F), usually for 2 h. Carbon and nitrogen, and sometimes small amounts of oxygen, diffuse into the surface to produce a hardened diffusion zone. The maximum hardness achieved in the process is in the range of 750 to 800 HV, falling progressively into the substrate, giving a case depth of about 50 μm. A uniform 10 μm is removed from the surface of the metal during the process. Components can usually be used in the as-coated condition, or they may be given a light pickle to remove the black surface.

Localized heat sources, such as a plasma torch combined with a nitrogen atmosphere, can be used to produce a superficial nitrogen-enriched surface region, but quality control is extremely difficult.

Carburizing of titanium and titanium alloys may be achieved in nonoxidizing, carburizing environments. The phase equilibrium system for Ti-C differs from those for Ti-O and Ti-N in that there is very little solid solubility for carbon in titanium. Hence, compound layer formation of TiC may result, but there is no significant diffusion zone beneath the TiC. Carburizing is accomplished in pack processes using carbonaceous media such as calcium carbonate, or following evacuation and heating to 1050 °C (1920 °F), a carburizing gas is introduced and is used for cooling. Carburizing has been used for the creation of wear-resistant surfaces on components such as engine valves.

Boronizing of titanium-base materials is similar to carburizing in that it results in the formation of an extremely hard compound layer with a negligible diffusion zone. TiB_2 is usually the outermost layer, although other borides are also formed. Wear resistance of boronized titanium has been studied (Ref 34), and in comparison with other surface treatments, it has performed very well in lightly loaded gear tests (Ref 35), compared to similar materials.

Siliconizing of titanium alloys can be achieved, for example, by using an atmosphere of 3 vol% silane in argon mixture at 1100 °C (2010 °F) for 2 h, which produces a 10 μm Ti_3Si_5 compound layer. The objective of this process is to improve oxidation resistance by changing the oxidation product. TiO_2 has been observed after oxidation in both air and oxygen at a range of temperatures. At low temperatures (<875 °C, or 1600 °F), the oxidation product was a dense mixture of TiO_2 and SiO_2, but at temperatures in excess of 900 °C (1650 °F), the outer layer consisted of pure TiO_2 (Ref 36). Titanium silicide surface layers have also been obtained using a pack process, the pack comprising of silicon with aluminum fluoride or sodium fluoride as the activator (Ref 37).

Metallic Elements

Aluminizing has been carried out via pack processes or deposition and diffusion processes to improve the oxidation resistance of titanium alloys. In a pack process, the compound layers formed depend on the processing parameters. For example, at 760 °C (1400 °F) for 20 h, 50 μm of $TiAl_3$ is formed; 900 °C (1650 °F) for 16 h produces $TiAl_3$ at the surface and thinner layers of TiAl and Ti_3Al form sequentially toward the substrate of $TiAl_2$. Cracks through the compound layers

are often present, and Kirkendall porosity occurs in some cases. Diminution of the $TiAl_3$ layer by inward diffusion of aluminum at the oxidizing temperature is faster than the consumption of the coating by oxidation. Cracking of the aluminide coating, thought to occur on cooling after the aluminizing process, is a significant problem. Large, deep, open cracks form during the oxidation of pre-existing ruptures. Other pre-existing cracks that remain virtually closed are oxidized to a lesser degree. There are also closed cracks that seem to form during cooling from the oxidation temperature.

Nonetheless, at 900 °C (1650 °F) the weight gain of the aluminized coatings has been found to be 50 times less than for pure titanium, 30 times less than for Ti-6Al-4V, and 5 times less than for a silicide coating. After 10 h, assuming a linear rate, the oxidation of the aluminide coating was 300 times slower than for the pure titanium (Ref 38). Between 850 and 1000 °C (1560-1830 °F) and room temperature, cyclic oxidation of aluminized titanium also allowed the diffusion of aluminum to continue during the oxidation experiments (Ref 39), but at lower temperatures, the beginning of rapid oxidation was delayed. The $TiAl_3$ surface layers provided better oxidation resistance than the TiAl layer. Successful pack aluminizing of Ti-14Al-24Nb has been achieved (Ref 40). Similar pack-aluminized, intermetallic material has been subjected to cyclic oxidation, and excellent protection from cyclic oxidation resistance was measured to 1000 °C (1830 °F). Thicker coatings were found to offer limited resistance to oxidation because of cracking of the coatings after about five cycles; after more cycles, large growths were observed. Optimum coating thicknesses were found to be 40 to 70 μm (Ref 41).

Pack-aluminized layers are considered to be much thicker than is necessary for protection against oxidation. Thinner aluminized coating can be obtained by duplex routes, for example, by electron beam evaporation followed by a diffusion anneal (Ref 42).

Nickel diffusion treatments have been attempted for improvements in tribological behavior. In one case, an electrodeposition process was followed by a diffusion treatment in order to form the compound layers Ti_2Ni (600 HV) and $TiNi_3$ (1000 HV), from which the excess nickel layer was subsequently removed by a chemical process (Ref 43). No particular attention was paid to the potential of the diffusion zone.

Electrodeposited nickel on a titanium alloy substrate that was subsequently diffusion heat treated produced nickel penetration to a depth of ~200 μm (20 h at 850 °C, or 1560 °F). The specimens were then solution treated at 900 °C (1650 °F) and water quenched. Aging at 500 °C (930 °F) for 2 h resulted in hardnesses of ~600 HV in the diffusion zone (Ref 44).

The fact that nickel diffusion into titanium readily occurs implies that the use of overlay coatings based on nickel (or iron or cobalt) are of limited use for oxidation resistance, both because of loss of the coating to the substrate and because some of the reaction products may degrade critical mechanical properties.

Copper diffusion has been achieved by both electroplating and ion plating copper onto the surface of titanium alloys, followed by a diffusion heat treatment. In one case a heat treatment of 800 °C (1470 °F) for 12 h followed by furnace cooling was used, which resulted in an outer compound layer of Ti_2Cu, beneath which there was a Ti_3Cu layer and a diffusion zone. The Ti_2Cu layer has been shown to perform well in wear testing, comparable with plasma-nitrided titanium and physical vapor deposited TiN. No optimization of the diffusion zone was carried out. The maximum diffusion zone hardness was 650 HV at 5 μm below the surface, dropping to a core hardness of 450 HV at 15 μm below the surface (Ref 45). Nickel and copper diffusion treatments involving electroplating followed by heat treatment are relatively low-cost surface engineering systems for wear resistance. The nickel diffusion treatment has been looked at as a possibility for a seal ring and a titanium alloy control rod couple in a nuclear power station; the surface treatment allows a reduction in friction and a longer component lifetime. Titanium alloy valves have been treated by nickel diffusion in the seat area in order to improve the cavitation erosion resistance of the components for use in chemical and power generation plants.

References cited in this section

16. Wolfson Institute for Surface Engineering, University of Birmingham, "Surface Engineering of Titanium Components," Final Report, BRITE/EURAM Contract RI. 1B.0151C(H), Feb 1991
22. S.R. Seagle and H. Kessler, "Principles of Alloying Titanium," ASM Battelle Memorial Institute, Columbus, OH, Vol 3, 1968
23. H.W. Worner, Surface Hardening of Titanium, *Australasian Engineer,* Nov 1950, p 52-55

24. R.W. Hanzel, Surface Hardening Processes for Titanium and Its Alloys, *Metal Progress*, March 1954, p 89-96
25. E.S. Machlin and W.R. Yankee, Friction of Clean Metals and Oxides with Special Reference to Titanium,*J. Appl. Physics*, Vol 25, 1954, p 576-581
26. W.R. Yankee and E.S. Machlin, Influence of Oxygen and Nitrogen in Solution in Alpha Titanium on the Friction Coefficient of Copper on Titanium, *Transactions AIME,* Sept 1954, p 989-990
27. E. Mitchell and P.J. Botherton, Surface Treatments for Improving the Wear Resistance and Friction Properties of Titanium and Its Alloys, *J. Instit. Metals,* Vol 93, 1965/65, p 381-386
28. A. Gaucher and B. Zabinski, Nouvelles Possibilities de Frottement des Alliages de Titane: Le Tifran, *Entropie,* No. 63, 1975, p 36-41 (in French)
29. R.M. Streicher, H. Weber, R. Schon, and M. Semlitsch, New Surface Modification for Ti-6Al-7Nb Alloy: Oxygen Diffusion Hardening (ODH), *Biomaterials,* Vol 12, 1991, p 125-129
30. M. Mushiake, K. Asano, N. Miyamura, and S. Nagano, "Development of Titanium Alloy Valve Spring Retainers," SAE Technical Report Series, No. 910428, 1991, p 41-49
31. F. Preissner and P. Minarski, Results on Nitriding Titanium and Ti6Al4V with a New Thermochemical Treatment Under High Gas Pressure, *Titanium '92, Science and Technology,* F.H. Froes and I. Caplan, Minerals, Metals and Materials Society, 1993, p 1979-1988
32. J. Marshall, M.H. Jacobs, G.R. Armstrong, and B.A. Rickinson, The Application of HIP Processing for Rapid Gas Nitriding, *Hot Isostatic Pressing '93,* L. Delaey and H. Tas, Ed., Elsevier, 1994, p 317-324
33. B. Finnern, Wear Resistant Surfaces on Titanium and Titanium Alloys Achieved by Treatment in a Salt Bath, *Harterei Tech. Mitt.,* Vol 26, 1971, p 47-52
34. T.S. Eyre and H. Alsalim, Effect of Boronizing on Adhesive Wear of Titanium Alloys, *Tibology International,* Oct 1977, p 281-285
35. R.A. Rowntree, Surface-Treated Titanium Alloy Gears for Space Mechanisms, *Proceedings Second European Space Mechanisms and Tribology Symposium,* Oct 1985, (Meersburg, Germany), p 167-171
36. A. Abba, A. Galerie, and M. Caillet, High Temperature Oxidation of Titanium Silicide Coatings on Titanium, *Oxidation of Metals,* Vol 17 (No. 1), 1982, p 43-54
37. J. Guille, L. Matini, and A. Clauss, Obtention of Silicide Coatings on Titanium by Pack-Cementation, *Titanium Science and Technology, Proceedings 5th International Conference on Titanium,* G. Lutjering, U. Zwicker, and W. Bunk, Ed., Deutsche Gesellschaft für Metallkunde, 1985, p 973-977
38. R. Strieff and S. Poize, Oxidation of Aluminide Coatings on Unalloyed Titanium, *International Conference on High Temperature Corrosion* (San Diego, CA), March 1981, p 591-597
39. J. Subrahmanyam and J. Annapurna, High Temperature Cyclic Oxidation of Aluminide Layers on Titanium, *Oxidation of Metals,* Vol 26 (No. 3/4), 1986, p 275-285
40. J. Subrahmanyam, Cyclic Oxidation of Aluminized Ti-14Al-24Nb Alloy, *J. Mat. Sci.,* Vol 23, 1988, p 1906-1910
41. J.L. Smialek, M.A. Gedwill, and P.K. Brindley, Cyclic Oxidation of Aluminide Coatings on Ti3Al+Nb, *Scripta Met. Mat.,* Vol 24, 1990, p 1291-1296
42. R.K. Clark, J. Unnam, and K.E. Wiedemann, Effect of Coatings on Oxidation of Ti-6Al-2Sn-4Zr-2Mo Foil, *Oxidation of Metals,* Vol 29 (No. 3/4), 1988, p 255-269
43. M. Thoma, Wear Protection of Titanium Alloys by Coatings, *Proceedings International Conference Designing with Titanium,* Institute of Metals, 1986, p 155-159
44. J. Lanagan and T. Bell, University of Birmingham, unpublished report, May 1986
45. M. Salehi, "Tribological Characterisation of Surface Engineered Titanium Alloys," Ph.D. thesis, University of Birmingham, 1990

Coatings

Chemical Conversion Coatings

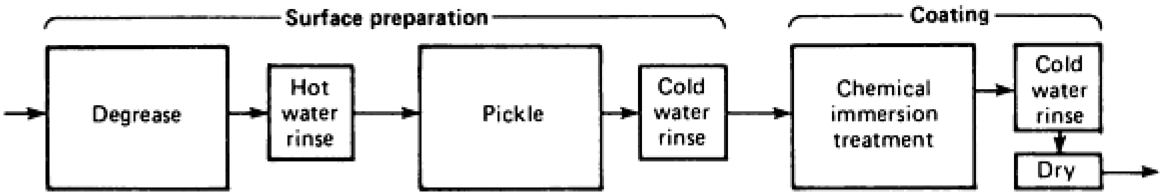
Chemical conversion coatings are used on titanium to improve lubricity by acting as a base for the retention of lubricants. Titanium has a severe tendency to gall, and lack of lubricity creates serious problems in applications involving the contact of moving parts in various forming operations (Ref 1).

Conversion coatings are applied by immersing the material in a tank containing the coating solution. Spraying and brushing are alternate methods of application. One coating bath consists of an aqueous solution of sodium orthophosphate, potassium fluoride, and hydrofluoric acid, which can be used with various constituent amounts, immersion times, and bath temperatures. The resultant coatings are composed primarily of titanium and potassium fluorides and phosphates. Several solutions are listed in Table 5. The flow chart in Fig. 12 indicates a processing sequence for the coating of titanium alloys.

Table 5 Conversion coating solutions for titanium alloys

Bath No.	Bath solution	Composition	Amount		Temperature		pH	Immersion time, min
			g/L	oz/gal	°C	°F		
1	Degreasing solution	$Na_3PO_4 \cdot 12H_2O$	50	6.5	85	185	5.1-5.2	10
		$KF \cdot 2H_2O$	20	2.6				
		HF solution[(a)]	11.5	1.5				
2	Pickling solution	$Na_3PO_4 \cdot 12H_2O$	50	6.5	27	81	<1.0	1-2
		$KF \cdot 2H_2O$	20	2.6				
		HF solution[(a)]	26	3.4				
3	Chemical immersion solution	$Na_2B_4O_7 \cdot 10H_2O$	40	5.2	85	185	6.3-6.6	20
		$KF \cdot 2H_2O$	18	2.3				

(a) Hydrofluoric acid, 50.3% by weight



Type of solution	Composition	Operating temperature		Cycle time, s
		°C	°F	
Degreasing	Alkaline cleaner	Boiling point		60-120
Pickling	15% HNO_3, 1% HF in water	23	75	10-60
Chemical immersion	[a]	. . .	. . .	. . .

(a) See Table 5.

Fig. 12 Processing sequence used in the chemical coating of titanium alloys

Cleanliness of the part before immersion is critical, and all preliminary cleaning and handling operations must be closely controlled for good results. Finger marks or residual grease on the surface of a part will interfere seriously with the coating process.

The appearance of the baths varies widely during the coating reaction, ranging from rapid bubbling to relative dormancy. Some coatings rub off when still wet; others are adherent. The various solutions produce coatings of approximately the same dark gray or black color.

The control of pH and immersion time is important. Dissolved titanium and the active fluoride ion make it impossible to use glass electrodes for pH measurements. Indicator paper and colorimetry are the most satisfactory methods for measuring in the degreasing and chemical immersion baths, which are held at 5 to 7 pH. The pickling bath is quite acid, and titrametric analysis offers the most practical method of control. When the bath is in the proper coating range, a 20 mL (0.70 fluid oz) sample in 100 mL (3.4 fluid oz) of water will neutralize 11.8 to 12.0 mL (0.4 to 0.41 fluid oz) of normal sodium hydroxide, using a phenolphthalein indicator.

Coating thickness depends on immersion time. In all three baths, a specific time is reached after which the coating weight remains essentially constant. In the fluoride-phosphate baths, a maximum coating weight is reached at some time before this equilibrium point. The maximum coating weight is obtained in about 2 min in the low-temperature bath and in about 10 min in the two other baths (Fig. 13).

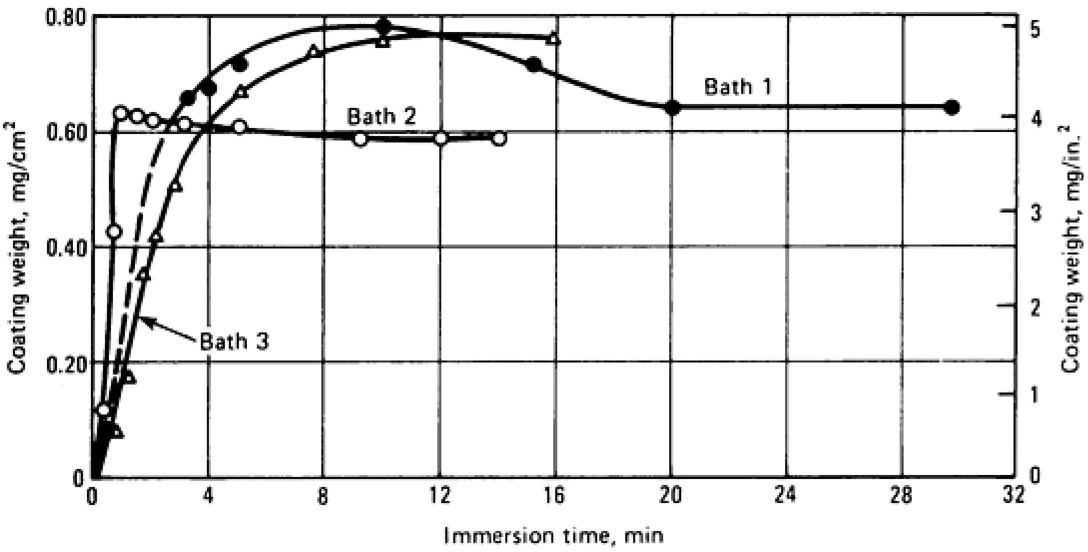


Fig. 13 Weight of conversion coating as a function of immersion time. See Table 5.

Results of extensive wire-drawing experiments (Table 6) illustrate the effectiveness of conversion coatings when used with various lubricants. Reciprocating wear tests showed that conversion coatings and oxidized surfaces provided some improvement in wear characteristics, but when conversion-coated samples were also oxidized, a marked improvement was noted. The conversion coating increases the oxidation rate of titanium at about 425 °C (800 °F) and may increase oxidation rates at temperatures up to 595 °C (1100 °F). The original coating is retained above the titanium oxide layers. High-speed rotary tests have indicated marked improvement in the wear characteristics of the metal after conversion coating and lubricating with one part of molybdenum disulfide and two parts of thermosetting eponphenolic resin.

Table 6 Comparison of conversion coatings used with various lubricants in wiredrawing of titanium

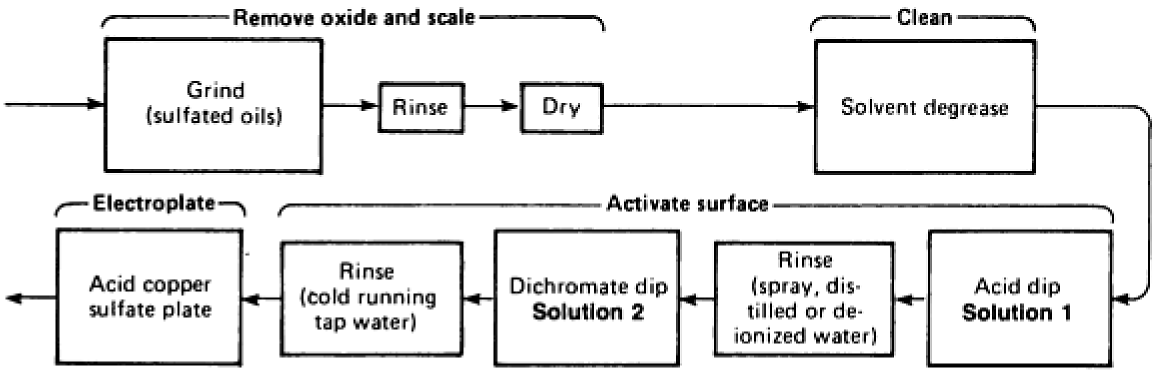
Coating	Drawing compound	Total reduction, %	No. of passes	No. of coats	Final condition
Bare	Molybdenum disulfide with grease	. . .	0	. . .	Galled
Bare	Soapy wax	. . .	0	. . .	Galled
Degreasing bath	Molybdenum disulfide with grease	85	8	2	Smooth
Pickling bath	Molybdenum disulfide with grease	94	17	7	Smooth
Pickling bath	Soapy wax	68	7	3	Galled
Pickling bath[(a)]	Molybdenum disulfide with grease	70	7	1	Smooth
Chemical immersion bath	Lacquer molybdenum disulfide	63	8	2	Smooth
Chemical immersion bath	Molybdenum disulfide with grease	63	8	3	Smooth

(a) Coating heated for 1 h at 425 °C (795 °F)

Conversion coatings are easily removable without excessive loss of metal by pickling in an aqueous solution containing 20% nitric acid and 2% hydrofluoric acid by weight.

Plating

Copper Plating. The electrodeposition of copper on titanium and titanium alloys provides a basis for subsequent plating. A flow chart outlining the processing sequence for copper plating titanium is shown in Fig. 14. After cleaning and before plating, the surface of the titanium must be chemically activated by immersion in an acid dip and a dichromate dip to remove the passivating oxide film and obtain adequate adhesion of the plated coating. The compositions and operating temperatures of these activating solutions are shown in the table with Fig. 14.



Solution No.	Type of solution[a]	Composition of solution
1	Acid dip	60% HF, 1 vol, 69% HNO_3, 3 vol
2	Dichromate dip	$Na_2Cr_3O_7 \cdot 2H_2O$, 290 g/L (33 oz/gal), 60% HF, 55 g/L (6.2 oz/gal), H_2O, remainder[c]

Solution No.	Operating temperature		Cycle time, s
	°C	°F	
1	Room temperature		[b]
2	82-100	180-212	20

(a) For preparation of Ti-6Al-4V and Ti-4Al-4Mn.

(b) Immerse to evolution of red fumes.

(c) Distilled or deionized water

Fig. 14 Processing sequence for electroplating copper on titanium alloy parts

Water purity is critical for the composition of activating solutions. Chemicals of technical grade are as effective as, and may be substituted for, chemically pure grades. In both the acid and dichromate baths, the hydrofluoric acid content is critical and must be carefully controlled.

After proper activation, titanium may be plated in a standard acid copper sulfate bath. The adhesion of the deposited copper is better than that of 60-40 solder to copper, and the deposit successfully withstands the heat of a soldering iron. The normal thickness of the plated deposit is about 25 μm (1 mil).

Copper-plated titanium wire is available commercially. The outstanding property of this material is the lubricity of its copper-plated surface. The wire can be drawn easily and can be threaded on rolls. Such wire has been used in applications that require electrical surface conductivity.

The titanium wire is plated continuously at a speed of about 60 m/min (200 ft/min) in a copper fluoborate acid bath at a current density of 7.5 to 12.5 A/dm^2 (75 to 125 A/ft^2). The final copper deposit is a thin flash coating. Higher current densities up to 150 A/dm^2 (1500 A/ft^2) have been tried, but if the copper coating is too thick, adhesion is poor.

Platinum Plating. Although titanium is not satisfactory as an anode material because an electrically resistant oxide film forms on its surface, application of a thin film of platinum to titanium results in a material with excellent electrochemical properties. Theoretically, the thinnest possible film is sufficient to give the highly desirable low overvoltage characteristics of platinum; furthermore, the film need not be continuous or free of defects to be effective.

The greatest immediate use for platinum-coated titanium is for anodes in the chlorine-caustic industry. Some horizontal-type chlorine cells use expanded metal anodes. From 1.3 to 2.5 μm (0.05 to 0.1 mil) of platinum is applied to the anode surface. Replating of the anodes may be required after about 2 years, depending on the operating conditions. The attrition rate for platinum appears to be about 0.6 g/tonne (0.5 g/ton) of chlorine.

Several platinum and electrode suppliers have developed reliable methods for platinum plating of titanium; most use proprietary solutions. A platinum diamino nitrite bath has been used successfully to apply platinum to titanium. In this and other procedures, certain precautionary steps are required to achieve adherent, uniform plates. The surface must be cleaned thoroughly and etched in hydrochloric or hydrofluoric acid to produce a roughened surface. Some procedures also involve a surface activating treatment just before plating. Immersion for 4 min in a solution of 895 mL (30 fluid oz) of glacial acetic acid containing 125 mL (4 fluid oz) of 52% hydrofluoric acid, followed by a prompt rinse, appears to be an effective activating treatment if performed immediately before plating. A postplating treatment, consisting of heating to 400 to 540 °C (750 to 1000 °F) for 10 to 60 min, stress relieves the plate and improves adhesion. This treatment can be done in an air atmosphere, and a light oxide film forms on unplated areas.

Coatings for Emissivity. Electrodeposits and sprayed coatings of gold on titanium are used to provide a heat-reflecting surface that reduces the temperature of the base metal. Gold-coated titanium has been used for jet engine components.

The gold coating is applied by spraying a gold-containing liquid on chemically clean titanium sheet. This is followed by a baking treatment. Normal coating thickness is about 25 μm (0.1 mil).

Coatings for Wear Resistance. Plating of hard chromium and electroless nickel are the most widely used on ferrous substrates for wear-resistant applications. However, in wear situations the thin oxide layer present on titanium alloys can make satisfactory adhesion of these coatings to titanium substrates difficult to achieve. Measures taken to overcome this problem include (Ref 46):

- In situ formation of alkali metal halogen complexes that protect from further oxidation and are later dissolved in acid plating solution
- Surface cleaning with an etchant, followed by rinsing in a water solution containing anions of cyanides, tartrate, citrate, and acetate complexing or chelating ions, followed by heat treatment
- Cathodic cleaning of the surface, activation in stannous chloride solution, coating in copper-reducing solution or gold chloride dip, electroplating copper, and copper striking from copper cyanide solution
- Chemical etching, immersion plating in a mixture of hydrofluoric acid, zinc sulfate, and sodium dichromate, followed by rinsing and conventional chromium plating
- Oxide removal in hydrofluoric acid/fluoboric acid solution, then transfer to a fluoborate plating solution to prevent reoxidation
- Immersion in nitric acid and sodium citrate solution; alkaline electroless nickel plate
- As above, abrade in hydrochloric acid, then Woods nickel strike, copper strike, chromium plate

These are some of the many procedures that have been attempted. An additional concern is that contact with acidic solutions allows hydrogen embrittlement of the titanium alloys.

Another approach to activation involves the dissolution of some microstructural constituents prior to plating. These are the aluminum-rich α-Ti phase and in Ti-6Al-4V, precipitated Ti_2Cu in Ti_2Cu and precipitated impurities at the grain boundaries of unalloyed titanium. Postplating heat treatment to 480 °C (895 °F) allows further improvements in adhesive strength, associated with diffusion of nickel into titanium and vice versa (Ref 47).

Heat treatment has been successfully used for enhancement of adhesion of hard chromium plating of titanium alloys. A 700 °C (1290 °F) temperature was used for the heat treatment, which resulted in a loss of hardness of the hard chromium, so a second chromium plating was applied to the initial, adherent, heat-treated chromium surface. Degradation in fatigue properties was ameliorated by the use of shot peening. Components treated using this procedure have included oil seal collars, racing car flywheels, bearing housings, and pistons (Ref 48).

Physical Vapor Deposition

Physical vapor deposition (PVD) is a term that covers several processes (including evaporation, ion plating, and various forms of sputtering) to deposit metals, alloys, compounds, or metastable materials on a wide variety of substrates. The most successful engineering application is the coating of tool material substrates by reactive ion plating or reactive sputtering of TiN and related materials.

The PVD treatment of titanium alloy substrates has found limited application so far, but arc evaporation has been used to deposit 4.5 μm of TiN, and sputter deposition has been used to deposit 0.5 μm of TiN on gears for space mechanisms. The thinner coating suffered from problems of adhesion, whereas the thicker coating eventually failed through galling (Ref 31). Pin-on-disc wear tests have demonstrated reductions in coefficients of friction for TiN and TiC on titanium substrates against 440C stainless steel (Ref 49, 50). Electron beam source and arc source ion plating have been used to produce 1 to 2 μm of TiN on the surface of Ti-6Al-4V.

The failure of conventionally applied TiN coatings on titanium alloy substrates under load-bearing wear situations was evaluated and modifications were made to produce a better PVD TiN process. Initially, a coating produced using an electron beam evaporative source was found to perform significantly better than an arc source coating in lubricated Falex tests against steel jaws. The poor performance of the arc source coating was caused by removal of small splats of titanium from the coating and the introduction of titanium into the wear couple. This problem was negated by lightly polishing the arc source coating before testing. Survival of the electron beam source coating at higher contact stresses was achieved by an improved sputtering process at a higher-than-normal temperature (700 °C vs. 450 °C, or 1290 °F vs. 840 °F) before evaporation of the titanium component of the coating commenced (Ref 51, 52). This process is tradenamed Nitron and is provided by Tecvac UK, Ltd. The improvements in load-bearing wear situations of the modified process is demonstrated by the Falex wear test data shown in Fig. 15. Engineering components routinely coated with TiN include brake pistons and other components for racing cars, aerospace components for which titanium is used because of its strength-to-weight ratio, and pump parts and valve components for oil, chemical, and food industries for which titanium is used because of its corrosion resistance.

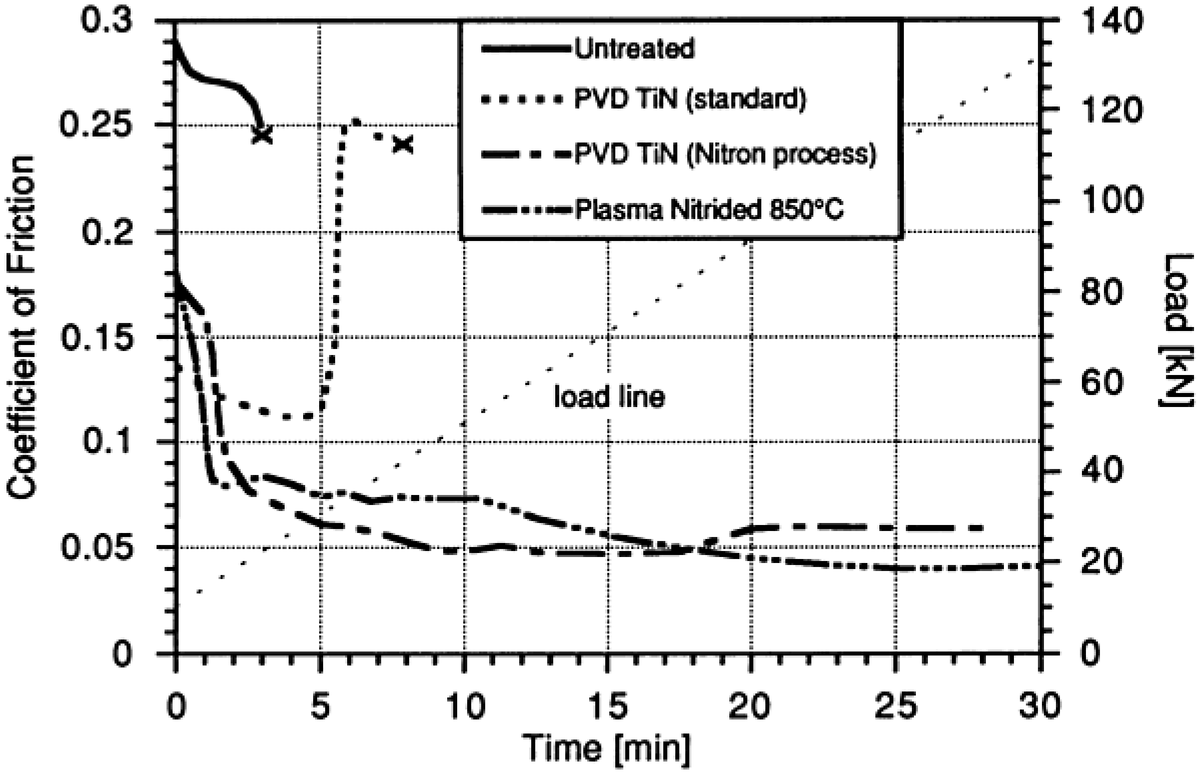


Fig. 15 Results from lubricated Falex wear tests for untreated and plasma-processed Ti-6Al-4V; carbon steel jaws. Source: Ref 16

One very active area of surface engineering research, mentioned above in the discussion of ion implantation, is in the area of surgical implants, where mechanical and chemical properties make titanium a useful material but its tribological properties require improvement. TiN deposition has been widely researched and is routinely employed by commercial coaters. Surface roughness of the component is a critical parameter in this type of wear couple, and polishing is usually required after TiN deposition (Ref 53).

In the same field of application (surface engineering of prosthetics), amorphous diamond-like carbon (DLC or ADLC) is stimulating interest. Optimization of the wide range of properties available from these coatings is essential, and, as in DLC coating of other substrates, adhesion problems must be overcome. The very low coefficients of friction and wear rates exhibited by these coatings are very promising, and the coatings have performed well in reciprocating abrasion wear tests against bone cement in Ringer's solution, as have TiN coating and zirconia (Ref 53) (Table 7).

Table 7 Results of polymethyl methacrylate abrasion tests of various metals and ceramic coatings following 10^6 wear cycles

Material	Coating	Surface hardness, DPH	Initial R_a, µm	Final R_a, µm	Wear track depth, µm
Ti-6Al-4V	. . .	330	0.06	4.15	27.5
Ti-6Al-4V	N^+ implantation	700	0.05	3.30	30.5
Co-Cr-Mo	. . .	400	0.05	0.13	0.08

316L S.S.	. . .	230	0.06	0.80	48.0
Ti-6Al-4V	TiN	1630	0.05	0.08	0.50
Ti-6Al-4V	ADLC	2850	0.02	0.16[(a)]	0.3[(a)]
Zr	ZrO_2	1430	0.02	0.02[(a)]	0[(a)]
ZrO_2	. . .	1430	0.02	0.02[(a)]	0[(a)]

Source: Ref 53

(a) 10^7 abrasion cycles.

Sprayed Coatings

Sprayed coatings may be applied to titanium alloy substrates as they are to many other materials; no special pretreatment is required for titanium-base materials. Sprayed coatings are mainly deposited using plasma spraying, but detonation gun, high-velocity oxyfuel (HVOF), and vacuum plasma spraying are also used. There is a vast range of materials that can be sprayed onto titanium substrates if so desired.

The main function of sprayed coatings on titanium is for wear protection in aerospace engines and other gas turbine applications. In the low-pressure compressor, titanium alloy midspan support faces are sprayed with tungsten carbide-cobalt for protection against fretting wear. Wear protection is also afforded to blade roots, location lugs and fan dampers by means of a "soft" coating (Cu-Ni-In) to protect the titanium components (Ref 54). The coating is very dense, has a very low oxide content, and resists fretting wear. The coating wears at a predetermined rate and the components can be removed and the coating resprayed after an establisher service period. The value of such a soft coating to combat fretting wear of titanium alloys has been demonstrated in laboratory tests in which a copper-base electroplated deposit outperformed many other surface treatments (Ref 55). In the intermediate-pressure compressor, abradable coatings are used for a variety of seals. These coatings, blends of aluminum-silicon and polyester powders, are worn away by, for example, blades. A good seal is maintained by partial wear of the coating and essentially no blade-tip wear occurs. Plasma-sprayed anti-fretting-wear coatings for titanium alloys, usually of tungsten carbide-cobalt, are also widely used.

Another major use of sprayed coatings is in repair of components. Some large, very expensive titanium components undergoing final machining operations are damaged, chiefly due to tool wear. Rather than scrap such components, plasma-sprayed coatings of Ni-Al-Mo are used to rebuild critical volumes. When titanium alloying processing vessels used in the production of dry-cell batteries undergo corrosion, they are repaired using plasma-sprayed tantalum.

Returning to the area of prosthetics, titanium implants are sprayed with hydroxyapatite (HAP). This compound is the ceramic constituent of bone, and when it is deposited with appropriate amounts of porosity and surface roughness, bone growth can occur and cementation between the bone and the HAP coating results. This material is commonly sprayed onto femoral stems, dental implants, knee implants, and acetabular caps (wherever a titanium prosthesis comes into contact with bone). The other widely used sprayed deposit in this area of application is titanium itself. Again, appropriate surface roughness and porosity are important because, although not a constituent of bone, titanium is biocompatible and does not discourage bone growth. Therefore, when a successful implant is carried out, the bone will grow, resulting in mechanical keying of the new bone and the porous titanium.

Other Coatings

Anodizing of titanium and titanium alloys enhances the wear resistance of the material. It produces layers of TiO_2 less than 100 nm thick. Such coatings are unable to withstand more than relatively light loads, but they do produce significant improvements over untreated titanium. The process is frequently used on titanium fasteners and can be considered the

basic minimum treatment for any titanium component subjected to a rubbing action. The range of interference colors produced by anodizing at different voltages is also used to obtain decorative effects on titanium jewelry and other items.

Sol-gel coatings on titanium alloys are being studied for use as oxidation protection surface treatments. A range of surface coatings on a Ti_3Al-Nb-based alloy, including sputtered oxides of magnesium, yttrium, zirconium, and hafnium, sputtered fluorides of calcium and yttrium, and 1 μm thick layers of silicon, aluminum, and boron oxides were applied both by sputtering and from sols, and calcium, sodium, and phosphorus oxides were also applied from sols (Ref 56). A reaction barrier undercoat expected to be stable with the titanium alloy was combined with oxidation barrier topcoats. Weight gains for various systems after 1 h at 982 °C (1800 °F) in air are shown in Fig. 16. The measured values for weight gain are indicative of the relative film integrity after exposure; sputtered coatings were often cracked. A sputtered yttria coating was improved by dipping in boric acid, which, during heating, forms boron oxide, which was believed to fill the cracks in the yttria layer, consequently improving the protection achieved.

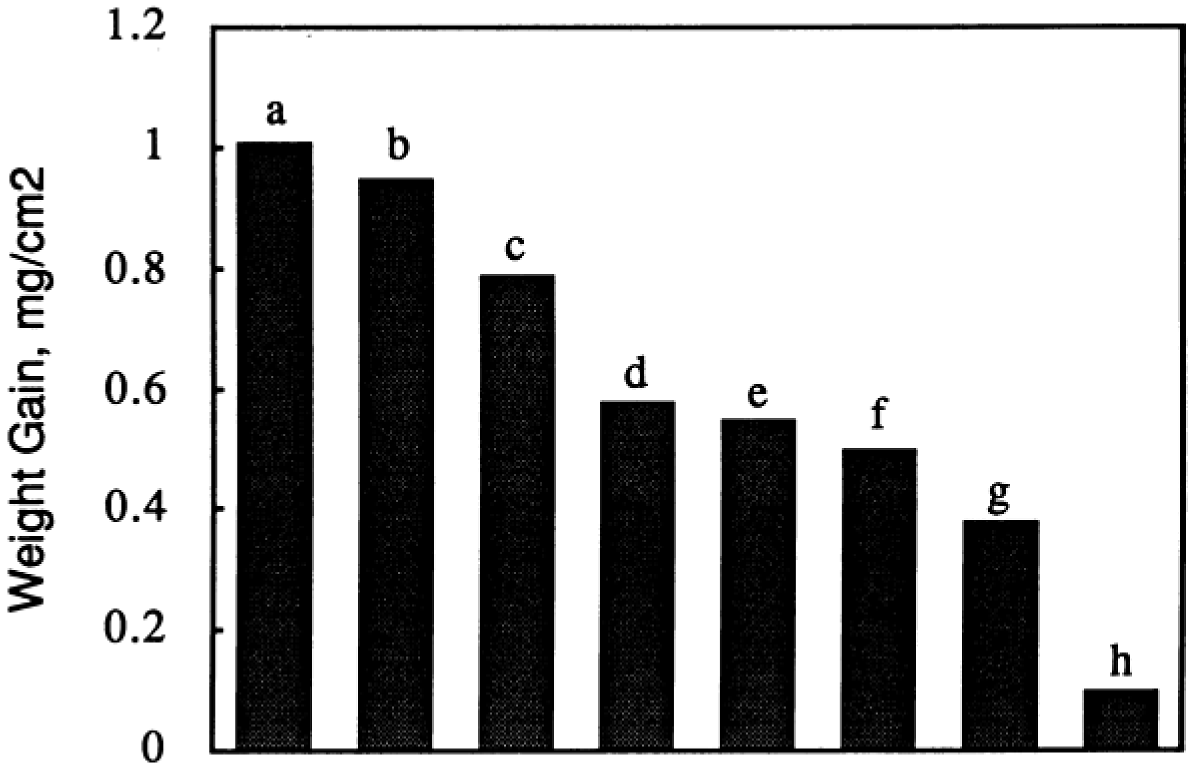


Fig. 16 Weight gain for 1 h at 982 °C (1800 °F) in air for (a) uncoated alloy, (b) sputtered yttria, (c) boron oxide from solution, (d) sodium aluminum borophosphate from solution, (e) calcium phosphate from solution, (f) calcium aluminate from solution, (g) calcium aluminophosphate from solution, and (h) magnesium silicophosphate from sol-gel. Source: Ref 56

A multilayered system involving 1 to 2 μm of reaction barrier coating is applied (either barium titanate or yttrium-stabilized zirconia), over which is a diffusion-barrier coating containing magnesium phosphate and silica glasses. In cyclic oxidation tests to 980 °C (1800 °F), the performance of this coating equaled and exceeded that of other, thicker reaction coatings (Ref 57).

Chemical vapor deposition (CVD) coatings are seldom applied to titanium-base substrates. However, some work has been done, again with the object of improving oxidation resistance (Ref 58). Sputtered silica and CVD silicate layers, both with and without aluminum base coats, have been tested for relatively low temperatures. The best results were obtained from the combined aluminum coating, which diffuses to form $TiAl_3$ and sputtered silica.

Another type of coating for γ-titanium aluminides is based on the Ti-Cr-Al system, within the composition range for which an alumina film is formed on the surface in elevated-temperature oxidation. Methods of application used are slurry fusion, low-pressure plasma spraying, HVOF spraying, and sputtering. Good oxidation behavior has been noted, but significant interdiffusion of the coating and the substrate occurs at the oxidation temperature (Ref 59).

Contemporary Developments

Plasma immersion ion implantation (PI^3) has been developed at the Australian Nuclear Science and Technology Organisation. It is an innovative process that combines and exploits the advantages of the established techniques of both ion implantation and plasma nitriding to produce surface-modified components with optimum performance characteristics. As such, it offers the potential expansion of the surface engineering market to applications that are prohibitively expensive with current ion-beam technology (Ref 60).

Specifically, PI^3 involves surrounding the sample by the ion source, in the form of a radio-frequency generated plasma. This enables a steady-state sheath to form around the target. A series of short, high-voltage, negative pulses are then applied directly to the workpiece, causing ions to be accelerated from the plasma to bombard the target from all sides simultaneously at approximately normal incidence. Therefore the line-of-sight restriction of conventional ion implantation is eased and the sputtering effects are reduced, allowing uniform coverage to be achieved on complex shapes at a lower unit cost.

The technology results in a modified layer of much greater depth than in conventional ion implantation. As well as implanting ions into the first 0.2 μm to obtain a surface layer with unique tribological properties, there is the additional possibility at elevated temperatures of producing a strengthened diffusion-enhanced "tail" of up to 100 μm thickness that supports the implanted layer.

Work on the effects of PI^3 on titanium alloys has so far been limited to studies on the Ti-6Al-4V alloy. Samples have been treated in a nitrogen atmosphere at between 350 °C and 550 °C (660 and 1020 °F), for either 3 or 5 h. Preliminary investigations indicate that under these conditions, considerable increases in surface hardness can be achieved. At temperatures of 500 °C (930 °F) and above, the surface Knoop hardness of Ti-6Al-4V increases by 150 to 170% at 25 g load. Furthermore, samples treated at all temperatures in the range were hardened to some degree.

These findings were reflected in significant improvements in the wear resistance of the alloy. Pin-on-disc wear testing has been carried out at low loads (2 N) and in the presence of ethanol. Samples treated at 350 and 450 °C (660 and 840 °F) showed some decrease in wear volume, compared to the untreated material. However, the Ti-6Al-4V disc that had been treated at 500 °C (1020 °F) for 5 h exhibited no measurable wear after the test had been completed.

One drawback of PI^3 is its effect on the surface roughness of samples during treatment. Unlike conventional ion implantation, the PI^3 process results in significant increases in surface roughness that are greater as temperature and time of treatment are increased.

Plasma source ion implantation (PSII) was developed simultaneously at the University of Wisconsin. Whereas the PI^3 unit has a radio-frequency generated plasma, the PSII process employs a filament discharge (direct current source) that ionizes the gas.

Research using titanium alloy substrates has concentrated on implantation at ambient temperatures (i.e., not greater than 100 °C), with nitrogen implanted at 50 keV to a fluence of 3×10^{17} atoms/cm^2, to produce a peak concentration of nitrogen of about 40 to 50% at the surface and a treated depth in the region of 2000 to 3000 Å.

Transmission electron microscopic analyses of the implanted layers show fine precipitates of TiN dispersed throughout the structure. However, in more recent work, comparing x-ray electron dispersive spectra for implanted and unimplanted Ti-6Al-4V, it has been concluded that this is more realistically represented by Ti(V)N, because the vanadium is thought to substitute for the titanium. Pin-on-disc wear testing has been carried out under extremely low loads (0.1 to 0.2 N) in both corrosive and lubricated conditions. Again, significant improvements in wear resistance have been exhibited by the surface-modified Ti-6Al-4V, comparable to those achieved by conventional ion implantation (Ref 61, 62).

Duplex Treatments. Plasma nitriding or modified PVD TiN coating provides a titanium surface with improved resistance to sliding contact under moderately high contact stresses. However, neither process is capable of providing a sufficiently deep case for use in bearings and gears. Deep hardened layers provided by laser or electron beam surface alloying are able to withstand the high stresses encountered in these applications but do not resist sliding motion.

Some work has been carried out to combine deep hardening with a subsequent surface treatment to enable the material to withstand the action of high load in mixed rolling/sliding and, in particular, to resist scuffing failure. Electron beam surface alloying of Ti-6Al-4V with silicon and carbon has been followed by surface grinding and then plasma nitriding.

Samples tested using a minidisc scuffing test with 54% slip (slide-roll ratio of 0.37) and a contact pressure of 1.3 GPa (Ref 16) demonstrated a dramatic improvement in scuffing resistance for the duplex-treated sample over and above that of the electron beam SiC-alloyed material alone. No visible signs of wear, other than a slightly polished appearance, resulted on the duplex-treated sample, whereas there was severe scoring on the surface-alloyed treated sample. The combination of a deep hardened case, able to resist high contact stresses, with a plasma-nitriding treatment to alter the chemical as well as physical and mechanical nature of the surface is capable of providing titanium alloys with a surface treatment of great potential value under severe wear conditions. The improvements to Ti-6Al-4V substrates produced by these surface engineering processes are summarized in Fig. 17.

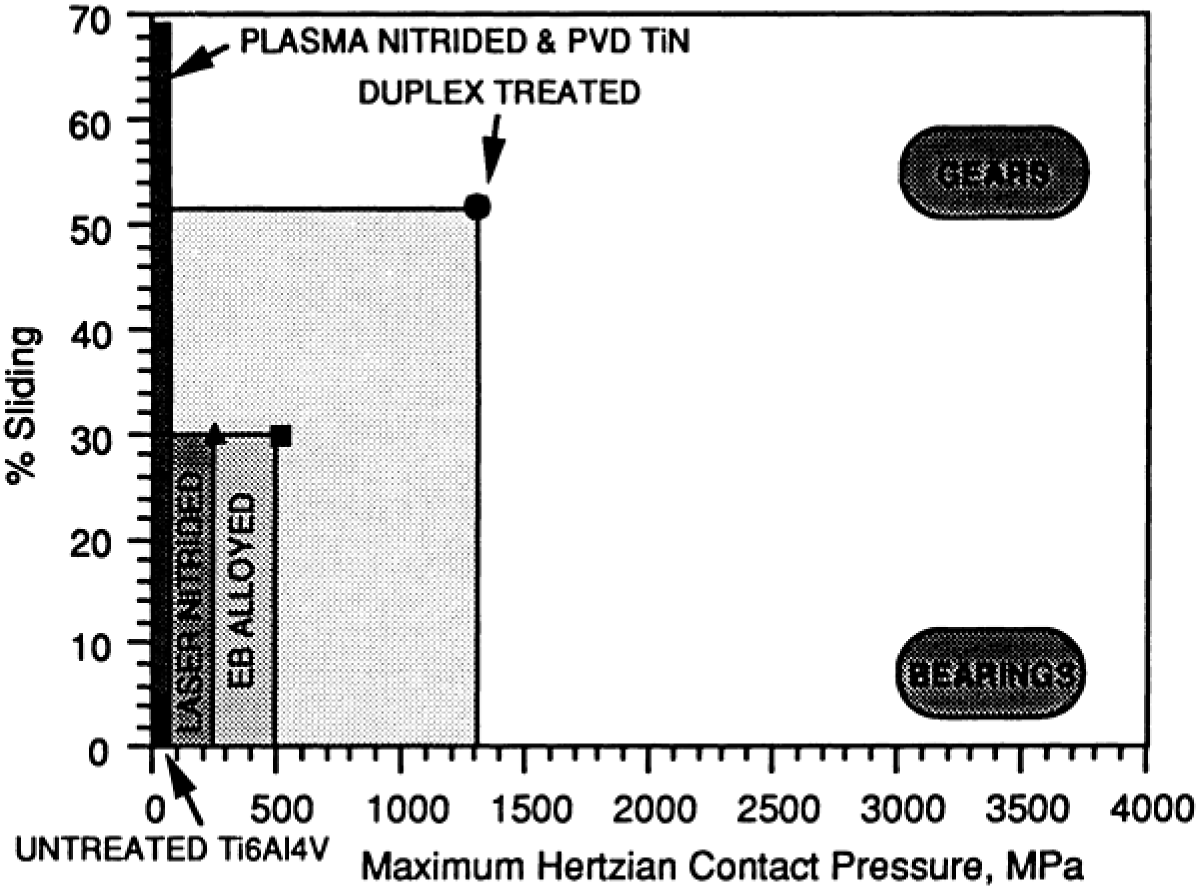


Fig. 17 Survival of wear tests described by percentage sliding and contact stresses for surface-engineered Ti-6Al-4V. Source: Ref 16

References cited in this section

1. *Surface Cleaning, Finishing, and Coating,* Vol 5, 9th ed., *Metals Handbook,* American Society for Metals, 1982, p 650-668
16. Wolfson Institute for Surface Engineering, University of Birmingham, "Surface Engineering of Titanium Components," Final Report, BRITE/EURAM Contract RI. 1B.0151C(H), Feb 1991
31. F. Preissner and P. Minarski, Results on Nitriding Titanium and Ti6Al4V with a New Thermochemical Treatment Under High Gas Pressure, *Titanium '92, Science and Technology,* F.H. Froes and I. Caplan, Minerals, Metals and Materials Society, 1993, p 1979-1988
46. E.W. Turns, J.W. Browning, and R.L. Jones, Electroplates on Titanium: Properties and Effects, *Plating and Surface Finishing,* May 1975, p 443-451
47. M. Thoma, Plating on Titanium, *Plating and Surface Finishing,* May 1983, p 96-98
48. C.G. John, Electroplated Coating of Titanium for Engineering Applications, *Proceedings International Conference Designing with Titanium,* Institute of Metals, 1986, p 160-165

49. A.K. Suri, R. Nimmagadda, and R.F. Bunshah, *Thin Solid Films,* Vol 64, 1979, p 191
50. T. Jamal, R. Nimmagadda, and R.F. Bunshah, *Thin Solid Films,* Vol 73, 1980, p 245
51. J. Lanagan, "Plasma Surface Engineering of Titanium Alloys," Ph.D. thesis, University of Birmingham, 1988
52. M. Salehi, T. Bell, and P.H. Morton, Load Bearing Capacity of Plasma Nitrided and Ion Plated Titanium Alloys, *Surface Modification Technologies IV,* T.S. Sudarshan, D.G. Bhat, and M. Jeandin, Ed., TMS, 1991, p 991-1002
53. J.A. Davidson and A.K. Mishra, Surface Modification Issues for Orthopaedic Implant Bearing Surfaces, *Surface Modification Technologies V, Proceedings of the Fifth International Conference,* T.S. Sudarshan and J.F. Braza, Ed., Institute of Materials, 1992, p 1-14
54. C. Chamont, Y. Honnorat, Y. Berthier, M. Godet, and L. Vincent, Wear Problems in Small Displacements Encountered in Titanium Alloys Parts in Aircraft Turbomachines, *Sixth World Conference on Titanium,* P. Lacombe, R. Tricot, and G. Beranger, Ed., Societe Francaise de Metallurgie, Cannes, June 1988, p 1883-1893
55. M. Thoma, Influence on Fretting Fatigue Behaviour of Ti6Al4V by Coatings, *Sixth World Conference on Titanium,* P. Lacombe, R. Tricot, and G. Beranger, Ed., Societe Francaise de Metallurgie, Cannes, June 1988, p 1877-1881
56. K.E. Wiedemann, P.J. Taylor, R.K. Clark, and T.A. Wallace, "Thin Coatings for Protecting Titanium Aluminides in Hot-Corrosion Environments," presented at TMS fall meeting, 1990, Detroit, MI
57. NASA Langley Research Center, Ultra-Thin Coatings Protect Titanium From Adverse Environments, *Adv. Mat.,* Vol 23, 1992, p 4
58. K.E. Wiedemann, S.N. Sankaran, R.K. Clark, and T.A. Wallace, Static and Dynamic Oxidation of Ti-14Al-21Nb and Coatings, *Oxidation of High Temperature Intermetallics, Proceedings of Workshop,* Warrendale, PA, Metal and Materials Society, 1989, p 195-206
59. R.L. McCarron, J.C. Schaeffer, G.H. Meier, D. Berztiss, R.A. Perkins, and J. Cullinan, Protective Coatings for Titanium Aluminide Intermetallics, *Titanium '92,* F.H. Froes and I. Caplan, Ed., Minerals, Metals and Materials Society, 1993, p 1971-1978
60. G.A. Collins, R. Hutchings, and J. Tendys, Plasma Immersion Ion Implantation of Steels, *Mat. Sci. Eng.,* Vol A139, 1991, p 171-178
61. X. Qui, A. Chen, R.A. Dodd, J.R. Conrad, and F.J. Worzala, Wear Corrosion Behaviour of Nitrogen Implanted Ti6Al4V, *ASM Conf. on Wear-Corrosion Interactions in Liquid Media,* (Indianapolis, IN), Oct 1989, A.A. Sagues and E.I. Meletis, Ed., ASM International, p 109-121
62. X. Qui, J.R. Conrad, R.A. Dodd, and F.J. Worzala, Plasma Source Nitrogen Ion Implantation of Ti6Al4V, *Met. Trans. A,* Vol 21A, June 1990, p 1663-1667

Surface Engineering of Zirconium and Hafnium

Revised by R. Terrence Webster, Metallurgical Consultant

Introduction

ZIRCONIUM AND HAFNIUM SURFACES may require cleaning and finishing for reasons such as preparation for joining, heat treatment, plating, forming, and producing final surface finishes. Special surface preparation and cleaning is generally not required for corrosion resistance because the naturally formed surface oxide protects the metal regardless of surface condition. They are difficult to electroplate via traditional methods, but plating can be accomplished using special alternative processes.

Surface Soil Removal

Grease, oil, and lubricants used in machine forming and other fabricating operations may be removed by a number of techniques. Alkaline or emulsion cleaners used in simple soak tanks or with ultrasonic cleaning, acetone or

trichloroethylene solvent washing, or vapor degreasing and detergents are all widely used. For light soil removal, hand wiping is done with solvents such as acetone, alcohol, trichloroethylene, or various alternatives to trichloroethylene (which is not environmentally attractive). Electrolytic alkaline cleaning is also used. In the electrolytic system, the work can be either anodic or cathodic polarity, provided the voltage and current can be controlled to avoid anodizing or spark discharge, and subsequent pitting. Removing these soils is essential before acid etching to provide uniform acid attack. The soils must be removed before heat treatment and joining to prevent contamination and consequent loss of ductility.

Blast Cleaning

Mechanical descaling methods such as sandblasting, shot blasting, and vapor blasting are used to remove hot work scales and hard lubricants from zirconium and hafnium surfaces. Aluminum oxide, silicon carbide, silica sand, and steel grit are satisfactory media for mechanical descaling. Periodic replacement of used media may be required to avoid excessive working of the surfaces by dull particulates. Roughening of exposed surface areas occurs from grit or shot impingement, depending on the grit size used. Any abrasive or shot blast cleaning may induce residual compressive stresses and warpage in the surface of the material, particularly thin sheet. Warpage also may occur in sections that are subsequently chemical milled or contour machined.

Blast cleaning is not intended to eliminate pickling procedures. Abrasive blasting does not remove surface layers contaminated with interstitial elements such as carbon, oxygen, and nitrogen. Generally blast cleaning is followed by a pickling step to ensure complete removal of surface contamination and cold-worked layer and to produce a smooth, bright finish.

Chemical Descaling

Some scale, as well as forming lubricants, can be removed by proprietary water solutions of strong caustic compounds, or by the use of molten alkaline-based salt baths. The salt baths operate at temperatures of 650 to 705 °C (1200 to 1300 °F) and must be used carefully according to manufacturer instructions. Salt bath descaling is accomplished by a series of cycles through the salt, a water rinse, and a sulfuric acid bath to remove scale before final pickling.

Pickling or Etching

Metal removal by a chemical bath of nitric-hydrofluoric acid is used most commonly, although other baths have been used. The usual bath for zirconium, Zircaloys, and hafnium is composed of 25 to 50% nitric acid, 70 vol%; 2 to 5% hydrofluoric acid, 49 vol%; and the remainder water. The acid bath for zirconium-niobium alloys consists of 28 to 32% sulfuric acid, specific gravity 1.84; 28 to 32% nitric acid; 5 to 10% hydrofluoric acid; and the remainder water.

Bath temperatures should not exceed 65 °C (150 °F) during pickling, to help prevent excessive pickup of the hydrogen that forms during the pickling. Zirconium and hafnium are very sensitive to small amounts of hydrogen, which lowers their fracture toughness markedly.

To help prevent formation of insoluble fluoride surface stain, a stop bath consisting of 70% HNO_3, and 30% H_2O can be used. The article is pickled in the nitric-hydrofluoric acid bath and is immediately dipped in the stop bath. Thorough rinsing in cold water follows the stop bath.

The hydrofluoric acid attacks the zirconium and hafnium, and the nitric acid oxidizes the hydrogen formed by the reaction and prevents its absorption by the metal. The ratio of nitric to hydrofluoric acid should not be less than 10 to 1 normality. Except for the zirconium-niobium alloys, the rate of metal removal is linear with hydrofluoric acid concentration and doubles as the bath temperature rises from 43 to 71 °C (110 to 160 °F).

Material etched in the nitric-hydrofluoric acid bath must be rinsed quickly and completely with flowing water, to prevent an insoluble fluoride surface stain from forming. This stain is extremely detrimental to corrosion resistance in hot water and steam environments of nuclear reactors. Extreme precautions to ensure a rapid and effective rinse are required for this service. A rapid temperature rise during the transfer to the rinse water can lead to redeposition of the etching product.

Anodizing and Autoclaving

Zirconium and hafnium oxidize readily in air and aqueous solution, but the tenacious oxide layer generally protects the metal from further oxidation. Methods to produce a dense oxide layer to serve as a protective coating for zirconium and hafnium are anodizing and autoclaving. Before anodizing, the article should be cleaned in a 50% nitric acid/50% water solution and then in water with the assistance of ultrasonic vibration.

The anodizing solution used for zirconium and hafnium consists of:

- 45.4 vol% absolute ethanol
- 26.5 vol% water
- 15.2 vol% glycerine
- 7.6 vol% lactic acid, 85% concentration
- 3.8 vol% phosphoric acid, 85% concentration
- 1.5 vol% citric acid

Voltage during anodization is raised slowly from about 20 V to 200 to 300 V. A rapid rise in voltage may overload the amperage and/or power capabilities of the equipment. A wide variety of anodization films with different thicknesses and colors can be produced. Voltage governs the thickness of the oxide layer, which determines the color (first gold, then red, green, blue, and black with increasing thickness). This technique can be employed to decoratively color zirconium and hafnium alloys and to enhance metallographically prepared surfaces for light microscope observation. See P.E. Danielson's articles on color metallography and the metallography of zirconium, hafnium, and titanium in Volume 9 of the *ASM Handbook.*

Caution should be exercised during the anodizing process, especially when the high voltage is reached. Operators should wear rubber gloves. Rubber floor mats are also advisable.

Autoclaving is a standard test for zirconium and hafnium for the nuclear industry. Testing is conducted to determine proper processing history and/or surface cleanliness for critical applications. Specific (surface area basis) weight gain and/or visual standards are used to determine compliance. The test for zirconium and Zircaloys is carried out at 400 °C (750 °F) under a steam pressure of 10 MPa (1.5 ksi) for 1 to 14 days. The test for hafnium is carried out at 360 °C (680 °F) under a water pressure of 18.6 MPa (2.7 ksi).

Autoclaving procedure may be used to produce a dense oxide coating for zirconium and hafnium. The water used should have a pH value of 6 to 8, with a resistivity of 1×10^4 Ω· m (1×10^6 Ω· cm) minimum when corrected to 22 °C (72 °F). The autoclave should be constructed of type 300 series stainless steel, and should be fitted with a pressure gage, pressure records, thermocouples, a safety blowout assembly, and a high-pressure venting valve. In preparation for anodizing, the article should be detergent cleaned, followed by solvent cleaning with reagent grade acetone, trichloroethylene, or perchloroethylene. The article should be cleaned further by acid pickling as described in a previous section. Upon completion of the designated pickling time, the article should be immediately and rapidly transferred to the first water rinse tank with a temperature maintained at 27 °C (81 °F) and a flow rate of at least two bath changes per minute. It should then be transferred to the second water rinse tank at the same temperature for at least 15 min. After this, the article should be transferred to the third rinse tank containing water at 80 °C (175 °F) minimum. All rinse water, especially in the third rinse tank, should have a pH of 7 (±1) and a resistivity of 5000 Ω· m (500,000 Ω· cm) minimum. After rinsing, the article should be dried by a method that prevents water marks, stains, or contamination on the surfaces of the article, by wiping with a clean, lint-free cloth, and blowing with dry air. Autoclaved zirconium and its alloys show a dense, shiny black coating of oxide, while hafnium shows a dense, iridescent coating of oxide, the color of which ranges from purple or blue to gold.

Oxide Layer for Low Friction Surfaces. A thick, dense, and adherent oxide layer can be produced on zirconium and hafnium by heat treatment. The resultant oxide layer will have low friction resistance and will resist galling and seizing, while retaining excellent corrosion resistance. For small precision-shaped components, compensation must be made for oxide buildup as well as stress-induced changes (see "Selected References" for citations on oxide growth).

The treatment consists of cleaning the surface, followed by heating for 4 to 6 h at 550 °C (1022 °F) in air. The resultant oxide layer will be approximately 5 μm (0.0002 in.). Thicker oxide films can be produced by heating in a controlled atmosphere of inert gas and oxygen in an air furnace, a fluidized bed furnace, or molten equimolar NaCl and KCl fused salts.

Polishing and Buffing

The polishing and buffing of zirconium is accomplished with the same methods used for titanium. Polishing is frequently done wet, using mineral oil lubricants and coolants. Silicon carbide abrasive cloth belts have been effective. It is common to polish in two or more steps, using a coarser grit initially, such as 60 or 80, to remove gross surface roughness, followed by polishing with 120 or 150 grit to provide a smooth finish. Zirconium and titanium tend to wear the sharp edges of the abrasive particles and to load the belts more rapidly than steel. Frequent belt changes are required for effective cutting. A good flow of coolant improves polishing and extends the life of the abrasives.

Dry polishing is more appropriate than wet for some applications. For these operations, belts or cloth wheels with silicon carbide abrasive may be used. Soaps and proprietary compounds may be applied to the belts to improve polishing and to extend belt life. Abrasive belt materials that incorporate solid stearate lubricants offer improved results for dry polishing operations. *Caution: Accumulation of zirconium and titanium fines can be pyrophoric.*

Fine polishing of zirconium and titanium articles for extremely smooth finishes requires several progressive polishing steps with finer abrasives until pumice or rouge types of abrasive are applied. With the softer grades, such as unalloyed titanium or zirconium material, fine polishing requires more time and care to prevent scratching. Harder grades can be polished more readily to a surface of high reflectivity. If a matte finish is desired, wet blasting with a fine slurry may be used after initial polishing.

The purpose of buffing is to improve the surface appearance of the metal and to produce a smooth, tight surface. Buffing is used as a final finishing operation and is particularly adaptable to finishing a localized area of a part. Parts such as body prostheses, pacemakers, and heart valves require a highly buffed, tight surface to prevent entrapment of particles. Close-fitting parts for equipment, such as the modern guidance systems, and electronics applications require highly polished surfaces obtained by buffing. In addition, sheet sizes too large to be processed by other abrasive finishing methods, such as mass finishing or wet blasting, can be economically processed by buffing.

The principal limitations of buffing are distortion, caused by the inducement of localized stress; surface burning, resulting from prolonged dwell of the buff; an inability to process inner or restricted surfaces; and the feathering of holes and edges. Proper care of the buffing wheel is essential. Buffing with insufficient compound or a loaded wheel produces burning or distortion of the part. After buffing, no further cleaning of parts is required except degreasing to remove the buffing compound. Further information may be found in the Section "Finishing Methods" in this Volume.

Vapor Phase Nitriding

Other surface modification techniques employ reactive gases such as nitrogen to form a surface layer that diffuses into the surface under temperature. The nitrogen must be extremely pure (less than 100 ppm oxygen with a dew point of -45 °C, or -50 °F). The part to be surface treated is heated in nitrogen, which forms a substoichiometric nitride layer on the surface. Depending on temperature and time, the nitride layer will form to a depth of several thousand angstroms. The coating thus produced is a light gold color for zirconium and its alloys. Typical temperatures are in the range of 850 to 1050 °C (1560 to 1920 °F) with times ranging from several minutes to 30 min at temperature. The operation may be performed in a vacuum furnace that is compatible with the introduction of nitrogen.

High-temperature vapor-phase synthesis (HVS) is used to form reactive layers of carbides, nitrides, and carbonitrides on the surface of zirconium, hafnium, tantalum, niobium, and their alloys. The ceramic surfaces of HVS-processed materials provide both wear and corrosion resistance, protecting the unreacted interior of the host material. The properties of the reacted material can be tailored to meet the requirements of a range of applications. In general, however, the materials have relatively high thermal conductivities and, unlike conventional oxide ceramics, are not particularly susceptible to thermal shock.

Metal-refining applications of HVS-processed materials are particularly promising. Most molten metals do not wet these ceramics, and they also resist both abrasion and corrosion. Other potential applications include transfer tubes for routing abrasive or reactive chemicals and gases, at high or low temperatures, and components of high-strength, high-stiffness structures. Property and performance testing are currently in progress.

Electroplating

Hafnium, zirconium, and Zircaloys (zirconium-tin alloys), are difficult to coat with an adherent electroplate because they form a tenacious oxide film in air and aqueous solutions. There are alternative processes for plating nickel on zirconium.

In the first process, the zirconium article is etched in either an ammonium bifluoride sulfuric acid, 45 g/L (6 oz/gal) of ammonium bifluoride + 0.5 mL (0.02 fluid oz) of sulfuric acid aqueous solution for 1 min at 22 °C (72 °F), or an ammonium bifluoride solution, 45 g/L (6 oz/gal) of ammonium bifluoride aqueous solution for 3 min at 22 °C (72 °F). For nickel plating, the electrolyte consists of 81 g/L (11 oz/gal) of nickel as in $Ni(NH_2SO_3)_2$, 1.0 g/L (0.13 oz/gal) of nickel chloride, and 40 g/L (5.2 oz/gal) of boric acid in an aqueous solution, with an ideal surface tension of 0.038 N/m (0.003 lb/ft). The pH value should be kept at 3.8 to 4.0, with the current density of 2.15 A/dm^2 (21.5 A/ft^2), and the temperature at 50 °C (120 °F). Preheating is required to improve bond strength. Carry the treatment at 700 °C (1300 °F) in vacuum for 1 h with the plated article placed in a molybdenum alloy, TZM ring, or constrained case. Because the coefficient of thermal expansion for molybdenum is lower than that of zirconium and nickel, it provides a stress on the plating as the assembly is heated.

In the alternate process, the zirconium article is etched with an aged aqueous activating solution of 10 to 20 g/L (1.3 to 2.6 oz/gal) of ammonium bifluoride and 0.75 to 2.0 g/L (0.1 to 0.26 oz/gal) of sulfuric acid, for about 1 min at ambient temperature. The solution is aged by immersion of a piece of pickled zirconium for at least 10 min at ambient temperature. The next step is to remove any loosely adhering film or smut formed on the article in the activating step. This can be accomplished in one of the following methods:

- Using a chemical solution which is either an aqueous solution of 2 to 10 vol% fluoboric acid or a hydrofluosilic acid of a similar concentration. The solution is maintained at about 25 °C (77 °F), and the article is immersed in the solution for about 1 min
- Submerging the article in water and applying ultrasonic energy of 20,000 to 30,000 cycles/s for 1 to 2 min
- Swabbing the loosely adhering film from the article by rubbing the surface with cotton, paper, or a brush

An optional step of rinsing the article in water can be practiced by using deionized water to free the article of any residual traces of the material used in previous steps.

Preferred metals to be deposited on the article include copper, nickel, and chromium. The chemical compositions and conditions used for the different electrolytes are shown in Table 1. Similar procedures can be used for electroplating metals on hafnium, although information in this respect is sparse. Some work has been done on advanced surface treatments for the purpose of enhanced corrosion resistance, appearance, resistance to hydrogen uptake, texture control, and other features. (See, for example, selected references by Sabol and McDonald.)

Table 1 Electrolyte compositions and conditions for plating on zirconium

Electrolyte	Composition	Amount		Temperature		Current density		Heat treatment[(a)]	
		g/L	oz/gal	°C	°F	A/dm^2	A/ft^2	°C	°F
Copper	$CuSO_4{\cdot}5H_2O$	150-250	20-33	32-42	90-110	16-22	160-220	149-204[(b)]	300-400[(b)]
	H_2SO_4	45-110	6-14	. . .	. . .	. . .	. . .	. . .	. . .
	$NH_2{\cdot}CS{\cdot}NH_2O$	0.002-0.005	0.0003-0.0007	. . .	. . .	. . .	. . .	. . .	. . .
	H_2O	bal	bal	. . .	. . .	. . .	. . .	. . .	. . .

Chromium	CrO_3	200-300	26-39	30-50	86-120	10-20	100-200	. . .	. . .
	H_2SO_4	2-3	0.3-0.4	. . .	. . .	. . .	. . .	. . .	. . .
	H_2O	bal	bal	. . .	. . .	. . .	. . .	. . .	. . .
Nickel	$NiSO_4 \cdot 6H_2O$	320-340	42-44	45-65	115-150	2.1-10	21-100	700[(c)]	1290[(c)]
	$NiCl_2 \cdot 6H_2O$	40-50	5-7	. . .	. . .	. . .	. . .	. . .	. . .
	H_3BO_3	36-40	4.6-5.2	. . .	. . .	. . .	. . .	. . .	. . .
	H_2O	bal	bal	. . .	. . .	. . .	. . .	. . .	. . .

(a) After plating.

(b) 3 h.

(c) 1 h

Surface Engineering of Refractory Metals and Alloys

Revised by John A. Shields, Jr., Climax Specialty Metals

Introduction

THE REFRACTORY METALS include niobium (also known as columbium), tantalum, molybdenum, tungsten, and rhenium. With the exception of two of the platinum-group metals, osmium and iridium, they have the highest melting temperatures and lowest vapor pressures of all metals. The refractory metals are readily degraded by oxidizing environments at moderately low temperatures, a property that has restricted the applicability of the metals to low-temperature or nonoxidizing high-temperature environments. Protective coating systems have been developed, mostly for niobium alloys, to permit their use in high-temperature oxidizing aerospace applications.

Refractory metals at one time were limited to use in lamp filaments, electron tube grids, heating elements, and electrical contacts; however, they have since found widespread application in the aerospace electronics, nuclear and high-energy physics, and chemical process industries. Each of the refractory metals, with the exception of rhenium, is consumed in quantities exceeding 900 Mg (1000 tons) annually on a worldwide basis.

This article describes surface cleaning, finishing, and coating methods used with molybdenum, tungsten, tantalum, and niobium. Because of similarities in processes and applications, molybdenum and tungsten are discussed together, as are tantalum and niobium.

Surface Engineering of Molybdenum and Tungsten

The surface engineering processes used for molybdenum and tungsten are largely similar to those used for steels and heat-resistant alloys (see the articles "Surface Engineering of Carbon and Low-Alloy Steels" and "Surface Engineering of

Heat-Resistant Alloys" in this Volume). This section describes exceptions, modifications, and special practices for treating molybdenum and tungsten surfaces.

Mechanical Cleaning and Polishing of Molybdenum and Tungsten Surfaces

Abrasive Blasting. The oxides of tungsten and molybdenum become volatile at relatively low temperatures. Oxides formed on the metal surface during hot working are porous. To remove these oxides, abrasive blasting is not generally required. It can be useful, however, to remove surface oxides from large or bulky components such as forgings to prepare them for machining. Grit sizes ranging from 36 to 120 mesh are commonly used.

Caution should be exercised when using this technique for two reasons. It is easy for particles of the abrasive medium to become embedded in the surface of the material, and it is not always possible to remove them if they are ceramic. If "iron" grit is used, embedded particles may be removed with hydrochloric acid, or by the nitric-hydrofluoric acid cleaning process described later in this section. When thinner sections such as sheet or plate are subjected to abrasive blasting on one side for an extended length of time without being turned over, the thermal stress caused by the temperature difference across the thickness of the plate may result in cracking of the metal.

Mechanical Grinding and Finishing. Belt grinding is commonly used to produce uniform surface finishes on both flat and round mill products of molybdenum and tungsten. The choice of equipment and abrasive are dictated in part by the equipment available and in part by the finish required. Wet grinding is preferred to avoid overheating and subsequent cracking. The liquid medium (water or a water-soluble coolant) also serves to minimize airborne dust and to lubricate the cutting medium. Table 1 summarizes recommendations for grinding molybdenum (Ref 1). Grinding wheels and papers should employ aluminum oxide or silicon carbide media. Emery paper is ineffective in grinding molybdenum and tungsten.

Table 1 Grinding recommendations for unalloyed molybdenum

	Surface grinding		**Cylindrical grinding**		**Bench grinding**	**Cutoff**	**Snagging portable**
	Surface grinding	**Form grinding**	**Roughing**	**Finishing**			
Wheel speed, m^2/min (ft^2/min)	510-605 (5500-6500)	510-605 (5500-6500)	510-605 (5500-6500)	510-605 (5500-6500)	885 (9500)	930 (10,000)	605 (6500)
Table speed, m/s (ft/min)	0.3 (50)	0.3 (50)	1/3[(a)]	1/6[(a)]	. . .	. . .	. . .
Work speed, m^2/min (ft^2/min)	. . .	. . .	6.5 (70)	10 (120)	. . .	. . .	. . .
Crossfeed, mm (in.)	0.813 (0.032)	. . .	. . .	. . .	. . .	. . .	. . .
Grinding fluid	Oil-water emulsion	Dry	Oil-water emulsion	Oil-water emulsion	Dry	Oil-water emulsion	Dry
Infeed/pass, mm (in.)	0.51 (0.002)	0.025 (0.001)	0.025-0.051 (0.001-0.002)	0.025 + sparkout (0.001)	. . .	. . .	. . .
Wheel dressing	Open	Open	Open	Fine	None	None	None

Wheel grading grain	Dry-wet Al_2O_3	Al_2O_3	Al_2O_3	Al_2O_3	Al_2O_3	Al_2O_3	Al_2O_3
Grit size[(b)]	60 (F)	60 (SF) 100 (F)	465 (SF)	80 (SF)	203 (SF)	60 (T)	36 (T)
Grade[(b)]	H	J (SF) I (F)	K	K	R	N	L
Structure[(b)]	8	8 (SF) 5 (F)	6	6	Normal	6	6
Bond	Vitrified	Vitrified	Vitrified	Vitrified	Resinoid	Rubber	Vitrified
Carborundum gradings							
Dry	AA60-H8-V40	AA100-15-V40	. . .	. . .	. . .	. . .	A36-L6-V30
Wet	GA60-J8-V40	. . .	DA465-K6-V11	DA80-K6-V11	TA203-R-B65	A60-N6-RR	. . .

Source: Ref 1

(a) Width of wheel per revolution of work.

(b) Grain type: F, friable; SF, semi-friable; T, tough.

Chemical Cleaning and Polishing of Molybdenum and Tungsten Surfaces

Molten Caustic Process. To remove the heavy oxide scale from tungsten, molybdenum, and their alloys, the molten caustic process is used. The molten caustic bath can be sodium hydroxide (NaOH) containing 0.5 to 3% sodium nitrite ($NaNO_2$), or it can be molten potassium hydroxide (KOH) containing 10% $NaNO_2$. Individual plants may use slightly different formulations. The operating temperature ranges from 315 to 400 °C (600 to 750 °F), and the immersion time is from 5 to 20 min or until the bubbling reaction stops. Caution should be taken to avoid any water getting into the bath, or a violent reaction will occur. When the workpiece is removed from the caustic, it is rinsed immediately with a jet of hot water in order to blast off the dissolved material and attached salt.

In the molten salt bath room, a suction hood or other ventilation system should be installed. The operator should use a control in a separate room or be separated from the bath container by a partition. In the vicinity of the bath container, the operator should wear a respirator, a face shield, rubber gloves, and an apron. In case the skin or eyes come in contact with the salt, one should flush the eye or skin area with plenty of water for at least 15 min.

Acid Cleaning and Pickling. When tungsten and molybdenum are slightly oxidized on the surface or after the heavily oxidized workpiece is cleaned with molten caustic, acid cleaning is used. The acid solution consists of 50 to 70 vol% of concentrated HNO_3, 10 to 20% of concentrated HF, and the remainder water. The cleaning solution is best when maintained at temperatures of 50 to 65 °C (120 to 150 °F). The process of acid pickling is twofold. First the nitrogen dioxide generated by nitric acid oxidizes the metal surface. Then the oxide is dissolved in hydrofluoric acid. The nitric-hydrofluoric bath also dissolves iron-containing contaminants that may have become embedded or included in the metal surface during high-temperature processing.

In the pickling area, ventilation and drainage systems should be installed. For the pickling acid, a recycling system to remove the residues and to refresh the acid is recommended. In small operations without recycling, the acid solution should be disposed of in a manner consistent with environmental regulations.

The dangers of hydrofluoric acid cannot be overemphasized. Any personnel working with the material must be adequately protected with rubber gloves and garments. Emergency spill kits should be readily available to neutralize any acid spills and more importantly treat any acid burns. Hydrofluoric acid is a "calcium seeker" that can cause severe and permanent injury to bone, and even death if burns are not treated properly.

Tungsten normally receives no other acid cleaning treatments, but molybdenum is occasionally further acid cleaned in a nitric-sulfuric acid bath. Acid concentrations are normally 750 to 900 g/L (100 to 120 oz/gal) HNO_3 and 100 to 200 g/L (15 to 25 oz/gal) H_2SO_4. The bath is typically operated at ambient temperatures.

Thorough water rinses are necessary after all acid cleaning treatments to remove acid residues and dissolved species. The best approach is to employ clean water sprays; the effluent from all rinse operations must be handled carefully to conform with environmental and safety regulations.

Solvent Cleaning. To remove oil, grease, and other contaminants from the surface of tungsten or molybdenum, a common organic solvent such as trichloroethylene, acetone, or isopropanol may be used. Cleaning is usually performed at room temperature by immersing and soaking the part in the solvent. Ultrasonic vibration is sometimes used to loosen soils from deep recesses. For large parts, spraying or wiping with the solvent may serve the same cleaning purpose. A proper ventilation system should be installed in the room for solvent cleaning.

Electrolytic Cleaning. Two common methods for cleaning molybdenum and tungsten are acid electrolyte (aqueous solution of 5 to 50 vol% concentrated HF, using 5 V, 60 Hz alternating current) and alkaline electrolyte (aqueous solution of 2 to 10 wt% NaOH or KOH with a nickel cathode, using a current density of 230 A/dm^2, or 2300 A/ft^2).

Preparation of Molybdenum and Tungsten for Coating and Joining

Plating is a coating technique that generally requires very clean surfaces, and a number of techniques have been developed to produce such surfaces. Table 2 summarizes operating information for several electrolytic cleaning techniques that have been applied to molybdenum. Table 3 lists nonelectrolytic techniques that are also in use.

Table 2 Etching solutions and conditions for molybdenum

Solution composition	Amount		Anodic current density		Time, min	Temperature	
	g/L	oz/gal	A/dm^2	A/ft^2		°C	°F
Sulfuric acid, H_2SO_4	880	1140	2-10	20-100	2-3	21-32	70-90
Phosphoric acid, H_3PO_4	718	93					
Chromate trioxide, CrO_3	100	153	38	380	2	21-32	70-90
Sodium chromate, Na_2CrO_4	10	1					
Sulfuric acid, H_2SO_4	1180	153	22	220	$\frac{1}{2}$	21-32	70-90

Chromate trioxide, CrO_3	250	33	15.5	155	$\frac{1}{3}$	56	135
Sulfuric acid, H_2SO_4	2.5	0.3					

Table 3 Nonelectrolytic cleaning techniques for molybdenum

Solution	Temperature		Immersion time, min
	°C	°F	
Satisfactory preparation for electroplating			
Aqueous: 300 g/L (40 oz/gal) potassium ferricyanide	RT	RT	1
"Ultra-clean" surfaces for electronic applications			
Aqueous: 80% H_2O_2, 10% HCOOH	RT	RT	5-10
Alternate "ultra-clean" surfaces for electronic applications			
Concentrated H_2SO_4 and 3.5 vol% saturated $Na_2Cr_2O_7 \cdot 2H_2O$	90	195	1

Ion sputtering has been evaluated as a means for preparing molybdenum and tungsten for plating and has not been shown to have an advantage in producing adherent films. However, when sputter cleaning is combined with magnetron deposition of an underlayment coating, the strength of subsequently plated coatings is greatly improved (Ref 2, 3).

Cleaning is also critical to obtaining efficient joints in brazed or welded material. A two-step technique for cleaning molybdenum prior to brazing has been published by one brazing alloy manufacturer, as follows:

Bath No. 1 (wt%)	
Potassium permanganate	5
Sodium hydroxide	10
Water	85
Bath No. 2 (vol%)	

Sulfuric acid (concentrated)	15
Hydrochloric acid (concentrated)	15
Aqueous solution of chromic acid (6-10 wt% CrO_3)	70

Immerse the molybdenum in bath No. 1 for 5 to 10 min at 65 to 80 °C (150 to 180 °F), remove, and spray rinse. This will leave a black smut on the surface. Rinse with cold water, scrubbing off loose smut. Immerse the molybdenum in Bath No. 2 at room temperature for 5 to 10 min, remove, and spray rinse. This cleaning procedure will remove the oxides without attack of the base metal.

Several other processes have been developed for pre-welding cleaning of molybdenum:

Alkaline-Acid Procedure

1. Degrease with acetone.
2. Immerse for 5 to 10 min at 65 to 80 °C (150 to 180 °F) in alkaline solution of 10 wt% NaOH, 5 wt% $KMnO_4$, and 85 wt% distilled water.
3. Rinse with cold water, scrubbing off the loose smut.
4. Immerse for 5 to 10 min at room temperature in a bath of 15 vol% concentrated H_2SO_4, 15 vol% concentrated HCl, 70 vol% distilled water plus 6 to 10 wt% CrO_3.
5. Rinse in flowing cold tap water and allow to drain dry.

The last step has been modified to use distilled water after the flowing tap water rinse and then dried with forced hot air.

Dual-Acid Procedure

1. Degrease with acetone.
2. Immerse 2 to 3 min at room temperature in a solution of 15 vol% hydrochloric acid (37 to 38% HCl), 15 vol% sulfuric acid (95 to 97% H_2SO_4), 15 vol% nitric acid (90% HNO_3), and 55 vol% distilled water.
3. Rinse in flowing tap water.
4. Immerse for 3 to 5 min at room temperature in a solution of 15 vol% sulfuric acid (95 to 97% H_2SO_4) 15 vol% hydrochloric acid (37 to 38% HCl), 70 vol% distilled water, and 6 to 10 wt% chromium trioxide (Cr_2O_3).
5. Rinse in flowing tap water.
6. Rinse in distilled water.
7. Dry with forced hot air.

Cleaning Procedure for Heavy Oxide Films

1. Vapor degrease in trichloroethylene.
2. Virgo (Virgo is a proprietary molten descaling process) descale; 5 to 15 s at 470 ± 15 °C (875 ± 25 °F).
3. Cold water rinse until all Virgo salt is removed.
4. Dry; repeat steps 2 and 3 if oxides are not removed.
5. Cold water rinse, until all Virgo salt is removed.
6. Nitric acid pickle; 20 to 25 vol% of 42 °Bé acid (63 ± 3 °C, or 145 ± 5 °F), until a uniform dark coating is formed.
7. Cold water rinse.
8. Dip in potassium ferricyanide-potassium hydroxide solution:

Potassium ferricyanide, g/L(oz/gal)	300 (40.2)
Potassium hydroxide, g/L (oz/gal)	100 (13.4)
Temperature	Room
Time, s	30-60

9. Cold water rinse.
10. Chromic acid dip; 187 g/L (25 oz/gal) Cr_2O_3, 30 to 45 s, room temperature.
11. Cold water rinse.
12. Alkaline cleaner (90 ± 6 °C, or 190 ± 10 °F), 6 s maximum.
13. Cold water rinse.
14. Hydrochloric acid pickle; 20 to 22 °Bé (63 ± 3 °C, or 145 ± 5 °F),10 s maximum.
15. Cold water rinse.
16. Deionized water rinse containing 0.01 wt% of a chelating material (Sequestrene NA4, NA2, or equivalent material; product of Geigy Chemical Corporation).
17. Repeat step 16 in a second solution.
18. Methyl alcohol--25 vol% acetone rinse.
19. Repeat step 18 in a second solution.
20. Drain dry.
21. Wrap in clean plastic sheeting.

Cleaning Procedure for Nonvisible Oxide Films

1. Vapor degrease in trichloroethylene.
2. Alkaline soak clean:

Sodium hydroxide, g/L (oz/gal)	7.5 (1)
Sodium carbonate, g/L (oz/gal)	30 (4)
Sodium phosphate (Na_3PO_4), g/L (oz/gal)	15 (2)
Temperature, °C (°F)	88±5 (190±10)
Time, min	1-2

3. Cold water rinse.
4. HCl pickle; 20 to 22 °Bé (63 ± 3 °C, or 145 ± 5 °F), 10 to 15 s.

5. Cold water rinse.
6. Rinse in deionized water containing 0.01% by weight of chelating material (same as for above).
7. Repeat step 6 in a second solution.
8. Methyl alcohol--25% acetone rinse.
9. Repeat step 8 in a second solution.
10. Drain dry.
11. Wrap in clean plastic.

After cleaning, the parts are handled with clean, dry gloves until they are welded.

Acid Cleaning Procedure

1. Solution: 95.0 parts H_2SO_4, 4.5 parts HNO_3, 0.05 parts HF, and 18.8 g/L (2.5 oz/gal) Cr_2O_3.
2. Temperature 60 °C (140 °F).
3. Immerse specimens for 30 s.
4. Rinse with hot water.

Electropolishing Procedures for Cleaning Molybdenum Prior to Brazing

1. Solution: 2 parts concentrated H_2SO_4, one part water.
2. Solution temperature 55 °C (130 °F).
3. Current density, 62 to 78 A/dm^2 (4 to 5 A/in.^{2}).
4. Voltage: 10 to 11 V.
5. Polishing time: 2 min.

Plating and Coating of Molybdenum and Tungsten

Electroplating. Molybdenum and tungsten are difficult to plate because the natural oxides formed on the surface of these metals interfere with the adherence of coatings. Chromium has been a favored strike coating because its thermal coefficient of expansion is similar to that of molybdenum. It has good as-plated adherence, and the two metals diffuse to form a solid solution at elevated temperatures. Nickel has also found extensive use as a strike plating because its adherence can be enhanced by a post-plating diffusion anneal. The anodic etching procedure for activation of molybdenum is as follows:

1. Chromium is deposited in a chromic-sulfuric acid bath, 250 g/L (33 oz/gal) Cr_2O_3 and 2.5 g/L (0.3 oz/gal) H_2SO_4, at 90 ± 5 °C (195 ± 9 °F), using a current density of 100 ± 20 A/dm^2 (1000 ± 200 A/ft^2).
2. Nickel is deposited in a Watts-type bath over an acid chloride Wood's nickel strike plate, 240 g/L (31 oz/gal) nickel chloride·hexahydrate, 80 g/L (10 oz/gal) HCl at room temperature, using a current density of 3 to 10 A/dm^2 (30 to 100 A/ft^2), on the chromium-plated molybdenum.
3. Molybdenum plated with 25μm (1 mil) of chromium and 175 μm (7 mils) of nickel is protected in air for 1200 h at 980 °C (1795 °F), and for 100 h at 1200 °C (2190 °F).
4. Chromium-strike plated tungsten is carried out in the same bath as for molybdenum at 50 °C (120 °F), for 1 min with a current density of 5 to 15 A/dm^2 (50 to 150 A/ft^2). Watts nickel can be deposited over an acid sulfate strike on chromium-plated tungsten. This is carried out in a bath containing 240 g/L (31 oz/gal) nickel sulfate·hexahydrate and 40g/L (5 oz/gal) H_2SO_4 at room temperature for 2 to 5 min with a current density of 5 to 10 A/dm^2 (50 to 100 A/ft^2).

Another process intended to produce a hydride film as a basis for nickel plating is as follows:

1. Tungsten is treated cathodically at 1 to 11 A/dm^2 (10 to 110 A/ft^2) in approximately 2% acid or alkali, by weight, for 5 to 15 s.

2. Tungsten is rinsed, and nickel plated for 2 min in a Watts nickel bath, pH 4.0, at 65 °C (150 °F), with a current density of 5 to 11 A/dm^2 (50 to 110 A/ft^2).
3. The nickel-coated tungsten, after heating under vacuum at 450 to 750 °C (840 to 1380 °F) until gas evolution ceases, is cleaned and activated by strike plating in a Wood's nickel bath and then plated as desired.

Recent development shows that gold can also be used as a preplate for the subsequent deposition of other metal coatings. A process for molybdenum is detailed as follows:

1. Alkaline ferricyanide etch for 10 s at room temperature in a solution of 200 to 250 g/L (26 to 33 oz/gal) ferricyanide and 75 to 85 g/L (10 to 11 oz/gal) KOH.
2. Water rinse.
3. Hydrochloric acid, 50 vol%, dip for 10 s at room temperature.
4. Water rinse.
5. Acid gold strike, alkaline gold-cyanide-tartrate bath, 1 to 3 min at 0.1 A/dm^2 (1 A/ft^2), deposit 0.12 to 0.72 mg/cm^2 (0.78 to 4.7 mg/in.^{2}), 0.06 to 0.37 μm (2.4 to 15 μin.).
6. Water rinse and dry.
7. Diffuse in dry hydrogen at 830 °C (1525 °F) for 30 min.
8. Acid gold strike 4 min at 0.1 to 0.2 A/dm^2 (1 to 2 A/ft^2) to deposit additional 0.2 to 0.5μm (8 to 20 μin.).
9. Water rinse and dry. Diffusion in dry hydrogen at 830 °C (1525 °F) for 30 min.
10. Acid gold strike for 45 to 75 s at 0.1 to 0.2 A/dm^2 (1 to 2 A/ft^2).
11. Water rinse.
12. Plate desired metal coating. A thermal treatment in dry hydrogen at 830 °C (1525 °F) reduces the natural oxide to form a metal-metal interface and a diffusion bond.

Tungsten is first plated with about 0.2 to 2.0 μm (8 to 80 μin.) gold, heated at 1200 to 1370 °C (2190 to 2500 °F) under vacuum for 5 min, and then plated with gold or other metals to the desired thickness.

The TZM (0.5% Ti, 0.08% Zr, balance Mo) alloy has good strength properties at high temperature, but is subject to galling in threaded fasteners. Rhodium plating on molybdenum tends to eliminate galling. The process is detailed as follows:

1. Solvent degrease.
2. Alkaline clean at 80 °C (175 °F) for 5 min.
3. Water rinse.
4. Alkaline ferricyanide etch with agitation for 30 s at room temperature.
5. Water rinse.
6. Sulfuric acid, 5 to 10 vol%, dip for 10 s.
7. Rhodium strike at 1 to 2 A/dm^2 (10 to 20 A/ft^2) at 50 °C (120 °F) to deposit a 0.06 to 0.10 mg/cm^2 (0.40 to 0.65 mg/in.^{2}) in an acid rhodium sulfate bath.
8. Water rinse and dry.
9. Diffusion heat treat at 1000 °C (1830 °F) for 30 min, 10^{-4} torr (10^{-2} Pa) maximum, purge with helium.
10. Sulfuric acid dip for 30 s minimum at room temperature.
11. Rhodium plate at 1 to 2 A/dm^2 (10 to 20 A/ft^2) at 50 °C (120 °F) to thickness of 0.5 μm (2.0 μin.).
12. Water rinse and dry.

Application of the rhodium strike directly over the natural oxide to TZM is somewhat difficult to accomplish initially because of the usual high tensile stress in rhodium plate. Reducing this stress is more effective in achieving adherence of the rhodium strike than are efforts to reduce the thickness of the natural oxide on TZM.

Iridium coatings about 12 μm (475 μin.) thick, plated in a fused cyanide bath, over chromium on nickel over gold strike-coated molybdenum, offered oxidation protection for about $\frac{1}{2}$ h in air at 1000 °C (1830 °F).

A typical process for nickel plating is as follows:

1. Degrease.
2. Scrub in detergent.
3. Water rinse.
4. Etch 2 min in potassium ferricyanide.
5. Wipe smut with clean towel and detergent.
6. Cathodically clean in potassium cyanide solution (80 g/L KCN) at 4.65 A/dm^2 (0.30 A/in.^{2}).
7. Cold water rinse 1 $\frac{1}{2}$ min.
8. Strike plate in nickel sulfamate solution for 2 $\frac{1}{2}$ min at 0.78 A/dm^2 (0.05 A/in.^{2}):

$Ni(NH_2SO_3)_2 \cdot H_2O$, g/L (oz/gal)	335 (45)
$NiCl_2$, g/L (oz/gal)	45 (6)
H_3BO_3, g/L (oz/gal)	45 (6)
pH	3.4

9. Water rinse.
10. Hydrogen anneal for 10 min at 875 °C (1605 °F).
11. Water rinse.
12. Repeat step 6.
13. Cold water rinse.
14. Plate in solution of step 8 at 2.3 A/dm^2 (0.15 A/in.^{2}) for 16 min.
15. Water rinse.
16. Repeat steps 12 to 15 until desired thickness is attained.

Anodizing. For the anodizing of tungsten and molybdenum, an acetic-based electrolyte for vanadium may be used. It consists of acetic acid, 0.02 *M* sodium tetraborate-decahydrate, and 1.0 *M* additional water. When the water content is less than 1.0 *M,* the conductivity is reduced to an inconvenient extent. When the content is more than 2*M,* the film formed on molybdenum becomes excessively unstable. In the process, a platinum cathode is preferred, and the temperature is maintained around 25 °C (77 °F), with the presence of air.

The anodic film formed on molybdenum is so unstable that it will change interference colors and eventually disappear when exposed to air. It can be stabilized either by dipping in glacial acetic acid, followed by drying with filter paper, or by using a jet of compressed air immediately after its withdrawal from the electrolyte. Once stabilized, it can be stored in a desiccator almost indefinitely.

High-Temperature Oxidation-Resistant Coatings for Molybdenum. Ductile metallic overlays are among the first materials investigated as coatings for molybdenum. The materials and processes used are summarized in Table 4. The electrodeposition processes have been discussed in the electroplating section. Chromium is the most promising of the

metallic coatings for molybdenum. It offers excellent oxidation protection and is compatible with substrate; however, chromium is embrittled by nitrogen and will crack and spall on repeated thermal cycling. A nickel or nickel alloy overlay will protect chromium from nitriding. A duplex coating will give good service for molybdenum up to 1200 °C (2195 °F).

Table 4 Metallic coatings for molybdenum

Process type	Material	Thickness range	
		µm	µin.
Electrodeposition	Chromium, nickel, gold, iridium, palladium, platinum, rhodium	12.7-76.2	500-3002
Flame sprayed	Nickel-chromium-boron, nickel-silicon-boron, nickel-chromium, nickel-molybdenum	127-254	5004-10,007
Clad or bonded	Platinum, nickel, nickel-chromium, platinum-rhodium	50.8-508	2002-20,015
Molten bath	Chromium	12.7-25.4	500-1001

Noble metal coatings, such as platinum and iridium, can be used on molybdenum at temperatures to about 1425 °C (2595 °F). They provide a significantly longer useful life at all temperatures than the duplex chromium-nickel coatings.

Coatings based on compounds with aluminum, in initial attempts, were to develop molybdenum parts for aircraft gas turbines. Coatings of aluminum-chromium-silicon, aluminum-silicon, and aluminum-tin systems are indicated in Table 5. The aluminide coatings are applied as thick overlays, using a variety of spray or dip processes. The aluminide coatings provide good oxidation protection to molybdenum at temperatures up to 1540 °C (2805 °F). Life at higher temperatures is very short, less than 1 h, probably as a result of rapid interdiffusion.

Table 5 Aluminide coatings for molybdenum

Type	Compositions	Deposition process	Thickness range	
			µm	µin.
Aluminum-chromium	20% Al + 80% (55Cr-40Si-3Fe-1Al)	Thermal spray	178-254	7013-10,008
Aluminum-silicon	88% Al-12% Si	Thermal spray, hot dip	12.7-178	500-7013
Tin-aluminum	90% (Sn-25Al)-10% $MoAl_3$	Slurry dip or spray	50.8-203	2002-7998

Interest in coatings for molybdenum shifted from an aluminide to a silicide base in the mid 1950s. A list of the basic silicide coatings is shown in Table 6. Most of the silicide coatings are deposited by pack-cementation diffusion processes. A major deficiency in the performance of silicide-base coatings appears when the system is used in low-pressure environments. As shown in Fig. 1, silicide coatings that protect TZM substrate for 4 h at 1650 to 1760 °C (3000 to 3200 °F) in air at 1 atm cannot be used above 1480 °C (2695 °F) in air at pressure of 0.1 to 1.0 torr (13 to 130 Pa).

Table 6 Silicide coatings for molybdenum

Type	Deposition process
Molybdenum silicide	Fluidized bed, pack cementation, slip pack, plasma spray, electrophoresis
Molybdenum silicide and chromium	Pack cementation
Molybdenum silicide and chromium, boron	Pack cementation
Molybdenum silicide and chromium, aluminum, boron	Slip pack
Molybdenum silicide and tin-aluminum	Cementation and impregnation

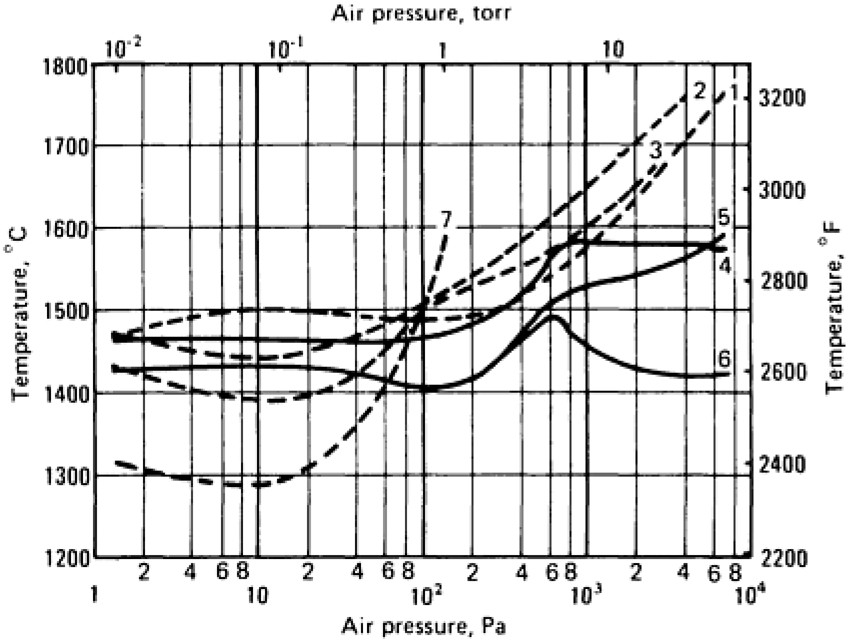


Fig. 1 The effect of air pressure on the maximum temperature for a 4 h life of silicide-coated refractory materials. Alloy/coating: 1, TZM/PFR-6; 2, TZM/Disil; 3, TAM/Durak-B; 4, Cb-752/PFR-32; 5, Cb-752/CrTiSi; 6, B-66/CrTiSi; 7, Ta-10W/Sn-Al

Refractory oxides or ceramics are the only materials suitable for the oxidation protection of molybdenum above 1650 °C (3000 °F) for any length of time. The types of oxide coatings that have been used on molybdenum are summarized in Table 7. Ceramic coatings suffer from one common problem. They crack on thermal cycling and tend to spall from the substrate. For only minutes, during single-cycle uses, such as for rocket motors, ceramic coatings provide useful protection from oxidation to 1930 °C (3505 °F) with Al_2O_3 and to 2200 °C (3990 °F) with ZrO_2.

Table 7 Oxide coatings for molybdenum

Type	Deposition process	Thickness range	
		μm	mils

Zirconium oxide-glass	Frit, enamel	130-760	5-30
Chromium-glass	Frit, enamel	130-250	5-10
Chromium-alumina oxide	Thermal spray over chromium plate	200-380	8-15
Alumina oxide	Thermal spray	25-2500	1-100
Zirconium oxide	Thermal spray	25-2500	1-100
Zirconium oxide	Troweling	2500-7600	100-300

High-Temperature Protective Coatings for Tungsten. A more restrictive situation exists with tungsten. Silicide coatings are protective for a short time to 1925 °C (3500 °F). In the 1090 to 1650 °C (1995 to 3000 °F) range, lives of 10 to 50 h are attained.

Modifying the silicides with tungsten, zirconium, and titanium may be a more successful approach. A tungsten-modified silicide pack coating with HfB_2 additives is available commercially. A multi-element umbrella type, consisting of iridium electrodeposited from a fused salt bath, followed by a plasma-sprayed ZrO_2 layer prevents volatilization losses during very high-temperature oxidation. This may be serviceable at 1800 °C (3270 °F) for several hours. In the ceramic approach, a coating of ThO_2 over a tungsten wire mesh can be used at 2925 °C (5300 °F), and a coating of HfO_2 at 2700 °C (4890 °F).

References cited in this section

1. G.A. Timmons, *Machining Molybdenum,* Climax Specialty Metals, Cleveland, OH, 1993
2. T.G. Beat, W.K. Kelly, and J.W. Dini, Plating on Molybdenum, *Plat. Surf. Finish.,* Vol 75, Feb 1988, p 71-75
3. J.W. Dini, Providing Adherent Coatings on Tungsten and Tungsten Alloys, *Proc. Conf. Tungsten and Tungsten Alloys,* 15-18 Nov 1992 (Crystal City, VA), Metal Powder Industries Federation, 1993

Surface Engineering of Tantalum and Niobium

The processes and equipment for surface cleaning, finishing, and coating of tantalum and niobium, like those for molybdenum and tungsten, are similar to the processes and equipment used for steels and heat-resistant alloys. Important exceptions and special procedures are noted in this section.

Mechanical Cleaning and Polishing of Tantalum and Niobium Surfaces

Abrasive Blasting. To remove intermediate thickness of the oxide scale of tantalum or niobium, abrasive blasting is applied. The abrasives to be used are usually silicon carbide of grit sizes ranging from 36 to 120 mesh. A good ventilation system is required in the abrasive blasting room, and the operator should wear a mask during working.

Mechanical Grinding and Finishing. Although commercially pure tantalum or niobium is worked at room temperature, their alloys are usually worked at elevated temperatures. Heavy oxide scale is formed. To remove such heavy oxide scale, mechanical grinding is the most effective method. For coarse grinding, a vitrified-bond grinding wheel having a 46 to 60 mesh of aluminum oxide is used. For finishing, a finer grit, vitrified or resinoid-bond grinding wheel 60 to 120 mesh of silicon carbide is used. For the cutting of tantalum or niobium, an abrasive wheel is also preferred. The grinding operation usually is performed dry, but the abrasive cutting is used with water cooling.

A good ventilation system should be installed in a grinding or polishing room. The operator should wear a face shield, mask, and gloves during working. Emery cloth and paper are ineffective for polishing tantalum and niobium. They are seldom used for finishing the product of these metals.

Cleaning and Polishing of Tantalum and Niobium

Alkaline Cleaning. When oxide scale is combined with grease, graphite, molybdenum disulfide, and other lubricants on the workpieces of tantalum and niobium, an alkaline cleaning process is usually used. The starting product for the solution is a solid alkaline material that usually consists of 50 to 80% NaOH, with the remainder being sodium metasilicate and sodium carbonate. The solids are dissolved in water at a concentration of 0.6 to 1.2 kg/L (5 to 10 lb/gal), and the solution is kept at 65 to 80 °C (150 to 180 °F). The soaking time for the workpiece ranges from a few minutes to a few hours. After soaking, the workpiece should be immediately rinsed with a jet of water in order to blast off the loosened scale and attached salt. The operator should wear a face shield, rubber gloves, and an apron during working.

Acid Cleaning and Pickling. After mechanical grinding, abrasive blasting, or alkaline cleaning, tantalum and niobium are cleaned further with an acid solution. This consists of 40 to 60 vol% of concentrated HNO_3 to 10 to 30% of concentrated HF, and the remainder water. The cleaning solution is best when maintained at temperatures of 50 to 65 °C (120 to 150 °F). After acid pickling, the workpiece should be washed with water or rinsed thoroughly with a jet of water to remove any trace of acids.

Good ventilation and drainage systems should be installed in the acid pickling room. A recycling system to remove the residues and to refresh the acid is preferred both for economical and ecological reasons. For small operations without recycling, the acid solution should be disposed of in a manner consistent with environmental regulations.

The dangers of hydrofluoric acid cannot be overemphasized. Any personnel working with the material must be adequately protected with rubber gloves and garments. Emergency spill kits should be readily available to neutralize any acid spills and more importantly treat any acid burns. Hydrofluoric acid is a "calcium seeker" that can cause severe and permanent injury to bone, and even death if burns are not treated properly.

Solvent Cleaning. To remove oil, grease, and other contaminants from the surface of tantalum or niobium, a common organic solvent, such as trichloroethylene, acetone, or isopropanol can be used. Cleaning is performed at room temperature by immersing workpieces in solvent. Ultrasonic vibration is sometimes used to loosen soils from deep recesses. For large parts, spraying or wiping with the solvent may serve the same purpose. A proper ventilation system should be installed in the room for solvent cleaning.

Electrolytic Cleaning. Electrolytic etching may be used for the preparation and activation of tantalum and niobium before electroplating. The electrolytes usually used are as follows:

- For niobium, a concentrated hydrofluoric acid, 49% solution, with alternating current at 1 to 5 V and a current density of 22 to 108 A/dm^2 (220 to 1080 A/ft^2) for 1 to 3 min at room temperature is used.
- For tantalum, a solution consisting of 90% concentrated H_2SO_4 and 10% concentrated HF, used in the 25 to 40 °C (75 to 105 °F) range with a platinum cathode at a current density of 10 to 50 A/dm^2 (100 to 500 A/ft^2), gives excellent results.

Preparation of Tantalum and Niobium for Coating and Joining

Before electroplating, the substrate to be plated should be electrolytically cleaned or activated. The electrolytic cleaning processes for niobium and tantalum have been mentioned in a previous section. After this, the article may be dipped in an aqueous solution of 50% concentrated HNO_3 and 2% concentrated HF, at 20 to 30 °C (68 to 86 °F).

Plating and Coating of Tantalum and Niobium

Electroplating. Copper, chromium, gold, iron, nickel, and platinum are plated on niobium or tantalum. Conditions and solutions for these are given in Table 8.

Table 8 Solutions for plating niobium or tantalum

Solution	Constituent	Amount of constituent		Current density		Temperature	
		g/L	oz/gal	A/dm^2	A/ft^2	°C	°F
Copper	$CuSO_4 \cdot 5H_2O$	210	27	1.69	26.9	25	77
	H_2SO_4	80	10				
	Molasses	2.5	0.3				
Chromium	CrO_3	400	52	5.38	53.8	75	165
	H_2SO_4	4	0.5				
Gold	$KAu(CN)_2$	44	5.7	2.15	21.5	54	130
	$K_2C_4H_4O_5$	48	6.2				
	KOH	3	0.9				
	K_2CO_3	10	1.3				
	KCN[a]	30	4				
Iron	$Fe_2SO_4 \cdot 7H_2O$	300	39	3.23	32.3	60	140
	$FeCl_2 \cdot 4H_2O$	42	5.5				
	$(NH_4)_2SO_4$	15	2				
	NaCOOH	15	2				
	H_3BO_3	30	4				
	Wetting agent	1	0.13				
Nickel	$NiSO_4 \cdot 7H_2O$	300	39	1[b]	10	60	140
	$NiCl_2 \cdot 6H_2O$	50	6.5				

	H_3BO_3	30	4				
	Wetting agent	1	0.13				
Platinum	Bakers platinum solution No. 209	(c)	(c)	8.07	80.7	88	190

(a) pH, 12.1.

(b) 4.31 A/dm^2 (43.1 A/ft^2).

(c) Diluted to 4 g/L (0.52 oz/gal) of contained platinum made slightly ammoniacal

Iron and nickel deposits are fairly adherent. Other deposits easily peel off the niobium. The presence of a hydride layer between the plate and the niobium limits the strength of the bond, and heat treating is required to decompose the hydride. This involves heating in a vacuum for 1 h at 700 to 1100 °C (1290 to 2010 °F). Improved adhesion of the coating can also be obtained if the surface to be plated is first shot blasted and the flash coated with an undercoat of copper, deposited by chemical displacement from a specified electrolyte.

For plating gold on tantalum, heat treatment before and after the electrolytic plating will enhance the bonding. The temperature for preheating is 1955 °C (3550 °F), and the after-treatment is carried out at 1100 °C (2010 °F). Both treatments occur under vacuum.

For plating nickel, cathodic treatment at 2 A/dm^2 (20 A/ft^2) for 20 to 30 min in a solution of 2.5 vol% of 48% HF, 2.5 vol% of HCl, sp gr 1.16, and 95% absolute methanol at 40 to 50 °C (105 to 120 °F), gives a more uniform surface texture on tantalum. After this treatment, 0.3 μm (12 μin.) of nickel is deposited in a Watts bath, pH 4.0, vacuum heat treated at 500 to 600 °C (930 to 1110 °F), then nickel plated to 10 μm (390 μin.) thick, and again heat treated at 450 °C (840 °F).

Another procedure intended to produce a hydride film as a basis for electroplating with nickel on tantalum or niobium is as follows:

1. The metal is treated cathodically at 1 to 11 A/dm^2 (10 to 110 A/ft^2) in 2%, by weight, acid or alkali for 5 to 15 s.
2. The metal is then rinsed and nickel plated for 2 min in a Watts nickel bath, pH 4.0, at 65 °C (150 °F), with a current density of 5 to 11 A/dm^2 (50 to 110 A/ft^2).
3. After vacuum heating at 450 to 750 °C (840 to 1380 °F) until gas evolution ceases, the nickel-coated article is cleaned and activated by strike plating in Wood's nickel bath, and then plated as desired.

Anodizing is a process in which a current passes through an electrolyte from an inert cathode to the anode, on which a thin layer of the oxide forms during the process. The thin but dense oxide layer thus formed usually protects the metal from further oxidation in air and from abrasion. Anodic oxidation for tantalum and niobium is carried out at constant current density, about 1 to 15 A/dm^2 (10 to 150 A/ft^2), at room temperature either in 0.5 to 2 wt% ammonium citrate or in 0.5 wt% ammonium borate solution, with the pH kept at 9 by adding ammonium hydroxide.

Oxidation-Resistant Coatings for Niobium. The use of refractory metals at elevated temperatures is being pursued intensively by the aerospace industry. One of the major limitations to progress in this field is the need for coatings to protect the alloys from rapid oxidation and embrittlement at elevated temperatures. These coatings may be classified as intermetallic compounds, including silicides and aluminides that form compact or glassy oxide layers; alloys that form

compact oxide layers; noble metals that resist oxidation; and stable oxides that provide a physical barrier to the penetration of oxygen.

Many techniques have been used to form protective coatings on niobium alloys. They are as described below.

Pack Cementation. Immersion of the material to be coated in a pack consisting of inert filler, metal coating elements, and halide activator. Heat treatment is conducted in hydrogen or an inert atmosphere. Coating is formed by vapor transport and diffusion.

Vacuum Pack. Immersion of material to be coated in an all-metal pack of coating elements plus halide activator. Heat treatment is performed in dynamic vacuum or under a partial atmosphere of inert gas. Coating is formed by vapor transport and diffusion.

Slip Pack. Similar to the two processes above, substitution of thin disposable bisque for massive pack. Bisque is sprayed, dipped, or applied to the substrate surface in other ways.

High-Pressure Pack Cementation. Similar to pack cementation and vacuum pack, with utilization of inert gas pressure in excess of 1 atm (100 kPa).

Fused Slurry. Uniform application of a metal or alloy slurry to the substrate surface, followed by fusion of the slurry in an inert gas or vacuum environment. Coating forms by liquid-solid diffusion.

Slurry-Sinter. Spray or dip application of metal particles plus binder to substrate surface, followed by solid- or liquid-phase sintering in vacuum or inert environment.

Fused Salt. Electrolytic or nonelectrolytic deposition of metal ions from a fused metal salt solution, such as fluorides, chlorides, and bromides, on the substrate material. Pure or alloy coatings are formed.

Electrophoresis. Deposition of charged metal particles from a liquid suspension onto a substrate surface of opposite electrical potential. Synthesis of particulate deposit generally involves isostatic compaction followed by vacuum or inert atmosphere sintering.

Aqueous Electroplating. Electroplating of metal ions from aqeuous solution. Process can involve suspension of particulate materials in electrolyte and occlusion of these particles in metal deposit.

Fugitive Vehicle. Involves spray or dip application of metal slurry onto the substrate surface, followed by vacuum heat treatment. Slurry contains coating elements and fugitive vehicle that is molten at the firing temperature. Fugitive vehicle has high solubility for coating elements and very low solubility for substrate. Coating forms by transfer of elements from the liquid solution to the substrate surface, with subsequent diffusion growth of the coating phase. Fugitive vehicle is eventually removed by evaporation.

Fluidized Bed. Immersion of the material to be coated in a heated fluidized bed of coating elements, using as the fluidizing gases mixtures of reactive halogen gases and hydrogen or argon. Coating forms by disproportionation of gaseous metal halides on substrate surface, followed by diffusion alloying.

Chemical Vapor Deposition (CVD). Entirely gaseous process. Metal halide gases, plus argon or hydrogen, pass over surface of metal to be coated. Coating forms by hydrogen reduction or thermal decomposition of metal halide at substrate surface, followed by diffusion-controlled coating growth.

Vacuum Vapor Deposition. Evaporation of a metal or alloy from a filament, liquid bath, or other source, followed by condensation of the metal vapor onto a cold or hot substrate surface. Post diffusion treatment is optional.

Hot Dipping. Immersion of material to be coated in a hot liquid bath of the molten coating elements. Coating forms by liquid-solid diffusion.

Hydride and Oxide Reduction. Spray or dip application of metal hydrides or oxides on substrate surface, followed by vacuum or hydrogen reduction, respectively.

Plasma Arc. Spray deposition of particulate metal or oxide particles using conventional plasma arc facility.

Detonation Gun. Patented gun detonation metal spraying process.

Gun Metallizing. Utilization of conventional wire or powder metallizing equipment.

Cladding. Bonding of thin sheet metal cladding to substrate surface by diffusion bonding, forging, rolling, extrusion, and other methods.

Coating systems and processes for niobium are shown in Table 9.

Table 9 Oxidation-resistant coating systems for niobium

System concept	Composition	Process
Silicide coatings		
Complex silicide multilayered	Cr, Ti, Si	Vacuum pack and vacuum slip-pack, fused slurry and pack, fluidized bed, electrophoresis, chemical vapor deposition, electrolytic fused salt
Modified silicide	Si + V, Cr, Ti	Fluidized bed
Modified silicide	Si	Pack cementation, iodine
Modified silicide	Si-B-Cr	Pack cementation, multicycle
Modified silicide	Si-Cr-Al	Pack cementation, multicycle
Modified silicide	Si + additives	Pack cementation, single cycle
Modified silicide	Si + Cr, Al, B	Pack cementation, single cycle
Silicide	Si	Chemical vapor deposition
Molybdenum disilicide	Si + Mo	MoO_3 reduction and chemical vapor deposition
Modified silicide	Si + additives	Pack cementation, fluidized bed, fused salt, slurry dip
Modified silicide	Si + additives	Pack cementation, single cycle
Liquid phase-solid matrix	Se, Sn, Al	Porous silicide applied by pack or CVD-impregnated with Sn-Al
Multilayered complex silicide	40Mo-40Si, 10CrB-10Al	Plasma spray-diffuse

Modified silicide	Si + additives	Pack cementation
Complex silicide	Si-20Fe-20Cr	Fused silicides
Complex silicide	Si-20Cr-5Ti	Fusion of eutectic mixtures
Complex silicide	Si + (Cr, Ti, V, Al, Mo, W, B, Fe, Mn)	. . .
Complex silicide	V-Cr-Ti-Si	Vacuum and high-pressure pack
Complex silicide	Mo-Cr-Ti-Si, V-Cr-Ti-Si, V-Al-Cr-Ti-Si, Mo-Cr-Si	Multicycle vacuum pack
Glass-sealed silicide	Si + glass	Silicide by pack cementation or CVD + glass slip overcoat
Multilayered	Mo, Ti + Si and glass	Slurry sinter application of Mo + Ti powder, pack silicide, glass slurry seal
Aluminide coatings		
Modified aluminide	Al + B	Pack cementation
Modified aluminide	88Al-10Cr-2Si	Fused slurry
Modified aluminide	Al-Si-Cr	Fused slurry
Modified aluminide	Al-Si-Cr, Ag-Si-Al	Hot dip
Multilayered systems	Fe, Cr, Al, Ni, Mo, Si, VSi_2, $TiCr_2$, $CrSi_2$, B + Al	Powder metallize + aluminum hot dip
Simple aluminide	Al	Pack cementation
Multilayered systems	Cr, FeB, NiB, Si, Al_2O_3, SiO_2, ThO_2 + Al	Electroplate dispersions in Ni + Al hot dip
Modified aluminide	Al + (Si, Ag, Cr)	Silver plate + Al, Cr, Si hot dip
Multilayered systems	Al_2O_3 + Ti + Al	(Al_2O_3 + TiH), Spray-sinter + Al hot dip
Oxide-metal composite	Al_2O_3 + Al	Slurry fusion of Al_2O_3-Al mixture

Aluminide	Al + additives	Fused slurry
Modified aluminide	Al + Sn	Hot dip
Zinc coating		
Self-healing intermetallic	Zn and Zn + Al, Ti, Co, Cu, Cr, Fe, Zr, Cu, Si	Vacuum distillation and hot dip
Oxide coating		
Glass-sealed oxide	Al_2O_3 + glass (baria, alumina, silica)	Flame spray Al_2O_3 + glass slurry
Nickel-chromium coating		
Oxidation-resistant alloy	Ni-Cr	Flame spray, detonation gun, plasma arc
Chromium carbide coating		
Carbide	Cr-C	Plasma spray
Noble metal coatings		
Clad	Pt, Rh	Roll bonding and hermetic sealing
Barrier-layer-clad	Pt, Rh + Re, Be, Al_2O_3, W, ZrO_2, MgO, SiC, Hf	Noble metal clad over barrier layer-diffusion couple study
Pure metal	Ir	Fused-salt deposition

Oxidation-Resistant Coatings for Tantalum. Much of the work on tantalum alloys is the outgrowth of approaches taken with niobium alloys. The development of coatings has come generally in the 1970s. Most of the emphasis is on the diffusional growth of intermetallic layers. A few commercial or semicommercial coatings are as follows:

- A series of tin-aluminum-molybdenum-base coatings are used by slurry process. These are limited primarily by poor resistance to reduced pressure and erosion at very high temperatures.
- Electrophoretical deposition of binary disilicides combined with a molybdenum-vanadium system shows no pest phenomenon during service. This process can be considered commercial for small parts.
- A fluidized-bed, three-step silicon-vanadium-silicon process may be used for niobium as well as Ta-10W.
- Complex titanium, molybdenum, tungsten, and vanadium modified silicide coatings can be applied by a two-step method: a slurry plus high-temperature sinter of an alloy layer followed by a straight silicide pack. Protection for hundreds of hours at 870 °C (1600 °F) and 1320 °C (2410 °F) in furnace tests has

been obtained.
- A fused-silicide coating system, particularly Si-20Ti-10Mo, appears practical for coating large, complex aerospace sheet metal components.
- A duplex coating consisting of a sintered hafnium boride-molybdenum silicide layer overlaid with a hafnium-tantalum slurry is serviceable at 1820 to 1870 °C (3310 to 3400 °F).

Surface Engineering of Nickel and Nickel Alloys

Revised by Russell C. Buckley, Nordam Propulsion Systems Division

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Introduction

NICKEL is a versatile element and will alloy with most metals. Complete solid solubility exists between nickel and copper; wide solubility ranges between iron, chromium, and nickel make possible many alloy combinations. The face-centered cubic structure of the nickel matrix (γ) can be strengthened by solid-solution hardening, carbide precipitation, or precipitation hardening. Nickel alloys are used for a wide variety of applications, the majority of which are designed to take advantage of the corrosion resistance and/or heat resistance properties of these alloys. The classification, physical metallurgy, and applications of nickel and nickel alloys are described in Volume 2 of *ASM Handbook;* information on heat-resistant nickel alloys and stainless steels is provided in Volume 1 of *ASM Handbook.* This article describes cleaning and finishing of nickel alloys; additional and related information is available in the articles "Diffusion Coatings," "Surface Engineering of Heat-Resistant Alloys," and "Surface Engineering of Stainless Steels" in this Volume.

Nickel alloys do not require special techniques or precautions for the removal of shop soils such as soap, drawing compound, oil, grease, cutting fluid, and polishing compound. Oxide, scale, tarnish, or discoloration can be removed from nickel and nickel alloys by mechanical methods, such as grinding or abrasive blasting, or by chemical methods, such as pickling. Conventional methods of cleaning with alkaline compounds, emulsions, or solvents or vapor degreasing may be employed. These processes are described in the articles "Alkaline Cleaning," "Emulsion Cleaning," "Solvent Cold Cleaning and Vapor Degreasing," and "Mechanical Cleaning Systems" in this Volume.

Pickling

Pickling is a standard method for producing bright, clean surfaces on nickel alloys, either as an intermediate step during fabrication or as a last step on finished parts. Procedures used for pickling nickel alloys are governed by both material composition and prior thermal treatment. The necessity of pickling can be avoided by using bright-heating practices, that is, the use of a protective inert and/or vacuum furnace atmosphere to prevent oxidation. Pickling should not be used to overhaul material by dissolving away appreciable amounts of metal. This practice can cause severe, irreversible damage such as pitting and intergranular attack. Significant material dimensional loss can readily occur if process parameters (e.g., continued maintenance of bath chemistry, temperatures, and immersion time) are ignored. Caution should be observed when pickling bimetallic items, weldments, and components with platings or coated surfaces, because selective, localized attack may occur, depending on system dynamics.

Oxidizing furnace atmospheres, high-sulfur-content fuels, and air leakage in furnaces during high-temperature operations can cause heavy scale to form on unprotected nickel alloys. Securely oxidized nickel alloys have a dull, spongy appearance. Hairline cracks are sometimes present, and patches of scale may break away from the surface. In such cases, the rough underlying metal will not allow an attractive finish to be attained by any pickling method. Table 1 provides selected formulas for pickling nickel alloys, and the table below will aid in preparing these formulas:

Acid	°Bé	Specific gravity	Concentration, wt%

HNO_3	42	1.41	67
H_2SO_4	66	1.84	93
HCl	20	1.16	32
HF	30	1.26	70

Table 1 Formulas for pickling nickel alloys

Formula No.	Reagents	Weight, %	Amount		Temperature	
			mL	oz	°C	°F
1	Nitric acid (HNO_3) 1.41 sp gr	20	300	10	70	160
	Water		1000	34		
2[(a)]	Nitric acid (HNO_3) 1.41 sp gr	10	133	4	75	170
	Sodium chloride (NaCl)	5	63 g	2		
	Water		1000	34		
3	Nitric acid (HNO_3) 1.41 sp gr	20	315	11	50	125
	Hydrofluoric acid (HF) 1.26 sp gr	2	34	1		
	Water		1000	34		
4	Sulfuric acid (H_2SO_4) 1.84 sp gr	25	200	8	80	180
	Water		1000	34		
5	Sulfuric acid (H_2SO_4) 1.84 sp gr	15	111	4	80	180
	Sodium chloride (NaCl)	5	63	2		
	Water		1000	34		
6	Sulfuric acid (H_2SO_4) 1.84 sp gr	15	119	4	20-40	70-100

	Sodium dichromate ($Na_2Cr_2O_7$)	10	135 g	5		
	Water		1000	34		
7	Sulfuric acid (H_2SO_4) 1.84 sp gr	12	82	3	Ambient	
	Sodium fluoride (NaF)	2	23 g	1		
	Water		1000	34		
8	Sulfuric acid (H_2SO_4) 1.84 sp gr	20	171	6	80	180
	Sodium chloride (NaCl)	5	73 g	3		
	Sodium nitrate ($NaNO_3$)	5	73 g	3		
	Water		1000	34		
9	Sulfuric acid (H_2SO_4) 1.84 sp gr	35	1200	41	20-40	70-100
	Nitric acid (HNO_3) 1.41 sp gr	30	1860	63		
	Sodium chloride (NaCl)	0.5	30 g	1		
	Water		1000	34		
10	Hydrochloric acid (HCl) 1.16 sp gr	6	200	7	60	140
	Water		1000	34		
11	Hydrochloric acid (HCl) 1.16 sp gr	12	535	18	80	180
	Cupric chloride ($CuCl_2$)	2	33 g	1		
	Water		1000	34		
12	Hydrochloric acid (HCl) 1.16 sp gr	1	30	1	Ambient	
	Ferric chloride ($FeCl_3$)	1	11 g	0.3		
	Water		1000	34		

13	Sodium hydroxide (NaOH)	15	188 g	7	80	180
	Potassium permanganate ($KMnO_4$)	5	63 g	2		
	Water		1000	34		
14	Ammonium hydroxide (NH_4OH)	2[(b)]	20	0.5	Ambient	
	Water		1000	34		
15	Alkaline cleaner		60-75 g/L	7-9 oz/gal	80	180
	Water		1000	34		
16	Agar-agar	1	10 g	0.3	20-65	70-150
	Potassium ferricyanide ($K_3Fe(CN)_6$)	0.1	1 g	0.03		
	Sodium chloride (NaCl)	0.1	1 g	0.03		
	Water		1000	34		

(a) An addition of at least 40 g of nickel per liter to Formula 2 will prevent overpickling of chromium-bearing alloys.

(b) Volume %

The best methods for removing heavy scale are mechanical removal techniques such as abrasive blasting or grinding, usually with aluminum oxide or silicon carbide, followed by flash pickling. Abrasive blasting requires a relatively low capital investment compared to pickling, considering the extensive equipment needed for pickling and the cost of complying with environmental regulations. Abrasive blasting also eliminates the need to use and dispose of acids and the need to treat the rinse water. However, the removed scale and spent media may be considered a solid waste for disposal purposes. An alternative method is to soak the oxidized material in hydrochloric acid pickle (Formula 11, Table 1), followed by flash pickling if brightening is required.

Precautions must be taken in handling pickling solutions, because noxious and sometimes toxic fumes are liberated. Positive ventilation, either the use of a ventilating hood over the bath or provision of a controlled draft, is required to remove the fumes. Pickling acids must be handled with care, particularly hydrofluoric acid. Protective clothing, face shields, and rubber gloves must be used at all times. When solutions are prepared, acid should always be added to the water. This is especially important when sulfuric acid is diluted. In preparing the solutions shown in Table 1, the ingredients should be added to the water in the order listed.

Bath Life. Pickling baths should be analyzed regularly to determine acidity. Only total acidity can be determined in baths composed of more than one acid; it is impossible to distinguish acidity contributed by one acid source from that contributed by another. However, when the acidity of a bath is being maintained, the ingredients should be added in the proportions used for the original solution. Bath analysis should be performed by a qualified individual, by either wet

chemistry or another acceptable means, on an established schedule. Subsequent additions should be made to maintain the bath at the initial acidity level.

With the exception of flash pickling solutions, bath solution should be disposed of when the total metallic content reaches 150 g/L (20 oz/gal). If the bath is used for only one type of alloy, only one element needs to be determined in the analysis. The remaining metallic elements can be determined from the percentage of each in the composition of the alloy. For example, in analyzing baths used for pickling nickel-chromium alloys, the nickel content determines whether the total metallic content is within the 150 g/L limitation.

Flash pickling solutions continue to perform satisfactorily even when nearly saturated with metal salts. Fresh solution should be made up only when salts begin to crystallize on the side of the bath container.

Alloy Groups

For the purpose of discussing pickling procedures, the nickel alloys can be divided into four groups:

- *High-nickel alloys* such as Nickel 200, Nickel 201, Nickel 270, and Duranickel alloy 301
- *Nickel-copper alloys* such as Monel alloys 400 and K-500
- *Nickel-chromium alloys* such as Inconel alloys 600, 625, 718, and X-750
- *Nickel-iron-chromium alloys* such as Incoloy alloys 800 and 825

All alloys within any one group have virtually the same pickling characteristics. However, the pickling procedures for alloys within a group must be varied to suit the surface condition of the metal.

Surface Conditions

Alloys within each composition group that have similar surface conditions are pickled in the same solutions using the same procedures. Three different surface conditions are generally encountered, primarily depending on the method of prior heating:

- *Bright annealed white surface* requiring removal of tarnish by flash pickling
- *Bright annealed oxidized surface* requiring removal of a layer of reduced oxide, sometimes followed by a flash pickle to brighten
- *Black or dark-colored surface* requiring removal of adherent oxide film or scale

Tarnish and dullness from bright annealed metal can be removed by flash pickling or bright dipping. Bright annealed white surfaces are generally found on drawn and spun shapes, cold-headed rivets, cold-drawn wire, and other cold-worked products. The white surface is a result of annealing in a reducing, sulfur-free atmosphere and cooling either out of contact with oxygen or by quenching in a 2 vol% alcohol solution.

Flash pickling solutions act rapidly, and care must be exercised to prevent overpickling and etching. These solutions are used at room temperature. If the bath is cold, it should be warmed slightly to prevent unduly slow action. Best results with flash pickling are obtained by warming the parts by dipping them in hot water, placing them in the acid for a few seconds, and rinsing them again with hot water. A second dip in acid may be used if necessary. Badly tarnished metal may require a total of 3 min in acid, but the material should be withdrawn frequently from the bath and inspected to prevent overpickling.

Reduced-oxide surfaces occur when hot-worked products, such as forged and hot-rolled material, are heated after hot working in a reducing, sulfur-free atmosphere and are cooled out of contact with air or quenched in an alcohol solution. On such products, pickling produces a clean surface for further processing by cold forming, or it produces the finished surface necessary for items such as rivets.

At annealing temperatures in reducing atmospheres, oxides formed on the high-nickel alloys, except those containing chromium, are readily converted to a spongy, tightly adherent layer. On nickel alloys, the layer consists of metallic nickel.

On Monel alloys the layer is a mixture of metallic nickel and copper. The oxide film formed on nickel-chromium alloys and nickel-iron-chromium alloys does not undergo complete reduction in reducing atmospheres, which makes pickling more difficult. The oxide on these alloys is selectively reduced to a mixture of metallic nickel and chromic oxide. The surface color ranges from the characteristic chrome green of chromic oxide to dark brown.

Oxidized or scaled surfaces are present on all hot-worked products and heat-treated material cooled in air. This type of surface also occurs on the nickel-chromium and nickel-iron-chromium alloys in all conditions except bright heated. The oxide film forms on properly heated nickel and nickel-copper alloys during contact with air after the work is withdrawn from the furnace. The nickel-chromium and nickel-iron-chromium alloys form oxide films even when heated and cooled in atmospheres that keep other alloys bright. Thus, the usual pickling procedure for Inconel and Incoloy alloys is designed to remove oxide and scale.

Nickel-Copper Alloys

Depending on the methods of prior heating and cooling, nickel-copper alloys can have any of the surface conditions discussed previously. Accordingly, the appropriate pickling procedure depends on the surface condition of the material.

Tarnish is best removed from bright annealed nickel-copper alloys by pickling in two solutions in sequence. First, the metal should be pickled thoroughly in Formula 2 (Table 1) in brief exposures and rinsed in water at 80 °C (180 °F). After rinsing, the metal should be dipped in Formula 1. The second dip should be followed by rapid rinsing of the workpiece and neutralization in a 1 to 2 vol% solution of ammonia (Formula 14). To dry, small workpieces should be dipped in boiling water and rubbed in sawdust or with a clean, dry cloth.

Reduced-Oxide Surfaces. Formula 8 is recommended for reduced-oxide surfaces on nickel-copper alloys if pickling is done on a large scale. This acid mixture is more destructive to tanks and racks than solutions used for steel or copper. Steel tanks lined with 4.8 mm ($\frac{3}{16}$ in.) thick natural rubber and a double layer of yellow acid bricks have proven to be the best and most economical containers for this corrosive solution. After pickling in Formula 8, the metal should be rinsed in hot water and neutralized in a 1 to 2 vol% ammonia solution. The Formula 8 pickling solution works best after a short period of use. Therefore, when new solutions are prepared, about 2 vol% of spent solution should be added to the fresh mixture to improve its action.

When a pickling room is not regularly operated, the time required for complete pickling of small lots in Formula 8 is usually a disadvantage. Adequate results in most cases can be obtained by using flash pickling solutions (Formulas 1 and 2). However, Formula 8 may be used for occasional small jobs if ceramic vessels or wooden barrels are used as containers. The solution can be heated and agitated by injecting live steam, either through a rubber hose or through a carbon pipe that has a perforated carbon-block end.

Oxidized or Scaled Surfaces. Oxidized nickel-copper alloys having a thin to moderately thick oxide are pickled by immersion in Formula 11, followed by brightening in Formula 6. After treatment in the first bath, the work should be rinsed in hot water before it is transferred to the brightening dip. The second dip in Formula 6 should be followed by rinsing the work in cold water and neutralizing it in a 1 to 2 vol% ammonia solution (Formula 14).

High-Nickel Alloys

Nickel 200, Nickel 201, Nickel 270, Duranickel alloy 301, and similar alloys can have any of the three types of surface conditions. With the exception of flash pickling, high-nickel alloys are pickled in the same solutions used for Monel alloys. However, maintaining separate baths for the two groups of alloys is usually advisable.

Tarnish. Only one dip, Formula 9, is required to remove tarnish from bright annealed high-nickel alloys. The metal should first be dipped in hot water to warm it. Immersion in the acid bath for 5 to 20 s is usually sufficient to produce bright, clean surfaces. After the metal is removed from the pickling solution, it should be rinsed in hot or cold water and neutralized in a dilute ammonia solution.

The pickling action of Formula 9 can be retarded, if necessary, by decreasing the amount of acid to as little as one-third the volume that is added to the standard formula [e.g., as low as 400 mL (13.5 oz) of sulfuric acid or 620 mL (21 oz) of nitric acid]. Normally, however, the formula gives the best results in the proportions given in Table 1.

Reduced-Oxide Surface. The solution used to pickle reduced-oxide surfaces on nickel-copper alloys, Formula 8, is also used for high-nickel alloys. The procedure is the same as the procedure for reduced-oxide surfaces, described in the section "Nickel-Copper Alloys" in this article. If both groups of alloys are being pickled, separate baths should be maintained. Formula 8 may be used for occasional small lots, but suitable results can usually be obtained in less time by flash pickling in Formula 9.

Oxidized or scaled surfaces on high-nickel alloys can be pickled with the hydrochloric acid/cupric chloride solution (Formula 11) used for nickel-copper alloys. A longer time is required, however. Immersion from 1 to 2 h is necessary to obtain a good pickle on high-nickel alloys. After removal from the pickling bath, the work should be rinsed with hot water and dipped for a few seconds in Formula 9, if brightening is required. The brightening dip should be followed with a cold-water rinse and neutralization in a dilute ammonia solution.

Nickel-Chromium and Nickel-Iron-Chromium Alloys

Tarnished or reduced-oxide surfaces are usually not encountered on nickel-chromium or nickel-iron-chromium alloys. These alloys can only be bright annealed in very dry hydrogen or in a vacuum. Oxides formed on their surfaces in other atmospheres do not undergo complete reduction. Oxide or scale is the usual surface pickled on nickel-chromium and nickel-iron-chromium alloys.

Pretreating in a fused-salt bath is strongly recommended to facilitate pickling of oxidized or scaled surfaces. However, if the metal has been properly heated and cooled, it will usually have a surface suitable for direct pickling in Formula 3. If a fused-salt bath is used for pretreating, the following procedure should be used for pickling nickel-chromium and nickel-iron-chromium alloys:

1. Treat in fused-salt bath.
2. Quench in and spray with water.
3. Immerse in Formula 4.
4. Withdraw from bath and rinse with water.
5. Immerse in Formula 1.
6. Withdraw from bath and rinse with water.
7. Pickle in Formula 3 as required.

As with the nickel-copper alloys and high-nickel alloys, an alternative procedure employing a salt bath and Formula 8, with 10 g/L (1 oz/gal) of ferric chloride added to the formula, effectively removes oxide from hot-rolled or annealed Inconel alloys 601 and 671, and from Incoloy alloys 804 and 903. The procedure for the use of a salt bath is described in the section "Nickel-Copper Alloys" in this article.

If the oxide film cannot be readily removed by pickling directly in Formula 3, or if a fused-salt bath is not available, Formula 13 is a useful pretreatment. The work should be soaked for 1 to 2 h in Formula 13, removed, rinsed to remove all of the caustic solution, and pickled in Formula 3. On highly refractory oxides, it is sometimes necessary to repeat the cycle. Adding 7 to 10 g/L (0.9 to 1 oz/gal) of iron to Formula 3 decreases the danger of overpickling. This can be done conveniently by adding the proper weight of scrap iron to the bath when it is prepared.

The nitric acid/hydrofluoric acid bath (Formula 3) must be used with care. Nickel-chromium and nickel-iron-chromium alloys are subject to intergranular attack in this solution if they have been sensitized by heating in, or slowly cooling through, the 540 to 760 °C (1000 to 1400 °F) temperature range. Time in the bath should be kept to a minimum, and bath temperature must not exceed 50 °C (125 °F). Stress-relieved and age-hardened material can also be sensitive to intergranular attack if the heat treatment involved exposure to sensitizing temperatures.

Salt Baths

Pretreatment baths of fused salts aid in the pickling of many alloys. They are particularly effective in pickling nickel-chromium and nickel-iron-chromium alloys. Several proprietary baths are commercially available; information on their use can be obtained from manufacturers.

Precautions must be taken in handling salt baths. Protective clothing, face shields, and suitable gloves should be used. Room-temperature solution, or powder residue, may cause severe chemical burns. Extreme temperatures of working salt baths exacerbate the need for constant vigilance. Operators should avoid mixing salt bath constituents with those of pickling baths. Typically, rinse water should be used after salt bath processing and prior to pickling. Tank carryout should be minimized by sufficient draining. *Caution: Operators should not dispose of salt bath and pickling bath materials in the same container without approval from a qualified supervisor.*

Bath Life. Salt baths are basically alkaline and not acid in constitution. Bath maintenance should be in accordance with the supplier's instructions. Bath monitoring and control will be similar to that described in the section "Pickling" in this article.

Salt baths are of three types: reducing, oxidizing, and electrolytic. Oxidizing baths are usually the least expensive to operate and the easiest to control, whereas reducing baths are no longer in common use. Electrolytic baths, although more expensive to install and operate, are quite effective for nickel alloys.

Oxidizing salt baths have a base of either sodium hydroxide or potassium hydroxide. Other salts, such as sodium nitrate and sodium chloride, are added to provide controlled oxidizing properties. The sodium hydroxide bath is operated at temperatures of 425 to 540 °C (800 to 1000 °F); a temperature of 480 °C (900 °F) is preferred for descaling nickel alloys. The potassium hydroxide bath operates at lower temperatures, usually 200 to 260 °C (400 to 500 °F). Treatment time in oxidizing baths is usually 5 to 20 min. In the operation of continuous strand pickling lines, the time may be as short as 15 to 60 s.

The salt bath oxidizes the lower oxides on the surface of the work to form soluble salts and water. Quenching after treatment removes part of the scale and loosens the remainder so that it is easily removed by appropriate acid dips. Oxidizing salt baths are also effective cleaners. They remove oil, grease, organic materials, and some inorganic substances from metal surfaces.

Electrolytic salt baths have a sodium hydroxide base and contain other salts, such as sodium chloride and sodium carbonate, that form reducing agents at the cathode and oxidizing agents at the anode when electrically activated. Baths are usually operated at about 480 °C (900 °F), and although electrolytic salt baths can be used as a batch process, they are more suitable for continuous operations such as descaling of strip. Two tanks are normally used for continuous processes. The work is made anodic in the first tank and cathodic in the second.

Specialized Pickling Operations

Although pickling is most often used to remove the oxide or scale formed during heating, it is also used to remove foreign metals and other substances. Several procedures specifically designed for such purposes are applicable to nickel alloys.

Removal of Lead and Zinc. Lead and zinc embrittle high-nickel alloys at elevated temperatures. Consequently, when the alloys are formed in dies made of materials containing lead and zinc, all traces of the die material picked up during forming should be removed. When parts will be given intermediate anneals for processing, or when they will be exposed to high temperatures during service, removal of lead and zinc becomes especially important.

Formula 10 is used to remove lead and zinc from nickel and nickel-copper alloys. For nickel-chromium and nickel-iron-chromium alloys, a bath of nitric acid similar to Formula 1 (but with the concentration of nitric acid increased to 30%) is used. After being immersed in the appropriate bath for 15 min, the work is removed, rinsed in water, and dried.

Detection and Removal of Embedded Iron. During mechanical operations such as rolling to shape or hot pressing, small particles of iron may become so firmly embedded in the surfaces of nickel alloys that they cannot be removed by the cleaning methods normally used for dissolving grease or cutting compounds. Under certain corrosive conditions, such iron particles can initiate local attack. For that reason, it is often necessary to test for iron traces and remove them.

For large-scale testing, a solution of about 1% sodium chloride is effective. A chemically pure grade of salt should be used to prevent false results from iron that might be present in less pure grades. When compressed air is available, it is usually less expensive to keep the tank full of salt spray with an atomizer than to fill it with the solution. After 12 to 24 h in the dilute salt solution, any iron particles in the nickel alloy will appear as rust deposits.

The ferroxyl test works well for small-scale testing. A potassium ferricyanide solution, made up in approximately the proportions shown in Formula 16, is applied to the surface of the material. The ingredients are mixed in earthenware, glass, or ceramic vessels and then boiled until all of the agar-agar is dissolved and a clear liquor is formed. Chemically pure sodium chloride should be used to prevent iron contamination of the test solution. The warm solution is applied to the surface to be tested and allowed to remain for at least 1 h. The solution gels as it cools, and the presence of iron on the metal surface is indicated by blue spots in the gel.

The ferroxyl test is sensitive enough that minute particles of iron that collect on the surface in the form of shop dust will appear as small blue spots in the gel. Because the iron dust will be washed off with the gel, the small spots should be distinguished from the larger ones caused by embedded iron. If spots of relatively major proportions develop, large iron particles are probably present.

A solution of hydrochloric acid and ferric chloride, Formula 12, is used to remove embedded iron. This solution should be used cold and should remain in contact with the metal for only the minimum time required for iron removal, not exceeding 1 h. After the work is removed from the solution, it should be rinsed thoroughly in cold water, then rinsed again in warm water. The detection tests should be repeated to verify the removal of the iron.

Prevention and Removal of Copper Flash. Copper flash sometimes forms on the surface of nickel alloys during pickling. For copper deposits to form, copper ions in the solution must be in the cuprous state, or they must pass from the cupric to the cuprous state during the cementing process. Consequently, any agents in the pickling bath that tend to maintain the cupric state will help prevent coppering.

Oxidizing agents such as nitric acid and sodium nitrate promote the action of pickling solutions but become depleted with use. As the pickling bath ages, the concentration of copper ions increases while the concentration of oxidizing agents decreases. Thus, aging the bath facilitates coppering on areas where the reducing effect of the metal exceeds the oxidizing power of the bath.

When coppering occurs on Monel alloy 400 and other high-nickel alloys containing an appreciable amount of copper, the bath can be restored by adding small amounts of nitric acid or sodium nitrate. Nickel has greater reducing capacity than Monel alloy 400 and requires a greater concentration of oxidizing agents to prevent coppering in solutions containing copper salts. For this reason, Nickel 200 and similar alloys must not be pickled in solutions that have been used for nickel-copper alloys.

Patches of copper will plate out on nickel-copper alloys if steel contacts the alloys while they are wet with acid. Steel tongs or other devices used to handle the work are the usual sources of kippered areas. Coppering is prevented by using handling devices made of Nickel 200 or Monel alloy 400.

Copper flash is readily removed by immersing the alloy in an aerated, 4 to 5% ammonia solution at room temperature. The solution composition should be approximately 125 mL of ammonia to 1 L of water, or 1 pint of commercial aqua ammonia to 1 gal of water. The work should be immersed for about 1 min only, then rinsed in water.

Electrolytic Pickling. Light oxide films on any of the nickel alloys can be removed by electrolytic pickling in Formula 7. The work should be made anodic by using a current density of 5.4 to 10.75 A/dm^2 (50 to 100 A/ft^2). Electrolytic pickling is also useful for etching ground material to obtain a surface suitable for inspection.

Electropolishing of high-nickel alloys smooths the surface by removing metal through a controlled electrochemical process that is similar to, but essentially the reverse of, electroplating. When the alloy is immersed into an electrolyte and maintained anodic, metal is electrochemically removed ion by ion. This simultaneously deburrs the alloy, maximizes tarnish protection, and reduces surface fouling while producing a uniformly bright and smooth surface luster. Properly electropolished surfaces are microscopically featureless, non-contaminating, non-particulating, and effectively stress relieved. Such high-performance and high-purity metal surface finish properties are unattainable by more traditional mechanical finishing techniques.

High-quality electropolishing of the high-nickel alloys produces brilliant lustered reflectivity. Best results are obtained from metals with fine grain boundaries that are free of nonmetallic inclusions and seams. Electropolished surfaces should not exhibit frosting, shadows, streaks, stains, pitted areas, or an "orange peel" or pebbly appearance.

Important factors in final finish quality are proper electrolyte selection, bath temperature, and bath maintenance (specific gravity, acid concentration, and metals content) and direct current from a ripple-free source applied at optimum voltage and current density. More complex configurations require adequate cathode design for effective polishing in inaccessible areas, inside corners, and in other areas of low current density. Agitation of either the electrolyte or the metal may be necessary to prevent gas entrapment, gassing streaks, flow marks, or similar undesirable markings.

Cleaning of Springs. In general, cleaning of springs made of a high-nickel alloy is not recommended after heat treating. The oxide on heat-treated springs usually aids in resisting corrosion at high temperatures. When the oxide is removed, resistance to relaxation is often lowered. If cleaning is necessary for inspection of the springs, they should be treated in a salt bath, quenched in water, and rinsed to produce a good surface. Table 2 shows the effect of the cleaning method on resistance to relaxation of Inconel alloy X-750 springs that were age hardened at 730 °C (1350 °F) for 16 h.

Table 2 Effect of cleaning method on relaxation of Inconel alloy X-750 springs[(a)]

Cleaning method	Relaxation[(b)], %
No cleaning, as age hardened	10.0
Oxidizing salt bath plus Formula 3	11.5
Tumbling in sand and oil	12.8
Abrasive blasting (120 grit with water)	13.3
Shot peening	13.5
Abrasive blasting (standard sand, dry)	14.6

(a) Cold drawn (No. 1 temper) and age hardened at 730 °C (1350 °F) for 16 h.

(b) Relaxation after 250 h at 415 MPa (60 ksi) and 540 °C (1000 °F)

Cleaning for Welding. Before maintenance welding is done on high-nickel alloys that have been in service, products of corrosion and other foreign materials must be removed from the area to be welded. Clean, bright base metal should extend 50 to 75 mm (2 to 3 in.) from the joint on both sides of the material to prevent the corrosion products from embrittling at welding temperatures.

Cleaning can be done mechanically (by grinding with a fine wheel or disk) or chemically (by pickling). Mechanical cleaning methods usually use an abrasive medium containing either aluminum oxide or silicon carbide grit. Care must be taken to avoid embedding abrasive grit into the weldment surface. Sometimes wire brushing with an austenitic stainless steel brush and/or local macroetching with a Schantz etch, or similar flash pickling, is an appropriate procedure immediately prior to welding.

Flash pickling solutions are effective in cleaning before welding. The solutions can be applied by swabbing, brushing, or dipping, if the parts are easily handled. A single dip in Formula 2 is adequate for the nickel-copper alloys. Formula 1 is used for nickel alloys, and Formula 3 is useful for nickel-chromium and nickel-iron-chromium alloys.

Reactive Gas Ion Thermal Processing

Reactive gas ion thermal processing is high-temperature processing that introduces certain extremely reactive gases disassociated into ions, specifically hydrogen and fluorine. It has been shown to be effective in reducing tenacious oxides of aluminum and titanium and scale found on high-nickel alloy surfaces.

Although hydrogen, considered an industrial gas, is generally readily available, the source of the fluoride ion is a commercially available system: chromous fluoride (CrF_2,) polytetrafluoroethylene (PTFE), or hydrogen fluoride gas (HF). The process uses a heated reaction vessel, generally a retort, and the work and its holding fixtures are placed inside. Reaction temperatures for high-nickel alloys are typically around 1100 °C (2000 °F), although times and temperatures will depend on specific processing requirements. Forethought must be given to safety and environmental concerns.

Example: Repair of Gas Turbine Engine.

For acceptable repair of an aircraft gas turbine engine that had some high-nickel alloy components, it was necessary to use high-purity, dry hydrogen gas, introduced into a retort during an elevated-temperature run, to reduce most surface oxides. Subsequent establishment of next-generation braze repair technologies was possible on these alloys only after successful incorporation of fluoride ion processing. The significantly more reactive fluoride ion and its innate, aggressive reduction of oxides achieved surface, and even subsurface, cleaning with complete subsurface oxide/scale conversions in cracks as fine as 0.013 mm (0.0005 in.).

Results. Process parameter definition ensures repeatable oxide reduction without unacceptable substrate damage. Positive results are removal of surface oxide from exposed internal/external surfaces; effective cleaning prior to coating, welding, or brazing; removal of mill scale; and stripping of aluminide coating. Negative results are slight alloy depletion, typically of aluminum, molybdenum, and titanium constituents, on exposed surfaces; and slight intergranular attack on exposed surfaces.

Finishing

Nickel alloys can be ground, polished, buffed, or brushed by all methods commonly used for other metals. For high-nickel alloys, a series of operations is required to produce a satisfactory finish. The number and type of operations required depend on the initial finish of the material, the desired final finish, and the type of equipment used. The pressures and speeds of the finishing equipment must be closely controlled. The high-nickel alloys, particularly nickel-chromium and nickel-iron-chromium alloys, do not conduct heat away as rapidly as copper and aluminum. Excessive heat will destroy the true color of the metal and may warp flat, thin articles.

Some general recommendations for finishing operations are given in Table 3. Table 4 lists spindle speeds and corresponding surface speeds for various wheel diameters.

Table 3 Recommended finishing procedures

Operation	Wheel	Grit No.	Compound	Speed	
				m/s	sfm
Grinding	Rubber bond	24 or 36	None	40-45	8000-9000
	Vitrified bond	24 or 36	None	25-30	5000-6000
Roughing	Cotton fabric, sewn sections	60 or 80	None	30-40	6000-7500
Dry fining	Cotton fabric, sewn sections	100 or	None	30-	6000-

		120		40	7500
Greasing	64-68 unbleached sheeting, spirally sewn sections	150 or 180	Polishing tallow or No. 180 emergy grease cake	30-40	6000-7500
Grease coloring	88-88 unbleached sheeting, spirally sewn or loose disk; or quilted sheepskin	200 or 220	Polishing tallow or "F" emery grease cake	30-40	6000-7500
Bobbing and sanding	Leather wheel for two bobbing operations, second with medium-density felt wheel	. . .	Grout	25	5000
Cutting down	88 unbleached sheeting, loose spirally sewn sections or loose-disk wheel	. . .	Tripoli	40-45	8000-9000
Coloring					
Bright finish	88-88 unbleached sheeting, loose spirally sewn sections or loose-disk wheel	. . .	White aluminum oxide	50	10,000
Mirror finish	Loose-disk, 88-88 unbleached sheeting or Canton flannel	. . .	Green chromium oxide	50	10,000
Brushing	Tampico	. . .	"F" emery grease cake or grout	5-15	1200-3000

Table 4 Spindle speed for various surface speeds and wheel diameters

Surface speed		**Spindle speed, rev/min, for indicated wheel diameter**						
m/s	**sfm**	**150 mm (6 in.)**	**200 mm (8 in.)**	**250 mm (10 in.)**	**300 mm (12 in.)**	**360 mm (14 in.)**	**410 mm (16 in.)**	**460 mm (18 in.)**
15	3,000	1930	1450	1150	950	820	710	640
20	4,000	2550	1900	1500	1300	1100	950	850
25	5,000	3200	2400	1900	1600	1375	1200	1050
28	5,500	3500	2600	2100	1750	1500	1300	1175
30	6,000	3800	2850	2300	1900	1650	1425	1275
38	7,500	4800	3550	2850	2400	2100	1800	1600
40	8,000	5100	3800	3100	2550	2200	1900	1700

45	9,000	5750	4300	3450	2850	2450	2150	1900
50	10,000	6400	4750	3800	3200	2750	2400	2100

Grinding, often the first operation in a finishing sequence, is used to remove large surface imperfections and to rough-down welds prior to polishing and buffing. Rubber-bond grinding wheels are used for nickel and Monel nickel-copper alloys for their cutting effectiveness and for their relative softness, which reduces the heat generated. Rubber-bond wheels should be operated at a surface speed of 40 to 45 m/s (8000 to 9000 sfm). Vitrified-bond wheels are preferred for grinding harder alloys such as the Inconel and Incoloy alloys. These wheels should be operated at a surface speed of 25 to 30 m/s (5000 to 6000 sfm). Light welds can be ground efficiently with a No. 36 grit wheel, whereas a No. 24 grit is more practical for heavy welds.

Polishing. The first polishing operation should be done with very fine grit to remove all surface defects and give a base upon which to build the final finish. Wheels of No. 60 to 80 grit are usually required to remove heavy oxide or deep defects.

The first operation should be done dry. After the initial roughing, tallow should be used on all roll-head wheels of No. 150 grit or finer. Tallow clogs the wheel, giving a smoother finish and reducing the amount of heat generated.

When flat work is polished, each subsequent operation should be done with a grit 30 to 40 numbers finer than the previous one, until the surface is ready for the brushing or bobbing operations needed to prepare for buffing.

When possible, the scratches produced by the abrasive should cross the scratches left by the preceding operation. When polishing is done in only one direction, the finer abrasive will follow in the grooves made by the coarser abrasive, and the efficiency of the polishing wheels will be impaired.

Wheels for roughing and dry finishing should be made of tightly woven, unbleached cotton fabric. To prevent chattering, the wheels should be perfectly balanced and should have a soft or cushioned face. Fine grit wheels require more cushions than coarse wheels.

A more resilient and flexible wheel should be used for greasing operations. Greasing wheels should be made of 64- to 68-count unbleached sheeting and should have more cushion than the wheels used for coarser polishing. Grease coloring may be done on a full-disk, quilted sheepskin wheel or on a spirally sewn wheel made of fine-count (88-88) heavy sheeting. Compounds of artificial abrasives are preferred for roughing and dry finishing. Turkish emery is usually used for greasing and grease coloring.

Bobbing done with emery grout is more like burnishing than polishing, and if it is performed in one operation, it is best done with leather wheels. If it is done in two operations, the second should be done with a medium-density felt wheel, because felt wheels require less pressure. The best results are obtained from emery roll-head wheels at surface speeds of 33 to 38 m/s (6500 to 7500 sfm). The metal drags at slower speeds, and at excessive speeds, the wheel tends to pull up the surface of the metal.

Buffing. For good results in buffing, a high-quality wheel of the proper construction and material is essential. Wheels should be of sturdy, closely woven, high-count sheeting. The close weave gives good cutting, and the heavy threads provide good coloring.

Buffing is usually done in two operations. The first, the cutting-down operation, is done with a sewn buffing wheel operating at a surface speed of 40 to 45 m/s (8000 to 9000 sfm). The second, the coloring operation, is done with a loose-disk wheel operating at a surface speed of approximately 50 m/s (10,000 sfm). A loose disk, Canton-flannel wheel is best for buffing to a mirror finish. The high speeds used in buffing create a high heat. Consequently, less pressure is necessary than for polishing.

The cutting-down operation is normally performed with tripoli compound, which leaves a haze on high-nickel alloys. Buffing compound with less grease should be used to promote deep color. White aluminum oxide and green chromium

oxide compounds can be used for the final coloring. Chromium oxide compounds produce less friction and give a truer color.

Brushing. A tampico or wire wheel produces a brushed finish on the high-nickel alloys. Tampico wheels usually produce a better finish and higher luster, and because of their flexibility, they are better for irregular shapes. A tampico wheel is used with emery paste or grout to produce a satin finish, or with pumice and water or pumice and oil to produce a better finish. For wet brushing, tampico wheels should have wooden hubs.

Wire brushes can be used to produce a satin finish on sheet metal articles. Brushes should have a wire diameter of 0.10 to 0.20 mm (0.004 to 0.008 in.). They should not be made of steel or brass wire, because small particles from the brush are always embedded in the metal during the process. Steel particles rust, and brass particles discolor the nickel alloys.

Brushing is done at slower speeds than those used for polishing. Brushing speeds are normally 5 to 15 m/s (1200 to 3000 sfm), depending on the final finish desired. Higher speeds, 20 to 30 m/s (4000 to 6000 sfm), are required to produce a bright wire brush finish. Wire brushes operated at too slow a speed produce coarse, undesirable scratches.

Blasting. Abrasive media blasting has the ability to produce a cosmetically appealing, uniform, matte gray appearance that varies from dull to a high-sheen luster. The appearance depends on the medium chosen (aluminum oxide, silicon carbide, glass bead, steel shot, crushed plastic, etc.); particle size (No. 24 grit for rough finishes vs. No. 220 for smooth finishes); and particle shape (angular grit or cut shot for a dull appearance vs. crushed plastic, round glass beads, or cast steel shot for luster and sheen).

Nondestructive Inspection

Care must be taken in finishing high-nickel alloys when subsequent inspection will be performed with an ultrahigh-sensitivity, fluorescent penetrant nondestructive method. Under certain conditions, finishing operations using plastics, such as plastic blasting media, plastic brushes, or buffing pads with embedded grit, leave a residue of thin, smeared plastic on the surface that introduces high background fluorescence during fluorescent penetrant inspection. Similarly, coarse abrasive blasting may hamper the detection of surface flaws by penetrant methods. On the other hand, fine grit blasting (No. 60 or finer) has been successfully used to enhance detection of surface flaws, such as investment casting defects.

Surface Engineering of Zinc Alloys

Revised by Thomas P. Groeneveld, Battelle Columbus Operations

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Introduction

THE PRIMARY PRODUCT FORMS of zinc and zinc alloys requiring surface engineering prior to coating or use are die castings, wrought zinc alloys, and zinc-coated steels. The vast majority of die castings are nominally Zn-4Al alloys covered by ASTM B 86 (Ref 1). These alloys are known commonly as alloys 3, 5, and 7. However, during the 1980s, applications increased for zinc die castings containing higher aluminum contents, nominally 8, 12, or 27% (Ref 2). In addition to the increased use of electrogalvanized zinc-coated steel by the automotive industry, there has been a significant increase in other applications that use painted or powder-coated galvanized steel, particularly in the appliance industry (Ref 3, 4).

Because of their inherent corrosion resistance, zinc and zinc alloys can be used satisfactorily in many applications without subsequent finishing. However, a variety of finishes are used for improved corrosion protection or appearance: conversion coatings, such as chromate, phosphate, and anodize; organic paint of various types; and metallic coatings, including electroplating, electroless plating, and vacuum metallizing. The normal sequence of preparation steps prior to painting or electroplating of zinc alloy die castings includes:

- Mechanical finishing to smooth parting lines and rough or defective surfaces, plus buffing, if necessary
- Solvent degreasing or aqueous-based solution degreasing followed by rinsing
- Soak alkaline cleaning and/or alkaline electrocleaning followed by rinsing
- Acid dipping followed by rinsing

Guidelines for preparing zinc die castings for electroplating are contained in ASTM B 252 (Ref 5). If die cast parts are to be painted, they are often given a chromate or phosphate conversion coating treatment following alkaline cleaning to improve corrosion resistance and coating adherence. Wash primers also are used for those purposes.

Wrought zinc products are subjected to solvent cleaning, soak alkaline cleaning, and electrolytic alkaline cleaning prior to electroplating (Ref 6). Zinc-coated steel products (hot dip or electrogalvanized) typically are solvent cleaned to remove stamping and forming lubricants and general handling soils, then are alkaline cleaned and are given either a phosphate or chromate treatment prior to coating, to improve corrosion resistance and coating adherence.

Surface preparation and cleaning prior to plating or painting is considered by many to be the most important aspect of the finishing process. If surfaces are not properly prepared, defects in the base metal will show through the finished coating, and if the parts are not properly cleaned, coating adherence will be reduced and premature corrosion often results.

For die castings, proper runner and gating design and proper control of the die casting process, particularly die temperature control, can produce castings in which surface defects are minimized. Thus, preplating or prepainting surface preparation processes can be reduced with substantial savings in finishing costs. Similarly, proper trim die design and maintenance can reduce the amount of effort spent smoothing parting lines.

References

1. "Standard Specification for Zinc Alloy Die Castings," B 86-88, ASTM
2. J. Grach, D.K. Gross, and G.R. Adams, Secondary and Finishing Operations for Die Cast High-Aluminum Zinc Alloys, Paper G-T83-096, *Transactions 12th International Die Casting Congress and Exposition,* Society of Die Casting Engineers, 1983
3. M.A. Kuehner, Pretreatment for Powder Coating, *Plating and Surface Finishing,* Vol 71 (No. 9), Sept 1984, p 36-39
4. T.J. Miranda, Trends in Appliance Finishing, *Plating and Surface Finishing,* Vol 74 (No. 12), Dec 1987, p 36-38
5. "Standard Guide for Preparation of Zinc Alloy Die Castings for Electroplating and Conversion Coatings," B 252-92, ASTM
6. W.H. Safranek and E.W. Brooman, "Finishing and Electroplating Die Cast and Wrought Zinc," International Lead Zinc Research Organization, 1973

Mechanical Finishing

Finishing of Parting Lines. Of the various product forms of zinc alloys, die castings require the most extensive mechanical finishing prior to electroplating or painting. This situation results because the castings must be trimmed to remove gates and runners, overflows, vents, and flash. Grinding and polishing of the parting lines is the first step after the castings have been trimmed. Finishing of the parting lines is done on set-up wheels or abrasive belts, by tumbling with abrasive media, or by vibratory finishing. Wheels or belts with coarse grit (60- to 120-mesh) are used for heavy metal removal, if necessary (Ref 2). The parting line regions typically are finished with 220- to 300-grit abrasive wheels or belts (Ref 5, 6). A lubricant, such as paraffin, may be used to produce a finer finish. Set-up wheels are typically operated at peripheral speeds ranging from 1800 to 2400 m/min (6000 to 8000 ft/min). Abrasive belts should not be operated at speeds greater than 2100 m/min (7000 ft/min); speeds ranging from 1080 to 1200 m/min (3500 to 4000 ft/min) often are used (Ref 5, 6).

Tumbling in barrels loaded with abrasive media such as limestone, preformed and fused alumina, ceramic shapes, or abrasive-loaded plastic chips can be used to remove parting line burrs. A lubricant such as soap or detergent solution (alkaline cleaner) often is used during barrel tumbling. Tumbling cycle times to remove parting line burrs range from 4 to 12 h.

Vibratory finishing also is used to finish the parting line regions (Ref 7, 8, 9, 10, 11). Abrasive-loaded plastic chips usually are used for zinc die castings because they do not mar the casting surface. Ceramic media and steel media can be used, but these media, because they have greater densities than plastic media, will indent the casting surface, leaving an "orange peel" type of surface. Coarse grit abrasives (80-grit) can remove burrs in minutes during vibratory finishing.

Resin-bonded abrasive chips remove burrs in times ranging from 1 to 4 h. The speed of finishing in vibratory finishing is controlled by the frequency and amplitude of vibration. Frequencies from 700 to 2100 vibrations/min and amplitudes from 0.8 to 6.4 mm ($\frac{1}{32}$ to $\frac{1}{4}$ in.) are used to deburr zinc die castings. Traditionally, neutral to alkaline cleaners (lubricants) have been used during vibratory finishing of zinc die castings. Acidic solutions with pH from 2.5 to 4.5 also have been used to increase the speed of metal removal and thus shorten the process cycle time (Ref 7). If tumbling or vibratory deburring is used without a cleaner, the media must be cleaned periodically to remove contamination (Ref 9). If not maintained properly, the media will contaminate, rather than clean, the castings.

Surface Polishing. Many die castings have sufficiently smooth surfaces that require only buffing prior to the chemical treatments used in preparation for electroplating or painting. However, others may require spot or overall polishing to remove surface defects or roughness. Spot or surface polishing is done with set-up wheels or abrasive belts with 220-mesh or finer abrasive, run at the same speeds as those used for preparing the parting lines. The abrasive surface should be lubricated. The surface finish produced by abrasive wheels or belts typically ranges from 0.2 to 0.4 μm (8 to 16 μin.).

Polishing of the casting surfaces also can be accomplished by tumbling or vibratory finishing under the conditions described previously. Generally, vibratory finishing concentrates the finishing action on the casting corners and edges, although all surfaces receive some finishing action (Ref 8). Abrasive-loaded plastic media are used for die cast zinc because they do not mar the surface. Ceramic media, which are heavier than plastic media, also are used for surface finishing; however, they may produce a slight orange peel texture. Steel media, which are significantly heavier, result in burnishing of the surface to a high luster, but they are suitable for applications for which the surface finish is secondary (Ref 8). To produce a fine, smooth finish, abrasives with 400-mesh are used with commensurate increases in finishing time. The sizes of the media vary significantly, ranging from 1.5 to 50 mm (0.06 to 2 in.) in diameter (Ref 10). Generally, the larger the diameter of the media, the rougher the surface. With proper control of the media, vibratory finishing parameters, and cycle times, buffing prior to plating with a leveling electroplate often can be eliminated. Because of its higher hardness, Alloy 27 may require a longer vibratory finishing time to receive a finish comparable to those on the lower-aluminum-content alloys (Ref 2).

The surfaces of zinc die castings can be polished smooth in centrifugal barrel finishing equipment (Ref 5, 6, 8). The drums are rotated with a peripheral speed of about 600 m/min (1970 ft/min) in an abrasive material such as ground corn cobs or nut shells mixed with a lubricant. Finishing times typically range from 5 to 10 min, and the resulting surface finish is 0.1 to 0.2 μm (4 to 8 μin.), depending on the abrasive used (Ref 6).

Brushing with wheel-mounted filament or fiber strands, run dry or lubricated, also is used to polish casting surfaces, particularly functional castings (Ref 7). Brushing removes sharp edges and burrs and generates fine radii. It does not result in the heavy stock removal, as does abrasive belt polishing, because it does not abrade the surface; however, it reaches internal recesses to deburr, descale, and clean.

Controlled shot peening can be used to smooth rough or defective castings and to remove fins, burrs, and flash from the surface (Ref 5). This process plastically deforms and densifies the casting surface and near-surface layers. That action can seal surface pores, which can create problems in subsequent electroplating and conversion coating. The shot-peening process is described in MIL-S-13165C (Ref 12), which should be consulted for selection of the peening media, shot size, peening intensity, and coverage. Those selections are based on the casting configuration, the smallest-size radii and wall thickness, and the required surface finish and contamination limits, as detailed in the specification.

Buffing of zinc die castings is used to smooth rough areas, eliminate polishing scratches, and produce a mirror-like finish prior to plating with conventional solutions when good leveling plating solutions are not available. If the castings have good surface finish or can be uniformly polished to a finish of 0.25 μm (10 μin.), buffing can be omitted if solutions with good leveling power are used for plating copper and nickel (Ref 5, 6).

Buffing is accomplished on cloth wheels rotated at peripheral speeds up to 2150 m/min (7000 ft/min). Slower speeds, from 1000 to 1600 m/min (3500 to 5000 ft/min), are used for smaller die castings (Ref 4, 5). Buffing wheels (buffs) usually are made of cloth (muslin or canvas) with 34 to 37 threads/cm (86 to 93 threads/in.) (Ref 5, 6). The buffs should be sewn to provide a mushing action from 6.4 to 13 mm (0.25 to 0.5 in.) while remaining rigid through the remaining depth of the buff (Ref 7, 13). The typical buffing compound used for zinc is tripoli (amorphous silica) or lime mixed with 25 to 30 wt% tallow or stearic acid to form a bar. The lubricant used should be readily saponified or emulsified to aid in removal during subsequent cleaning. In addition, only as much lubricant as is necessary should be used to facilitate subsequent cleaning. The compound is applied manually or automatically to the buffing wheels. With automated buffing

systems, water slurries of fine abrasive particles and lubricants are applied to the wheels by dripping through controlled-flow tubes or by spraying. With these automated systems the castings advance through a series of buffs with varying diameters and widths, which smooth different areas of the casting surface. After buffing, the casting surfaces should be cleaned by passing them over a relatively clean, dry buffing wheel. Buffing produces surface finishes ranging from 0.025 to 0.05 μm (1 to 2 μin.) (Ref 5, 6, 14).

Buffed castings are more difficult to clean than vibratory-finished parts, especially when the buffing compounds packed in holes, grooves, and other recesses are not removed within a few hours of buffing. It is strongly recommended that the initial removal of the buffing compound and other soils in a precleaning operation be done as soon as possible after polishing and buffing. Most buffing compounds become substantially more difficult to remove after aging several days (Ref 5).

References cited in this section

2. J. Grach, D.K. Gross, and G.R. Adams, Secondary and Finishing Operations for Die Cast High-Aluminum Zinc Alloys, Paper G-T83-096, *Transactions 12th International Die Casting Congress and Exposition,* Society of Die Casting Engineers, 1983
4. T.J. Miranda, Trends in Appliance Finishing, *Plating and Surface Finishing,* Vol 74 (No. 12), Dec 1987, p 36-38
5. "Standard Guide for Preparation of Zinc Alloy Die Castings for Electroplating and Conversion Coatings," B 252-92, ASTM
6. W.H. Safranek and E.W. Brooman, "Finishing and Electroplating Die Cast and Wrought Zinc," International Lead Zinc Research Organization, 1973
7. A.V. Dickman, Jr. and J.R. Pinto, Die Casting Finishes, *Die Casting Management,* Vol 9 (No. 6), Dec 1991, p 26-28
8. E.H. Tulinski, Deburr by Design--From Die to Finish, *Die Casting Engineer,* Vol 31 (No. 6), Nov/Dec 1987, p 47-48
9. M.H. Quinn, Troubleshooting Cleaning Problems, *Die Casting Engineer,* Vol 29 (No. 3), May/June 1985, p 32-38
10. Vibratory Process Comes of Age as a Mass Finishing Technology for Today, *Die Casting Engineer,* Vol 32 (No. 2), March/April 1988, p 44
11. K.A. Fligge, In Vibratory Finishing, *Action* Counts, *Die Casting Engineer,* Vol 32 (No. 1), Jan/Feb 1988, p 32
12. "Shot Peening of Metal Parts," MIL-S-13165C (Standardization Documents Order Desk, Bldg. 4, Section D, 700 Robbins Ave., Philadelphia, PA, 19111-5094, Attn: NPODS)
13. W.G. Millman and R. LaVorgna, Finishing Zinc-Based Die Castings--An Art and Science, *Die Casting Engineer,* Vol 32 (No. 1), Jan/Feb 1988, p 34
14. R.A. Covert and G.A. Di Bari, Nickel Plating Zinc Die Castings--A Review, *Die Casting Engineer,* Vol 36 (No. 1), Jan/Feb 1992, p 20-26

Solvent Cleaning

Following the mechanical finishing of die castings or the forming of wrought zinc or zinc-coated steel, the parts are cleaned to remove finishing compounds, forming lubricants, and general shop and handling soils. Traditionally, the first step in the cleaning process is solvent degreasing, vapor degreasing, or emulsion cleaning. Solvent degreasing typically is done in chlorinated hydrocarbons, such as methylene chloride, 1,1,1-trichloroethane, trichloroethylene, and perchloroethylene. Many of the commonly used solvents are being banned from use, and exposure to their vapors is being strictly regulated for health, safety, and environmental reasons (Ref 5, 15, 16). Thus, before the solvent degreasing process is considered, federal, state, and local safety and environmental laws and regulations should be consulted. In addition, current safe exposure levels for various solvents should be determined prior to their use.

Cold solvents, such as mineral spirits, methylene chloride, trichloroethylene, perchloroethylene, and 1,1,1-trichloroethane, are used with brushing to loosen packed buffing compounds. Simple dipping in cold solvents often is ineffective in

removing soil; consequently, vapor degreasing with trichloroethylene or perchloroethylene is still widely practiced. Often buffed die castings are sprayed with, or dipped in, the hot solvent and then subjected to vapor degreasing to remove the last traces of grease and compound. This method is effective provided that adequate measures are taken to remove the fine abrasive and metallic particles from the parts (Ref 5).

References cited in this section

5. "Standard Guide for Preparation of Zinc Alloy Die Castings for Electroplating and Conversion Coatings," B 252-92, ASTM
15. M.L. Mounts, Converting from Vapor Degreasing to the Optimum Alternative, *Metal Finishing,* Vol 91 (No. 9), Aug 1993, p 15-17
16. S.D. Temple, A New Era for Aqueous Cleaning, *Product Finishing,* Vol 54 (No. 6), March 1990, p 77-83

Emulsion Cleaning

Emulsion cleaners can be used to soften and remove, to some extent, buffing compounds and other oils and greases (Ref 5, 6). Emulsion soak cleaners usually are made from a hydrocarbon base such as kerosene and a water solution that contains soaps, emulsifiers, and an inhibitor to prevent etching of the zinc and zinc alloy surfaces (Ref 14). They typically are used hot, at 80 °C (180 °F), and with agitation or brushing. The soak time varies from 2 to 5 min (Ref 5). A water-spray rinse should follow emulsion cleaning. The pH of emulsion cleaners should be kept between 7 and 10 to avoid attack of the zinc alloy surfaces.

The compounds not removed by an emulsion cleaner usually are sufficiently softened that they are easily removed in the alkaline spray wash that normally follows. The principal disadvantage of emulsion cleaners is the danger of carryover of hydrocarbon solvent into plating baths (Ref 5). Consequently, it is extremely important that proper alkaline cleaning and rinsing follow emulsion cleaning to ensure solvent removal from recesses and blind holes.

References cited in this section

5. "Standard Guide for Preparation of Zinc Alloy Die Castings for Electroplating and Conversion Coatings," B 252-92, ASTM
6. W.H. Safranek and E.W. Brooman, "Finishing and Electroplating Die Cast and Wrought Zinc," International Lead Zinc Research Organization, 1973
14. R.A. Covert and G.A. Di Bari, Nickel Plating Zinc Die Castings--A Review, *Die Casting Engineer,* Vol 36 (No. 1), Jan/Feb 1992, p 20-26

Aqueous Detergent Cleaning (Alkaline Cleaning)

Because of the increasing restrictions on the use of chlorinated hydrocarbon solvents for cleaning, water-based alkaline detergent cleaning systems are being used in place of, rather than in addition to, solvent cleaning systems (Ref 16, 17). No other solvents or cleaners match the desired characteristics of the chlorinated hydrocarbon solvents for degreasing, so much effort is being expended to develop suitable alternative cleaners.

For zinc and zinc alloy parts, a number of alkaline cleaning solutions are available and have been used after solvent cleaning processes. The aqueous-based detergents mix emulsifiers and surfactants (wetting agents) with mild alkaline phosphates, borates, or silicates to optimize properties such as oil emulsion, saponification, dirt suspension and dispersion, water softening, and rinsability. These cleaners are used as soak cleaners, often with ultrasonic agitation, or as power-spray cleaners. Some cycles employ a 2 to 3 min soak treatment followed by spray washing with the alkaline cleaner. The solution temperatures usually range from 70 to 80 °C (160 to 180 °F), but slightly lower temperatures may be more suitable for automated cleaning cycles that include more than 30 s of anodic cleaning (Ref 6). Alkaline cleaning solutions for zinc and zinc alloys are listed in Table 1. Proprietary alkaline cleaners also are available. The alkaline cleaners must have controlled pH and contain inhibitors to prevent attack of the zinc.

Table 1 Alkaline cleaning solutions for zinc die castings

Chemical	Soak cleaning	Power-spray cleaning	Anodic cleaning
Sodium hydroxide, g/L	. . .	1.5	0.5-2[(a)]
Sodium carbonate, g/L	. . .	3.5	18
Sodium triphosphate, g/L	35	1.0	5
Sodium metasilicate, g/L	. . .	4.0	30[(b)]
Wetting agent, g/L[(c)]	0.5	. . .	0.5
Temperature, °C	82	77	71-82
Current density, A/dm^2	. . .	. . .	1.4-2.3
Time, min	1 or 2	1 or 2	0.5

(a) Solutions with a higher concentration of sodium hydroxide or a pH>12 might cause etching and the formation of a loose smut difficult to remove by rinsing.

(b) Solutions containing silicates may be more difficult to rinse than nonsilicated cleaners.

(c) Usually an alkyl sulfonate, alkyl aryl ether alcohol, and/or sodium resinate

A typical alkaline precleaning cycle may include a 1 to 2 min washing period followed by a 0.5 to 1 min draining period, a 0.5 to 1 min spray-rinse period, and a final 0.5 to 1 min draining period (Ref 5). If a spray alkaline cleaning step does not follow the soak cleaning treatment, the soak treatment should be followed by a spray rinse with warm water before electrocleaning.

Following alkaline cleaning and rinsing, parts that will be painted are often given a chromate or phosphate conversion treatment in preparation for painting.

References cited in this section

5. "Standard Guide for Preparation of Zinc Alloy Die Castings for Electroplating and Conversion Coatings," B 252-92, ASTM
6. W.H. Safranek and E.W. Brooman, "Finishing and Electroplating Die Cast and Wrought Zinc," International Lead Zinc Research Organization, 1973
16. S.D. Temple, A New Era for Aqueous Cleaning, *Product Finishing,* Vol 54 (No. 6), March 1990, p 77-83
17. E.C. Groshart, Preparation of Basis Metals for Plating, *Metal Finishing,* Vol 92 (No. 1A), Jan 1994, p 176

Electrocleaning

The final cleaning step for zinc alloy or zinc-coated parts prior to electroplating is electrolytic, usually anodic, and is conducted in an alkaline bath (see Table 1). Electrocleaning is necessary to complete the removal of oil, grease, and soil and to ensure good electroplate adhesion (Ref 5, 6). Anodic cleaning of zinc alloys is preferred to cathodic cleaning, because the dissolution of the metal prevents the formation of nonadherent metal films resulting from impurities in the cleaning solution (Ref 6). Anodic electrocleaning also helps to remove metallic smut.

The anodic alkaline electrocleaning baths are operated at temperatures from 70 to 82 °C (160 to 180 °F) with a low direct-current voltage of 3 to 6 V and current densities of 1.4 to 3.2 A/dm^2 (15 to 30 A/ft^2) (Ref 6). The cleaning time varies from 25 to 45 s. Lower bath temperatures may be required if the cleaning time exceeds 45 s or if the transfer time to the first rinse is greater than 30 s. Operating an anodic electrocleaner at too dilute a concentration may overetch the zinc (Ref 6).

Rinsing following anodic electrocleaning should include a warm-water rinse, a cold-water rinse, and a water-spray rinse. The rinses should be agitated with air to aid in removal of the cleaner solution from holes, grooves, and other surface irregularities. Alkaline solution trapped in those features can result in process blisters following plating or painting. Rinse waters containing high concentrations of dissolved minerals should be avoided.

Electrocleaning may not be required as a pretreatment for the application of conversion coatings.

References cited in this section

5. "Standard Guide for Preparation of Zinc Alloy Die Castings for Electroplating and Conversion Coatings," B 252-92, ASTM
6. W.H. Safranek and E.W. Brooman, "Finishing and Electroplating Die Cast and Wrought Zinc," International Lead Zinc Research Organization, 1973

Acid Dipping

Prior to electroplating, the surfaces of zinc alloy parts are activated by acid dipping. This process removes oxides that formed during anodic cleaning and trace amounts of alkaline compounds that were carried over from the cleaning operations due to inadequate rinsing. Dilute sulfuric acid, 0.25 to 0.75 wt%, is most often used; the immersion time ranges from 25 to 45 s with the solution at room temperature (Ref 5, 6). Similar solutions of hydrofluoric acid or a mixture of sulfuric or hydrofluoric acids also are effective. For very mild acid dipping, citric acid can be used. All traces of black films or loosely adherent smut must be removed by the acid treatment. For die castings prone to smut, including alloys containing more than 0.25% Cu, ultrasonic agitation effectively prevents smut formation (Ref 6).

Thorough rinsing must follow acid dipping to remove all traces of acid from surface fissures, porous areas, or holes to prevent blistering of the parts at those locations after plating (Ref 5, 6, 17). A succession of two air-agitated rinses and a water-spray rinse is recommended after acid dipping. A final water-spray rinse should use deionized water that can be recycled for use in an initial rinsing stage.

Following cleaning, acid dipping, and rinsing, no water breaks should occur on the surfaces of the zinc alloy castings, wrought zinc, or zinc-coated parts (Ref 6). If water breaks occur, the parts should be recycled through the alkaline and/or electrocleaning steps after those processes have been checked for proper solution composition and temperature. Tests for cleanliness should be made routinely during production (e.g., wiping with a clean white cloth or paper should result in no soil or smut on the cloth). More sophisticated tests are available to determine the effectiveness of cleaning processes (Ref 18), but they typically are not suitable for assessing cleanliness on the line during production. Most are research tools that are used to assess new cleaning processes or modifications to cleaning solution formulations.

References cited in this section

5. "Standard Guide for Preparation of Zinc Alloy Die Castings for Electroplating and Conversion Coatings," B 252-92, ASTM
6. W.H. Safranek and E.W. Brooman, "Finishing and Electroplating Die Cast and Wrought Zinc," International Lead Zinc Research Organization, 1973

17. E.C. Groshart, Preparation of Basis Metals for Plating, *Metal Finishing,* Vol 92 (No. 1A), Jan 1994, p 176
18. L.J. Durney, Ed., *Electroplating Engineering Handbook,* Van Nostrand Reinhold Co., 1984, p 150

Conversion Coating Treatments

Zinc die castings that will be painted with organic coatings must be given a suitable phosphate or chromate conversion coating (Ref 19). Similarly, zinc-coated (galvanized) steel surfaces must be prepared for painting by phosphate or chromate conversion treatments, application of wash primers, annealing treatments, complex oxide treatments, or anodizing (Ref 3, 19, 20). Sometimes the zinc alloy or zinc-coated parts are used after chromating or anodizing without painting. Prior to the various conversion treatments, the zinc alloy or zinc-coated parts are degreased by solvents, alkaline cleaned, and acid dipped using the procedures described previously.

Two types of phosphate treatments are used for zinc alloy or zinc-coated parts: iron phosphate and zinc phosphate. The baths for the iron phosphate, which is applied to steel and sometimes to aluminum and zinc, are proprietary alkali metal phosphate solutions (Ref 3). The baths are operated at temperatures from 16 to 71 °C (60 to 160 °F). The phosphate coating formed is a mixture of oxides and phosphates of the base metal. Technically, there is little or no iron phosphate present on zinc alloys after treatment, but the generic name is commonly used to describe the process on all three metals. The coating weights range from 1.9 to 4.6 mg/m^2 (20 to 50 mg/ft^2). The baths are relatively simple to control, and the films that form improve the corrosion resistance and adhesion of paints and powder coatings.

Zinc phosphates are more commonly used on galvanized coatings and zinc die castings (Ref 3, 20, 21). The baths contain zinc oxide or phosphate and phosphoric acid in combination with accelerators, refining agents, and other proprietary ingredients. They produce heavier crystalline deposits than do the iron phosphate solutions. The best paint or powder coating adhesion is achieved when the coating weight is kept low, in the range from 9 to 28 mg/m^2 (100 to 300 mg/ft^2) (Ref 3).

Chromate treatments consist of a dip or spray in a dilute solution of chromium trioxide and other acids, with the proper accelerator for 5 to 30 s (Ref 20). The baths are operated at temperatures from room temperature to 54 °C (130 °F). The process produces a thin, amorphous chromate coating that increases corrosion resistance and paint adhesion.

Aqueous chromic-organic treatments, applied by dipping or roller coating, are solutions of certain water-soluble resins, properly formulated with chromium compounds (Ref 20). The film is cured or baked after application, whichever is required by the paint system to be applied.

A vinyl wash primer also is used to prepare the surfaces of galvanized parts for painting. It involves the application of an acid-bound resinous film 8 to 13 μm (0.3 to 0.5 mil) thick. The treatment is based on three primary components: a hydroxyl-containing resin, a pigment capable of reacting with the resin and an acid, and an acid capable of insolubilizing the resin by reacting with the resin, the pigment, and the zinc surface. This film usually is applied by spraying, but it may be applied by brushing, dipping, or roller coating. Under normal conditions it will dry sufficiently for recoating within 30 min, and within 8 h of application it will not be softened by organic solvents commonly used in paint coatings. It has good adhesion to the metal substrate and promotes good adhesion of most organic coatings.

Hot-dipped galvanized coatings may be given an annealing treatment under controlled conditions to alloy the coating with the base metal and to change the surface character of the zinc coating and make it more receptive to paint (Ref 20). Annealing treatments usually are performed in the mill shortly after galvanizing coils of steel. The surface produced by annealing can further be treated to enhance paint adhesion by the conversion treatment methods described previously.

The amorphous complex-oxide treatment consists of reacting to the zinc surface in an alkaline solution containing heavy metal ions for times between 5 and 30 s at 45 to 70 °C (115 to 160 °F) (Ref 20). The surface of the zinc is converted to a nonmetallic, amorphous, complex-oxide coating that inhibits corrosion and increases the adhesion and durability of paint finishes. This treatment can be carried out by immersion or spray.

Zinc die castings also can be anodized prior to use or prior to painting (Ref 21). Zinc anodizing produces an unusual fritted coating (Ref 22). Anodizing is conducted in a solution of chromic acid, phosphoric acid, and hydrofluoric acid. Alternating current is preferred, although direct current can be used (Ref 21). The anodizing process is conducted at a current density of 4.3 A/dm^2 (40 A/ft^2) and a bath temperature in the range from 66 to 82 °C (150 to 180 °F). The coating forms during an anodic spark discharge that starts at about 70 V (Ref 22). Because the anodized coating is dielectric, the voltage increases to about 200 V in order to maintain the current density as the fritted coating forms. When the power

reaches 200 V (5 to 7 min), the process is terminated. The coating formed is matte green. This coating has very unusual corrosion- and abrasion-resisting properties and can be readily painted.

Following the application of a conversion coating, most commonly zinc phosphate, the treated parts can be coated with most of the organic and water-based systems available. The choice of coating will depend on the service requirements of the coated part.

References cited in this section

3. M.A. Kuehner, Pretreatment for Powder Coating, *Plating and Surface Finishing,* Vol 71 (No. 9), Sept 1984, p 36-39
19. B. Johnson, Reliable Finishing Systems for Zinc Die Castings, Paper G-T83-095, *Transactions 12th International Die Casting Congress and Exposition,* Society of Die Casting Engineers, 1983
20. "Standard Practice for Preparation of Zinc-Coated Galvanized Steel Surfaces for Plating," D 2092-86, ASTM
21. R.E. Marce, Choosing the Right Finish to Finish It Right, Paper G-T81-072, *Transactions 11th International Die Casting Congress and Exposition,* Society of Die Casting Engineers, 1981
22. R.E. Marce and L.M. Weisenberger, Applications of Anodized Zinc, Paper G-T75-141, *Transactions 8th International Die Casting Congress and Exposition,* Society of Die Casting Engineers, 1975

Introduction

VITREOUS CERAMIC COATINGS are applied over substrates for a number of reasons (Ref 1). These coatings may be applied to a substrate surface to render the surface:

- Chemically more inert
- Impervious to liquids and gases
- More readily cleanable
- Smoother and more resistant to abrasion and scratching
- Mechanically stronger
- Decorative
- Aesthetically pleasing

Vitreous coatings are thin layers of glass fused onto the surface of the substrate. When the substrate is a ceramic, the coating is called a glaze. When the substrate is a metal, the coating is called a porcelain enamel. When the substrate is a glass, the coating is called a glass enamel. This article focuses on ceramic coatings for ceramic and glass substrates. Porcelain enameling is discussed in a separate article in the Section "Dip, Barrier, and Chemical Conversion Coatings," in this Volume.

The first requirement is for a strong bond between the coating and the substrate (Ref 2). The composition must fuse to a homogeneous viscous glass (or ceramic) at a temperature that is either coincident with the temperature at which the body matures or at a temperature sufficiently lower to prevent distortion of the substrate during glost firing.

During and after fusion of the coating materials, they must react with the substrate to form an intermediate bonding layer of proper thickness. If the bonding layer or interface is too thin, the coating will flake off after application and subsequent firing. If the bonding layer is too thick, the composition of the body or the coating may be degraded. The coating must also have a coefficient of thermal expansion that coincides or fits the substrate (Ref 3). When the fired ware is cooled, the coated substrate contracts. If the coefficients of thermal expansion of the coating and the substrate are not matched, stresses that lead to spalling or crazing of the coating will be introduced. The coating materials should have a low surface tension to minimize the crawling of the coating away from the edges or any holes present during firing.

The second group of properties are those associated with the use of the product, such as appearance, smoothness, porosity, and corrosion resistance to various liquids and gases. Almost all vitreous coatings are expected to be homogeneous, smooth, and hard and also to resist abrasion and scratching. Such a surface is also more apt to be impervious to liquids and gases and hence more readily cleanable. The sole exception to the desire for a smooth surface is the textured coating in which a pattern is applied for aesthetic purposes.

In many applications, chemical durability in severe service conditions is a principal reason for the selection of a ceramic coating (Ref 4). Vitreous coatings are formulated to be resistant to a variety of reagents ranging from acids, to hot water, to alkalis, to essentially all organic media. The only important exception is hydrofluoric acid, which readily attacks all silicate glasses.

For some applications, the finished ware is to be subjected to elevated temperatures while in service. This is a prime reason for the selection of ceramic coatings for cookware applications and for industrial and military applications.

The optical and appearance properties of any surface coating material are major considerations in determining which coating will be applied. Various possibilities exist for meeting the requirements of a particular application. Because vitreous coatings can be transparent or opaque; high gloss, satin, or matte; smooth, patterned, or textured; and monochrome or multicolored, the combination of requirements that meets each particular application is extensive.

Acknowledgements

Adapted from R.A. Eppler and L.D. Gill, Glazes and Enamels, *Engineered Materials Handbook,* Vol 4, *Ceramics and Glasses,* ASM International, 1991, p 1061-1068

References

1. R.A. Eppler, Chapt. 4, Glazes and Enamels, *Glass Science & Technology,* Vol 1, Academic Press, 1983, p 301-337
2. R.A. Eppler, Glazes and Enamels, *Commercial Glasses,* J.F. MacDowell and D. Boyd, Ed., Vol 18, *Advances in Ceramics,* American Ceramic Society, 1986
3. P. Rado, *Introduction to the Technology of Pottery,* 2nd ed., Pergamon Press, Oxford, 1988
4. R.A. Eppler, Chapt. 12, Corrosion of Glazes and Enamels, *Corrosion of Glass, Ceramics, and Ceramic Superconductors,* D.E. Clark and B.K. Zoitos, Ed., Noyes Publications, 1991, to be published

Glazes

A ceramic glaze is a vitreous coating applied to a ceramic substrate (usually a whiteware). A great variety of formulations are used as glazes (Ref 1). Ceramic ware is fired over a wide range of temperatures from 800 to >1400 °C (1470 to >2550 °F). No single glaze composition would be satisfactory over such a wide range of temperatures. A glaze that melts at low temperature will run off the substrate, react with the substrate, or volatilize if fired at a high temperature. A given glaze composition is generally useful over a temperature range of only 30 °C (55 °F). Typical firing temperatures for glazes based on application can be summarized as follows (Ref 5):

- Electronic substrates, ≈600 to 900 °C (≈1110 to 1650 °F)
- Artware glazes, ≈900 to 1050 °C (≈1650 to 1920 °F)
- Dinnerware and tile glazes, ≈1000 to 1150 °C (≈1830 to 2100 °F)
- Structural clay and sanitaryware glazes, ≈1180 to 1250 °C (≈2155 to 2280 °F)
- Porcelain glazes, ≥1300 °C (≥2370 °F)

Because of the toxicity of lead, glazes are often classified on the basis of the presence or the absence of litharge (PbO). Safe working practices require unfired glazes containing litharge to be handled carefully and to have an acceptable level of acid resistance in raw powdered form in the work environment. Finished tableware coated with a lead glaze must also possess an acceptable level of resistance to chemical attack.

Another way to classify a glaze is according to the way it is constituted. Raw glazes are prepared from mineral powders (usually oxides or carbonates) and are chemically limited to elements that can be obtained in materials having low water solubility. Frits are prepared to allow the use of water-soluble materials, which are first melted to an insoluble glass, and then quenched and broken up. For a partially fritted glaze, only the soluble materials and sufficient network former to make an insoluble glass are fritted. In an all fritted glaze, all components are melted into the frit except for necessary suspending agents.

Markets for Glazed Ceramics

The total whitewares market in the United States was reported to be $3.459 billion in 1989 (Ref 6). A breakdown of the U.S. market for products using glazes is shown in the chart of Fig. 1.

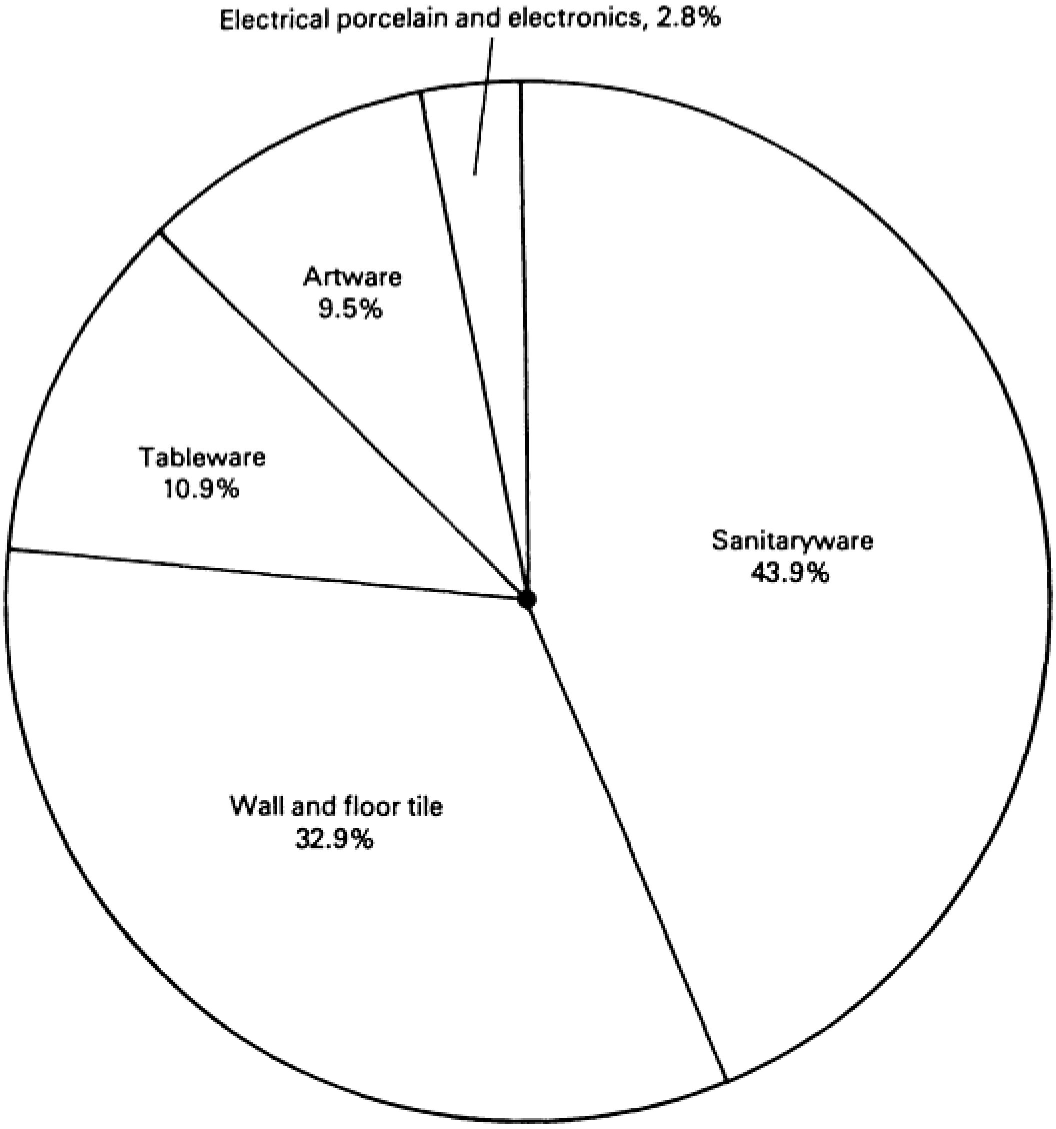

Fig. 1 Breakdown of key segments of the $3.46 billion glaze market in the United States (1989 data)

A ceramic coating typically makes up 10 to 15% of the total manufacturing cost of a ceramic product. The value of the properties provided by the coating usually far outweighs this cost. The protective, functional, and decorative surface that is obtained often serves as a primary selling feature of the end product.

Ceramic glazes find their way into a wide range of applications ranging from coffee mugs to automotive sparkplugs. The major markets for ceramic coatings have different requirements, but one common theme is corrosion resistance and cleanability.

Rarely sold in a ready-to-use form, ceramic glazes are usually formulated and processed for application by the end user.

Role of Specific Oxides in Glazes

The commonly used oxides in glazes are SiO_2, ZrO_2, Al_2O_3, B_2O_3, CaO, SrO, BaO, MgO, ZnO, PbO, Li_2O, Na_2O, and K_2O (Ref 7). Small amounts of fluorine are sometimes used as a partial substitution for oxygen.

Silicon Dioxide. Most glazes contain more silica than all the other constituents combined. Silica promotes low expansion, high durability, and abrasion resistance. Its only serious deficiency is its high melting point, T_m, of 1723 °C (3133 °F).

Alkali Oxides. The foremost reason for adding other oxides is to reduce the maturing temperature. The alkalis are powerful fluxes at all maturing temperatures, and their use is limited by the high thermal expansion they impart to a glaze.

Alkaline Earths. The alkaline earths and magnesia are effective fluxes only at >1100 °C (>2010 °F).

Zinc oxide is effective at >1000 °C (>1830 °F) and in modest amounts it improves the effectiveness of other fluxes.

Lead monoxide is a powerful flux from the lowest temperatures to ≈1150 °C (≈2100 °F), above which volatilization becomes excessive.

Boric oxide is effective at all temperatures. As a network former, it can be used with other oxides to get a high fluxing level. Above 15% B_2O_3 concentration, however, it seriously degrades the durability of the glaze.

Alumina contributes to the working properties of a glaze, improves acid durability, and suppresses phase separation and crystallization of the glaze.

Zirconia is added to a glaze to improve the alkaline durability, and, in higher concentrations, as an opacifier.

Leadless Glazes

Tables 1 and 2 give the formulas of a number of commercial ceramic coatings. The first eight of these are leadless glazes. In these glazes, the alkali and alkaline earth oxides, together with MgO, ZnO, and B_2O_3, are used to provide the fluxing action.

Table 1 Compositions of selected glazes based on mole ratio (Seger formula)

Oxide	Glazes						
	1 Hard porcelain	2 Soft porcelain	3 Sanitaryware	4 Bristol	5 Wall tile	6 Semivitreous dinnerware	7 Vitreous dinnerware
Li_2O	. . .	. . .	. . .	. . .	. . .	0.047	. . .
Na_2O	. . .	0.142	0.100	0.100	0.270	0.081	0.070
K_2O	0.30	0.135	0.100	0.100	0.040	0.115	0.069
MgO	. . .	0.043	. . .	0.200	0.010	0.066	0.037
CaO	0.70	0.680	0.600	0.400	0.350	0.580	0.391
ZnO	. . .	. . .	0.200	0.200	0.320	. . .	0.322
SrO	. . .	. . .	. . .	. . .	. . .	0.110	0.071
BaO	. . .	. . .	. . .	. . .	. . .	. . .	0.039
Al_2O_3	1.00	0.556	0.550	0.400	0.260	0.367	0.173

B_2O_3	. . .	. . .	. . .	. . .	0.050	0.171	0.188
SiO_2	10.00	4.570	3.000	3.500	2.650	2.721	2.224
ZrO_2	. . .	. . .	. . .	. . .	. . .	. . .	0.011
Ref	3	8	2	2	9	10	11

Oxide	**Glazes**						
	8 Low expansion	**9 Cone 4 dinnerware**	**10 Cone 06 artware**	**11 Electronic**	**12 Opacified**	**13 Zinc matte**	**14 Lime matte**
Li_2O	0.850	. . .	. . .	. . .	. . .	. . .	. . .
Na_2O	. . .	0.179	0.157	. . .	0.111	0.087	0.040
K_2O	0.150	0.066	. . .	. . .	0.083	0.052	0.059
MgO	. . .	. . .	. . .	. . .	. . .	0.097	. . .
CaO	. . .	0.494	0.218	. . .	0.407	0.152	0.524
ZnO	. . .	. . .	. . .	. . .	0.371	0.364	. . .
BaO	. . .	. . .	. . .	. . .	0.028	. . .	. . .
PbO	. . .	0.261	0.625	1.000	. . .	0.247	0.377
Al_2O_3	0.740	0.340	0.273	. . .	0.406	0.443	0.262
B_2O_3	0.200	0.314	0.507	. . .	0.143	0.142	0.176
SiO_2	2.510	3.369	2.792	0.500	2.019	1.566	1.746
ZrO_2	. . .	. . .	0.023	. . .	0.248	0.210	0.211
Ref	12	13	14	15	16	2	2

Table 2 Compositions of selected glazes based on weight percent

Oxide	Glazes						
	1 Hard porcelain	**2 Soft porcelain**	**3 Sanitaryware**	**4 Bristol**	**5 Wall tile**	**6 Semivitreous dinnerware**	**7 Vitreous dinnerware**
Li_2O	. . .	. . .	. . .	. . .	. . .	0.51	. . .
Na_2O	. . .	2.24	2.05	1.98	6.54	1.81	1.81
K_2O	3.67	3.24	3.12	3.01	1.47	3.92	2.71
MgO	. . .	0.44	. . .	2.57	0.16	0.96	0.62
CaO	5.10	9.71	11.15	7.16	7.67	11.76	9.16
ZnO	. . .	. . .	5.39	5.19	10.18	. . .	10.94
SrO	. . .	. . .	. . .	. . .	. . .	4.12	3.07
BaO	. . .	. . .	. . .	. . .	. . .	. . .	2.50
Al_2O_3	13.24	14.44	18.58	13.01	10.36	13.53	7.37
B_2O_3	. . .	. . .	. . .	. . .	1.36	4.30	5.47
SiO_2	78.00	69.90	59.71	67.09	62.25	59.09	55.79
ZrO_2	. . .	. . .	. . .	. . .	. . .	. . .	0.57

Oxide	Glazes						
	8 Low expansion	**9 Cone 4 dinnerware**	**10 Cone 06 artware**	**11 Electronic**	**12 Opacified**	**13 Zinc matte**	**14 Lime matte**
Li_2O	9.08	. . .	. . .	. . .	. . .	. . .	. . .
Na_2O	. . .	3.06	2.46	. . .	2.50	1.91	0.85
K_2O	5.05	1.72	. . .	. . .	2.84	1.73	1.91

MgO	. . .	. . .	. . .	. . .	. . .	1.38	. . .
CaO	. . .	7.65	3.09	. . .	8.29	3.02	10.08
ZnO	. . .	. . .	. . .	. . .	10.97	10.48	. . .
BaO	. . .	. . .	. . .	. . .	1.56	. . .	. . .
PbO	. . .	16.08	35.30	88.14	. . .	19.52	28.87
Al_2O_3	26.98	9.57	7.04	. . .	15.04	15.99	9.17
B_2O_3	4.98	6.04	8.93	. . .	3.62	3.50	4.20
SiO_2	53.91	55.88	42.45	11.86	44.07	33.31	35.99
ZrO_2	. . .	. . .	0.72	. . .	11.10	9.16	8.92

Hard Porcelain Glaze. Glaze 1 is a feldspathic glaze suitable for use only on the highest firing hard paste porcelains (Ref 3).

Soft Porcelain Glaze. For porcelains fired at lower temperatures, such as soft paste porcelain or hard stoneware, glaze 2 would be satisfactory (Ref 8). This glaze is typical of that used on medieval Chinese porcelains.

Sanitaryware Glaze. Glaze 3 is a sanitaryware glaze (Ref 5). It is derived from the soft paste porcelain glaze by the addition of ZnO in large quantities.

Bristol glaze (glaze 4) is used to produce an opaque white coating on stoneware and other dark-colored bodies.

Fast-fire wall tile glazes are derived from the Bristol glaze by increasing the amount of fluxes to increase the melting rate (Ref 9). Glaze 5 is a typical example.

Semivitreous Dinnerware Glaze. The development of glazes for dinnerware is more difficult because of the lower expansion of the bodies. Glaze 6 is an example of a glaze for semivitreous dinnerware (Ref 10). Several alkaline earths are used to improve the melting and surface properties.

Hotel China Glaze. Leadless glazes for vitreous hotel china (such as glaze 7) are a very recent development (Ref 11).

Low Expansion Glaze. Zircon and cordierite bodies are even lower in expansion, requiring a semicrystalline glaze, such as glaze 8 (Ref 12).

Lead-Containing Glazes

Litharge is used in glazes for several reasons (Ref 20). The strong fluxing action of PbO allows the formulation of glazes that mature at temperatures lower than their leadless counterparts, thus leading to greater flexibility in the formulation of the glaze to obtain low expansion, smooth surface, and maturing of the glaze over a wider firing range. Litharge imparts low surface tension for a smooth surface and a high index of refraction that results in a brilliant appearance. Glazes containing litharge heal over defects in the glaze surface more readily and are usually more corrosion resistant. This combination of desirable properties is difficult to achieve in leadless glazes on a production scale.

However, litharge also has disadvantages as a glaze constituent. Lead glazed ware must be fired in a strongly oxidizing atmosphere because lead is readily reduced. Lead oxide cannot be used above 1150 °C (2100 °F) due to volatility. Most importantly, litharge is highly toxic. Moreover, lead poisoning is very difficult to diagnose because its symptoms are similar to other ailments. Therefore, every possible precaution must be taken when preparing lead glazes to avoid poisoning, and ware intended for food contact should be tested as noted below to ensure consumer protection.

Cone 4 Dinnerware Glaze. Glaze 9 in Tables 1 and 2 is an example of a lead-containing dinnerware glaze for cone 4 (1100 °C, or 2010 °F) (Ref 13). (*Cone* refers to pyrometric cones, which are a traditional means of measuring time/temperature thermal cycles, and are still one on the most accurate methods for recording the amount of thermal "work" applied to a kiln of ware. Pyrometric cones are small, triangular pyramids prepared from carefully formulated ceramic compounds designed to soften and melt under precise conditions of temperature and time. A series of cones, which are given numbers corresponding to temperatures at which they soften, are placed in the kiln with the ware. The cones are observed during firing to assist in temperature control, and are examined after the fire to indicate and record the degree of firing achieved.)

Cone 06 Artware Glaze. Glaze 10 is an example of a clear glaze suitable for use on artware and hobbyware bodies at cone 06 (1000 °C, or 1830 °F) (Ref 14).

Electronic Glaze. The glazes used on alumina packages for integrated circuits (ICs) to seal the package represent the lowest firing lead-containing glazes. Glaze 11 is an example of such a glaze, which can be fired as low as 550 °C (1020 °F) (Ref 15).

Heavy-Metal Release

If lead-containing glazes are not properly formulated, they may be less resistant to acid attack, which results in the release of lead. If such glazes are used in contact with food or drink, lead poisoning of the user may result. Cadmium oxide, which is considerably more toxic than lead oxide (Ref 21), is only used in ceramic coatings in connection with the use of cadmium sulfoselenide pigments, which already contain large amounts of cadmium.

To control this problem under production conditions, standard tests have been developed for determining the lead and cadmium content released from glazed surfaces (Table 3). A sample is exposed to a 4% acetic acid solution for 24 h at room temperature while covered. The concentration in ppm of lead and cadmium in the solution is then determined.

Table 3 Standard test methods for determining the lead and cadmium content released from glazed and enamel surfaces used for food preparation when exposed to attack by acetic acid

ASTM standard	Test method	Ref
C 738	Lead and cadmium extracted from glazed ceramic surfaces	22
C 872	Lead and cadmium release from porcelain enamel surfaces	23
C 895	Lead and cadmium extracted from glazed ceramic tile	22
C 927	Lead and cadmium extracted from the lip and rim area of glass tumblers externally decorated with ceramic glass enamels	22
C 1034	Lead and cadmium extracted from glazed ceramic cookware	22

FDA Guidelines. The current United States Food and Drug Administration (FDA) standard limits for lead released are 7 ppm average for six samples of flatware, 5 ppm maximum of six samples of small holloware, and 2.5 ppm maximum of

six samples of large holloware (Ref 24). The standard limits for Cd are $\frac{1}{2}$ ppm average for six samples of flatware, $\frac{1}{2}$ ppm maximum of six samples of small holloware, and $\frac{1}{4}$ ppm maximum of six samples of large holloware. These limits are currently under review, and lower levels may possibly be applicable by the time this article is published (Ref 25). Because of statistical fluctuations in the measurements, operating standards must be less than half these guideline values (Ref 26).

In the FDA test, lead-containing commercial dinnerware glazes usually release $\frac{1}{2}$ to 2 ppm (Ref 20). Properly designed commercial artware will be somewhat higher. In contrast, ware implicated in health cases have all released in excess of 50 ppm Pb.

Most glazes have no added cadmium oxide. Those that do contain cadmium will release 0.1 to 0.2 ppm even when properly formulated (Ref 21). For this reason, it is best if CdS-Se colors are not used as surface decorations on glass surfaces that will come in contact with food or drink.

The issue of lead and cadmium release from glassware decorated with glass enamels has also been addressed through a voluntary quality-control program adopted by the ceramic industry (Ref 27). The lip and rim area (that is, the top 20 mm, or $\frac{25}{32}$ in.) of the decorated glass must not leach greater than 50 ppm Pb or 3.5 ppm Cd when analyzed by a modification of the existing ceramic ware test (see Table 3). Failure of one glass in a sample of six is cause for rejection.

Numerous factors must be considered in formulating and processing a glaze to achieve low lead and cadmium release:

- Total glaze composition
- Thermal history during processing
- Glaze application techniques
- Glaze-body solution at the interface during firing
- Atmospheric conditions that exist during firing

Of all these parameters, the most important is the glaze composition.

Heavy-Metal Release Performance Rating. A figure of merit (FM) has been developed to predict the heavy-metal release or acid resistance of a glaze from its composition (Ref 14). Silica, alumina, zirconia, and similar ions such as titania and tin oxide are effective in lowering the lead release (LR) of a glaze:

$$LR_A = 2[Al_2O_3 + [SiO_2] + [TiO_2] + [ZrO_2] + [SnO_2] \quad \textbf{(Eq 1)}$$

The concentrations given in Eq 1 are expressed in molar ratio. The factor 2 arises from the fact that there are 2 equivalents of aluminum ions per equivalent of Al_2O_3.

It has also been shown that alkalis, alkaline earths, B_2O_3, fluoride, phosphate, ZnO, CdO, and PbO are all more or less detrimental to the lead release in a glaze:

$$LR_B = ([Li_2O] + [Na_2O] + [K_2O] + [B_2O_3] + [P_2O_5]) + [MgO] + [CaO] + [SrO] + [BaO] + [F] + [ZnO] + [PbO] \quad \textbf{(Eq 2)}$$

Combining these terms gives the figure of merit:

$$FM = LR_A/(LR_B)^{1/2} \quad \textbf{(Eq 3)}$$

When the figure of merit is >2.05, the lead release is below the standard. When it is <1.80, some measurements are always greater than the standard. This figure of merit applies to all single-phase glazes. In a glass-crystal-line system, the formulation of the least durable component must be used in the calculation.

Opaque Glazes

In opaque glazes, the transmittance of the glaze has been reduced to hide the body. Opacity is introduced into ceramic coatings by the addition of a substance that will disperse in the coating as discrete particles to scatter and reflect the incident light (Ref 5). This dispersed substance must have a refractive index that differs from that of the clear ceramic coating.

The refractive index, n_D, of most glasses is 1.5 to 1.6. Typical opacifiers include SnO_2 (n_D = 2.04), ZrO_2 (n_D = 2.40), $ZrSiO_4$ (n_D = 1.85), and TiO_2 (n_D = 2.5 for anatase and 2.7 for rutile). Opacified glaze (glaze 12) in Tables 1 and 2 is an example of a glaze fired at >1000 °C (>1830 °F) where zircon is the opacifier of choice (Ref 16).

In coatings fired at <1000 °C (<1830 °F), titania in the anatase phase is the best opacifier because of its high refractive index. The temperature limit is the point at which anatase inverts to rutile. Rutile crystals are unsuitable because they grow too large in glass for opacification and then have a yellow color.

Satin and Matte Glazes

Satin and matte effects are also due to dispersed crystals in the glaze (Ref 5). The crystals must be very small and evenly dispersed if the glaze is to have a smooth velvet appearance. Matte glazes are always somewhat opaque. The amount of opacity depends on the difference in refractive index between glaze and crystal and can be fairly small. Glaze 13 in Tables 1 and 2 is an example of a zinc matte glaze where the crystal is willemite (Zn_2SiO_4) (Ref 2). Glaze 14 is a lime matte glaze with a wollastonite ($CaSiO_3$) crystal.

References cited in this section

1. R.A. Eppler, Chapt. 4, Glazes and Enamels, *Glass Science & Technology,* Vol 1, Academic Press, 1983, p 301-337
2. R.A. Eppler, Glazes and Enamels, *Commercial Glasses,* J.F. MacDowell and D. Boyd, Ed., Vol 18, *Advances in Ceramics,* American Ceramic Society, 1986
3. P. Rado, *Introduction to the Technology of Pottery,* 2nd ed., Pergamon Press, Oxford, 1988
5. F. Singer and W.L. German, *Ceramic Glazes,* Borax Consolidated, 1964
6. *Ceram. Ind.,* Aug 1990, p 36
7. D. Rhodes, *Clay and Glazes for the Potter,* Ref. ed., Chilton, 1973
8. R. Tichane, *Ching-th-Chen; Views of a Porcelain City,* N.Y. State Institute Glaze Research, 1983
9. W.H. Orth, Effect of Firing Rate on Physical Properties of Wall Tile, *Am. Ceram. Soc. Bull.,* Vol 46 (No. 9), 1967, p 841-844
10. J.E. Marquis and R.A. Eppler, Leadless Glazes for Dinnerware, *Am. Ceram. Soc. Bull.,* Vol 53 (No. 5), 1974, p 443-445, 449; Vol 53 (No. 6), 1974, p 472
11. E.F. O'Conor, L.D. Gill, and R.A. Eppler, Recent Developments in Leadless Glazes, *Ceram. Eng. Sci. Proc.,* Vol 5 (No. 11), 1984, p 923-932
12. E.F. O'Conor and R.A. Eppler, Semicrystalline Glazes for Low Expansion Whiteware Bodies, *Am. Ceram. Soc. Bull.,* Vol 52 (No. 2), 1973, p 180-184
13. J.E. Marquis, Lead in Glazes--Benefits and Safety Precautions, *Am. Ceram. Soc. Bull.,* Vol 50 (No. 11), 1971, p 921-923
14. R.A. Eppler, Formulation of Glazes for Low Pb Release, *Am. Ceram. Soc. Bull.,* Vol 54 (No. 5), 1975, p 496-499
15. R.R. Tummala and R.R. Shaw, Glasses in Microelectronics in the Information-Processing Industry, *Commercial Glasses,* J.F. MacDowell and D. Boyd, Ed., Vol 18, *Advances in Ceramics,* American Ceramic

Society, 1986

16. F.T. Booth and G.N. Peel, Principles of Glaze Opacification with Zirconium Silicate, *Trans. Brit. Ceram. Soc.,* Vol 58 (No. 9), 1952, p 532-564
20. R.A. Eppler, Chapt. 10, Formulation and Processing of Ceramic Glazes for Low Lead Release, *Proceedings of the International Conference on Ceramic Foodware Safety,* J.F. Smith and M.H. McLaren, Ed., Lead Industries Association, 1976
21. R.A. Eppler and D.S. Carr, Cadmium in Glazes and Glasses, *Cadmium 81, Proceedings of the 3rd International Cadmium Conference,* International Lead and Zinc Research Organization, 1982, p 31-33
22. Glass, Ceramic Whitewares, part 15.02, *Annual Book of Standards,* American Society for Testing and Materials
23. Metallic and Inorganic Coatings, part 2.05, *Annual Book of Standards,* American Society for Testing and Materials
24. Cadmium 7117.06, and Lead 7117.07, U.S. Food and Drug Administration Compliance Policy Guides
25. J.A. Calderwood, *Soc. Glass Ceram. Decorators 1988/89 Seminar Proceedings,* 1989, p 12-15
26. C.F. Moore, *Trans. J. Brit. Ceram. Soc.,* Vol 76, 1977, p 52-57
27. *Federal Register,* Vol 43 (No. 242), 15 Dec 1978

Glass Enamels

Glass enamels are applied to glass for decorative purposes and not to improve chemical durability or cleanability. Because these coatings are matured at temperatures below the deformation point of the glass substrate (540 to 650 °C, or 1000 to 1200 °F) and require larger quantities of fluxing elements, corrosion resistance can be difficult to obtain.

Glass enamels are produced in ready-to-use form (for example, paste, thermoplastics, spray media, and ultraviolet curable media) by a few select manufacturers. These enamels are rarely compounded by the end user and represent a specialty product that is more akin to organic paints than to other ceramic coatings.

The markets for this specialty product are categorized as tableware, glass containers, architectural, lighting, and automotive. There are no published figures on the value of the specific portion of the glass market that is decorated with glass enamels.

As supplied to the user, glass enamels are mechanical mixtures of pigments (see the section "Ceramic Decoration" in this article), fluxes, and organic suspending media. The requirement for low maturing temperatures necessitates the use of very high lead-oxide containing borosilicates for the flux. The industry relies on in-house control tests to ensure acceptable levels of lead release from decorated areas that might come in contact with food or drink (see the section on "Heavy-Metal Release" in this article).

The organic suspending media for glass enamels are similar to materials used to make organic paints.

Ceramic Decoration

Techniques for Coloring Vitreous Coatings. There are a number of ways to obtain color in a ceramic coating (Ref 28). In one method, certain transition metal ions can be melted into a glass when it is made. While suitable for bulk glass, this method is rarely used for coatings because adequate tinting strength and the purity of color cannot be obtained by this process.

A second method to obtain color is to induce the precipitation of a colored crystal in a transparent matrix. Certain materials dissolve to some extent in a vitreous material at high temperature. When the temperature is reduced, the solubility is also reduced and precipitation occurs. This method is used for opacification (that is, the production of an opaque white color). Normally, some or all of the opacifier added to the coating dissolves during the firing process and recrystallizes upon cooling. For oxide colors other than white, however, this method lacks the necessary control for reproducible results and is seldom used.

The third method to obtain color in a vitreous matrix is to disperse in that matrix one or more insoluble crystals that are colored. The color of the crystal is then imparted to the transparent matrix. This method is the one most commonly used to introduce color to vitreous coatings.

Pigment Systems. To be suitable as a ceramic pigment, a material must have a high tinting strength, a high refractive index, and be free of grayness. It must also possess stability under the high temperatures and corrosive environments encountered in the firing of glazes (Ref 29). Most ceramic pigments are complex oxides (see Table 4) with the lone exception being the cadmium sulfoselenide red pigments.

Table 4 Inorganic pigments to impart colors to ceramic coatings

Pigment system	CAS registry number[(a)]	Chemical formula	DCMA number[(b)]
Pink and purple			
Chrome-alumina-pink spinel	68201-65-0	$Zn(Al,Cr)_2O_4$	13-32-5
Chrome-alumina-pink corundum	68187-27-9	$(Al,Cr)_2O_3$	3-03-5
Manganese-alumina-pink corundum	68186-99-2	$(Al,Mn)_2O_3$	3-04-5
Zirconium-iron pink zircon	68187-13-3	$(Zr,Fe)SiO_4$	14-44-5
Chrome-tin orchid cassiterite	68187-53-1	$(Sn,Cr)O_2$	11-23-5
Chrome-tin pink sphene	68187-12-2	$CaOSnO_2SiO_2:Cr$	12-25-5
Brown			
Zinc-iron-chromite brown spinel	68186-88-9	$(Zn,Fe)(Fe,Cr)_2O_4$	13-37-7
Iron-chromite brown spinel	68187-09-7	$Fe(Fe,Cr)_2O_4$	13-33-7
Iron-titanium brown spinel	68187-02-0	Fe_2TiO_4	13-34-7
Nickel-ferrite brown spinel	68187-10-0	$NiFe_2O_4$	13-35-7
Zinc-ferrite brown spinel	68187-51-9	$(Zn,Fe)Fe_2O_4$	13-36-7
Iron brown hematite	68187-35-9	Fe_2O_3	3-06-7
Chrome-iron-manganese brown spinel	68555-06-6	$(Fe,Mn)(Fe,Cr,Mn)_2O_4$	13-48-7

Chromium-manganese-zinc brown spinel	71750-83-9	$(Zn,Mn)Cr_2O_4$	13-51-7
Yellow			
Zirconium-vanadium yellow baddeleyite	68187-01-9	$(Zr,V)O_2$	1-01-4
Tin-vanadium yellow cassiterite	68186-93-6	$(Sn,V)O_2$	11-22-4
Zirconium-praseodymium yellow zircon	68187-15-5	$(Zr,Pr)SiO_4$	14-43-4
Lead-antimonate yellow pyrochlore	68187-20-2	$Pb_2Sb_2O_7$	10-14-4
Nickel-antimony-titanium yellow rutile	71077-18-4	$(Ti,Ni,Sb)O_2$	11-15-4
Nickel-niobium-titanium yellow rutile	68611-43-8	$(Ti,Ni,Nb)O_2$	11-16-4
Chrome-antimony-titanium buff rutile	68186-90-3	$(Ti,Cr,Sb)O_2$	11-17-6
Chrome-niobium-titanium buff rutile	68611-42-7	$(Ti,Cr,Nb)O_2$	11-18-6
Chrome-tungsten-titanium buff rutile	68186-92-5	$(Ti,Cr,W)O_2$	11-19-6
Manganese-antimony-titanium buff rutile	68412-38-4	$(Ti,Mn,Sb)O_2$	11-20-6
Green			
Chromium-green hematite	68909-79-5	$(Cr,Fe)_2O_3$	3-05-3
Cobalt-chromite blue-green spinel	68187-11-1	$Co(Al_2Cr)_2O_4$	13-29-2
Cobalt-chromite green spinel	68187-49-5	$CoCr_2O_4$	13-30-3
Cobalt-titanate green spinel	68186-85-6	Co_2TiO_4	13-31-3
Victoria green garnet	68553-01-5	$3CaOCr_2O_33SiO_2$	4-07-3
Nickel-silicate green olivine	68515-84-4	Ni_2SiO_4	5-45-3
Blue			
Cobalt-aluminate blue spinel	68186-86-7	$CoAl_2O_4$	13-26-2

Cobalt-zinc-aluminate blue spinel	68186-87-8	$(Co,Zn)Al_2O_4$	13-28-2
Cobalt-silicate blue olivine	68187-40-6	Co_2SiO_4	5-08-2
Cobalt-zinc-silicate blue phenacite	68412-74-8	$(Co,Zn)_2SiO_4$	7-10-2
Cobalt-tin blue-gray spinel	68187-05-3	Co_2SnO_2	13-27-2
Cobalt-tin-alumina blue spinel	68608-09-3	$CoAl_2O_4/Co_2SnO_4$	13-49-2
Zirconium-vanadium blue zircon	68186-95-8	$(Zr,V)SiO_4$	14-42-2
Black			
Iron-cobalt black spinel	68187-50-8	$(Fe,Co)Fe_2O_4$	13-39-9
Iron-cobalt-chromite black spinel	68186-97-0	$(Co,Fe)(Fe,Cr)_2O_4$	13-40-9
Manganese-ferrite black spinel	68186-94-7	$(Fe,Mn)(Fe,Mn)_2O_4$	13-41-9
Copper-chromite black spinel	68186-91-4	$CuCr_2O_4$	13-38-9
Chromium black hematite	68909-79-5	$(Cr,Fe)_2O_3$	3-05-3
Chromium-iron-nickel black spinel	71631-15-7	$(Ni,Fe)(Cr,Fe)_2O_4$	13-50-9
Gray			
Cobalt-nickel gray periclase	68186-89-0	$(Co,Ni)O$	6-09-8
Titanium-vanadium-antimony gray rutile	68187-00-8	$(Ti,V,Sb)O_2$	11-21-8
Tin-antimony gray cassiterite	68187-54-2	$(Sn,Sb)O_2$	11-24-8

Source: Ref 28, 30

(a) CAS, Chemical Abstract Service.

(b) DCMA, Dry Color Manufacturers' Association.

Red Pigments. Orange, red, and dark red colors are obtained only by the use of the cadmium sulfoselenide pigments (Ref 21, 31). Because cadmium compounds are highly toxic (Ref 32), the cadmium sulfoselenide pigments should not be used in applications that will come in contact with food and drink. Moreover, these pigments must also be handled with great care to avoid the possibility of ingestion.

Pink and Purple Pigments. Chrome alumina pinks (Ref 33) impart pink shades in glazes suitably formulated. The manganese alumina pink is a very pure clean pink, but it is difficult to manufacture. The most stable pink pigment is the iron-doped zircon system (Ref 34) in which the shades of color extend from pink to coral. The chrome-tin system is the only family that can produce purple and maroon shades as well as a pink shade (Ref 35).

Brown Pigments. The zinc-iron-chromite spinels (Ref 36) produce a wide palette of tan and brown shades. The other browns are variations of this system for specific applications.

Yellow Pigments. Zirconia vanadia yellows are economical pigments for use with coatings fired at >1000 °C (>1830 °F) when high tinting strength is not required (Ref 37). Tin vanadium yellows are a strong yellow color but are very costly to produce (Ref 38). The praseodymium zircon pigments have excellent tinting strength in coatings fired to as high as cone 10 (Ref 34). For lower-temperature applications, the tinting strength of the lead antimonate pigment is unsurpassed with the exception of the cadmium sulfoselenides. The rutile pigments yield yellow, orange yellow, or maple shades useful in porcelain enamels and glass enamels.

Green Pigments. Green Cr_2O_3 may be used in a few applications (Ref 39). The zinc-alumina-chromite blue-green pigments give shades from blue to blue-green when used in strong masstones. The Victoria green gives a transparent bright green color. Because of difficulties inherent in the use of chromium-containing pigments, many green ceramic glazes are now made with zircon pigments (Ref 34). Stable greens are obtained with a blend of about 2 parts of the praseodymium zircon yellow to 1 part of the vanadium zircon blue.

Blue Pigments. Cobalt blues, both the spinel ($CoAl_2O_4$) and the silicate (Co_2SiO_4) forms, are the highest tinting strength colors used in ceramics (Ref 40). At the higher firing temperatures used for ceramic glazes, they often cause a bleeding defect. At these specific temperatures, the vanadium-doped zircon blue is used (Ref 34).

Black Pigments. Black ceramic pigments are formed by mixtures of several oxides to form the spinel structure (Ref 41). The one exception is the chromium black hematite, an inexpensive pigment suitable for use in zinc-free coatings (Ref 42).

Gray Pigments. The cobalt-nickel gray periclase uses zirconia or zircon as a carrier for various ingredients of blacks such as cobalt, nickel, iron, and chromium oxides. The titanium-vanadium rutile can be used in porcelain enamels.

Pigment Application in Coatings. When selecting pigments for a specific coating application, consideration must be given to the following parameters (Ref 43):

- Processing stability requirements
- Pigment uniformity and reproducibility
- Particle size distribution
- Compatibility of all materials to be used

An engobe or body stain must be stable to the bisque fire. (*Engobe* is a slip coating applied to a ceramic body for imparting color, opacity, or other characteristics.) An underglaze color or a colored glaze must be stable to the glost fire and to corrosion by the molten glaze ingredients. An overglaze or glass enamel must only be stable to the decorating fire and to corrosion by the molten flux used in the application.

For most ceramic pigments, uniform and reproducible manufacture requires great care. To avoid specking in a blend, no component should be <10% of the mix.

Most calcined ceramic pigments are in the 1 to 10 μm (40 to 400 μin.) range in mean particle size, with no residue on a 325 mesh (44 μm) screen. The optimum particle size for an application is the largest size that gives uniform dispersion and adequate strength in opacified coatings.

A ceramic pigment must function as a component in a glaze or porcelain enamel system. Thus, it must be compatible with the other components (that is, the glaze itself, the opacifier(s), and the other additives).

Pigment Cost Factors Availability. Owing to the limited market and the variety and complexity of the products, ceramic pigments are manufactured by specialty firms and not by the users. In 1991, the cost of ceramic pigments ranged from \$9 to \$50/kg (\$4 to \$20/lb) or even higher, depending on the elemental composition and the processing required.

References cited in this section

21. R.A. Eppler and D.S. Carr, Cadmium in Glazes and Glasses, *Cadmium 81, Proceedings of the 3rd International Cadmium Conference,* International Lead and Zinc Research Organization, 1982, p 31-33
28. A. Burgyan and R.A. Eppler, Classification of Mixed-Metal-Oxide Inorganic Pigments, *Am. Ceram. Soc. Bull.,* Vol 62 (No. 9), 1983, p 1001-1003
29. R.F. Patrick, Some Factors Affecting the Opacity, Color, and Color Stability of Titania-Opacified Enamels, *J. Am. Ceram. Soc.,* Vol 34 (No. 3), 1951, p 96-102
30. *DCMA Classification and Chemical Description of the Mixed Metal Oxide Inorganic Colored Pigments,* 2nd ed., Metal Oxides and Ceramic Colors Subcommittee, Dry Color Manufacturers' Association, 1982
31. R.A. Eppler, Ceramic Colorants, *Ullmann's Encyclopedia of Industrial Chemistry,* Vol A5, VCH Publishers, Weinheim, West Germany, 1986, p 545-556
32. N.I. Sax and R.J. Lewis, Sr., *Hazardous Chemicals Desk Reference,* Van Nostrand Reinhold, 1987
33. R.L. Hawks, Chrome-Alumina Pink at Various Temperatures, *Am. Ceram. Soc. Bull.,* Vol 40 (No. 1), 1961, p 7-8
34. R.A. Eppler, Zirconia Based Colors for Ceramic Glazes, *Am. Ceram. Soc. Bull.,* Vol 56 (No. 2), 1977, p 213-215, 218, 224
35. R.A. Eppler, Lattice Parameters of Tin Sphene, *J. Am. Ceram. Soc.,* Vol 59 (No. 9-10), 1976, p 455
36. S.H. Murdock and R.A. Eppler, Zinc-Iron-Chromite Pigments, *J. Am. Ceram. Soc.,* Vol 71 (No. 4), 1988, p C212-C214
37. F.T. Booth and G.N. Peel, Preparation and Properties of Some Zirconium Stains, *Trans. J. Brit. Ceram. Soc.,* Vol 61 (No. 7), 1962, p 359-400
38. E.H. Ray, T.D. Carnahan, and R.M. Sullivan, Tin-Vanadium Yellows and Praseodymium Yellows, *Am. Ceram. Soc. Bull.,* Vol 40 (No. 1), 1961, p 13-16
39. P. Henry, Ceramic Green Colors for Whiteware Glazes, *Am. Ceram. Soc. Bull.,* Vol 40 (No. 1), 1961, p 9-10
40. R.K. Mason, Use of Cobalt Colors in Glazes, *Am. Ceram. Soc. Bull.,* Vol 40 (No. 1), 1961, p 5-6
41. R.A. Eppler, Cobalt-Free Black Pigments, *Am. Ceram. Soc. Bull.,* Vol 60 (No. 5), 1981, p 562-565
42. S.H. Murdock and R.A. Eppler, The Interaction of Ceramic Pigments with Glazes, *Am. Ceram. Soc. Bull.,* Vol 68 (No. 1), 1989, p 77-78
43. R.A. Eppler, Selecting Ceramic Pigments, *Am. Ceram. Soc. Bull.,* Vol 66 (No. 11), 1987, p 1600-1604

Surface Engineering for Chemical Activity

Michel Deeba and Jennifer S. Feeley, Engelhard Corporation

Introduction

A CATALYST is a substance that accelerates the rate of a chemical reaction toward equilibrium without becoming consumed in the process. The process is cyclic, in that an active catalytic site first forms a complex with adsorbing reactants, and then forms products that desorb, restoring the original site. Catalysts are available in many physical forms,

including particulates (tablets, microspheres, etc.), powders for slurry-phase reactions, and washcoated honeycombs or monoliths for fixed-bed reactors. The form that is selected strongly depends on the process being catalyzed.

A catalyst must be designed to have high activity and selectivity. (The *activity* of a catalyst refers to the rate at which it causes the reaction to proceed to chemical equilibrium. *Selectivity* is a measure of the extent to which a catalyst accelerates the reaction to form one or more of the desired products.)

The chemical process being catalyzed should have a high productivity within a specified reactor volume, with high reaction rates for the desired reactions and low rates for undesired reaction pathways. A catalyst also must have sufficient durability, that is, a certain lifetime will be required of it, depending on the process in which it is used. Factors that can influence durability include thermal and hydrothermal stability, resistance to poisons, and mechanical strength. Potential poisons can be either inorganic in nature (sulfur, lead, or phosphorus) or organic (carbon deposition), depending on the process. The mechanical strength of a catalyst can sometimes be determined by measuring crushing strength, attrition resistance, or thermal shock.

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Catalyst Preparation

In the past, the manufacturing of catalysts was regarded to be more of an art than a science. Successful recipes were acquired by trial and error, rather than through scientific understanding and careful process design. However, since the 1980s, the design of catalysts with specific and controlled properties has become possible.

In many catalytic processes, the number of reactant molecules that are converted to products in a given time period is directly related to the number of catalytic sites available. To increase the availability of active sites to reactants, catalytic materials are often dispersed on a highly porous, high-surface-area, thermally stable carrier. This generally stabilizes the active sites by preventing their migration and coalescence.

The most commonly used method for preparing supported metal and metal oxide catalysts involves two steps. First, it is necessary to distribute precursor compounds containing the catalytic component (metal salts, cations, or clusters) within the pore structure of the high-surface-area carriers, using impregnation, ion exchange, or precipitation. Second, the supported precursors must be transformed into catalytically active phases using one or more of these pretreatment steps: drying, calcination (heating to high temperatures in air), reduction (treating with reducing agents such as hydrogen gas or hydrazine), and sulfidation.

In some catalytic applications, nonsupported metal oxides or mixed metal oxides can be used. Generally, these catalysts are prepared by precipitation from aqueous metal salt solutions. Some processes use nonsupported metal wire gauzes. For example, platinum-rhodium alloy gauzes are used for nitric acid production by the oxidation of ammonia.

Some important commercial processes that utilize catalysts prepared by the procedures described in this article are given in Table 1. This article is intended as a very short review of the most general catalyst preparation procedures. The references should be consulted as sources of more complete information.

Table 1 Industrial processes and relevant catalysts

Application	**Reaction**	**Active catalytic component**
Chemicals		
Steam reforming (H_2 production)	$CH_4 + H_2O \rightarrow 3H_2 + CO$	Ni/Al_2O_3 (pellet)
Methanol synthesis	$2H_2 + CO \rightarrow CH_3OH$	Cu, ZnO/Al_2O_3 (pellet)

Ammonia synthesis	$3H_2 + N_2 \rightarrow 2NH_3$	Bulk Fe (pellet)
Hydrogenation	(1) Fats and oils + H_2 $\rightarrow$ hydrogenated products	Ni/Al_2O_3 (powder)
	(2) Organic functional groups + H_2 $\rightarrow$ hydrogenated products	Pd or Pt/carbon (powder)
		$CuO\text{-}Cr_2O_3$ (powder)
Polyethylene synthesis	$CH_2{=}CH_2 \rightarrow CH_3(CH_2)_nCH_3$	Cr_2O_3/SiO_2 (powder)
Nitric acid synthesis	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	PtRh gauze
Sulfuric acid production	$SO_2 + O_2 \rightarrow SO_3$ H 2 O H_2SO_4	V_2O_5/SiO_2 (pellet)
Environmental processes: catalysts on monoliths		
Three-way catalyst automotive catalyst	CO + hydrocarbons + NO $\rightarrow CO_2 + H_2O + N_2$	Pt, Rh, $Pd/Al_2O_3/Ce$
Volatile organic compound destruction	Hydrocarbons + $O_2 \rightarrow CO_2 + H_2O$	Pt/Al_2O_3
Selective catalytic reduction of NO_x	$NH_3 + NO_x\ O_2N_2 + 3/2H_2O$	V_2O_5/TiO_2
Ozone abatement	$2O_3 \rightarrow 3O_2$	Pd/Al_2O_3
Petroleum processes		
Fluid catalytic cracking to produce gasoline	High- $\rightarrow$ low-molecular-weight hydrocarbon (C_5-C_{13})	Acidic *Y* zeolite in
		SiO_2/Al_2O_3 matrix (microspheres)
Catalytic reforming to produce high-octane gasoline	(1) Dehydrogenation	Pt, PtRe, or PtSn on acidified Al_2O_3 (pellet)
	(2)Isomerization	
	(3)Aromization	
Methanol to gasoline process	$CH_3OH \rightarrow$ aromatics	ZSM-5 zeolite (pellet)
Paraffin isomerization	Linear $\rightarrow$ branched hydrocarbons	Pt/H mordenite in alumina matrix (pellet)

Impregnation is one of the simplest ways to prepare a supported metal or metal oxide catalyst. A porous carrier with a high internal surface area, such as alumina, silica, and titania, is contacted with an impregnating solution, usually aqueous, of one or more metallic salts or compounds.

The carrier and the impregnated metal compound are then dried and subjected to further pretreatments, such as calcination and/or reduction before use. Drying at approximately 100 °C (210 °F) in air, followed by calcination to higher temperatures, is a common method used to decompose metal salts and to fix active metal oxide components on carriers. For example, silica can be impregnated with an ammonium metavanadate solution, and then dried and calcined to give a catalyst (vanadium pentoxide supported on silica) that is similar to the product used commercially in sulfuric acid production.

Incipient Wetness Impregnation. In this method, impregnating solution is used in a sufficient volume to completely fill the pores of the carrier, without excess solution. This allows the precursor to disperse evenly within the pore structure of the carrier.

In some cases, the active component can be precipitated onto the carrier by adjusting the pH of the impregnating solution. This will immobilize, or fix, the active material on the carrier. For example, it is common to treat noble metals (platinum, palladium, rhodium, etc.) on carriers with hydrazine, in order to reduce the metal, or with acids or bases, in order to neutralize the impregnating solution (i.e., the addition of ammonium hydroxide to a H_2PdCl_4 impregnating solution) and precipitate the metal oxide to obtain dispersions. This step is carried out after impregnation, but before drying and further processing.

Impregnation by Precipitation. One modification of the standard impregnation method is achieved by suspending the carrier material (powder or particulate) in a solution of the catalytic precursor materials. The catalytic material is then slowly precipitated onto the carrier by adjusting the pH of the liquid impregnating solution. The resulting catalyst is collected by filtration. Metal oxides supported on zeolites, such as CuO/ZSM-5, can be prepared using this method.

Eggshell Impregnation. Some catalytic reactions are conducted under conditions in which only the exterior of the catalyst particle contains the active component. Thus, the interior of the catalyst particle is inactive, and all of the reaction occurs on its exterior. This procedure is sometimes used to reduce the formation of byproducts and unwanted side reactions that can occur in a pore diffusion controlled reaction. It is also used to prepare catalysts containing expensive noble metals in order to increase the effectiveness per unit of noble metal.

In this process, a carrier, usually particulate, is coated with a thin layer of up to 200 μm (8 mils) of catalytic material. The procedure involves placing the carrier in a rotating drum along with the catalytic material. The degree to which the active component penetrates the carrier can sometimes be controlled by either adjusting the pH of the solution or varying the quantity of alkali metals present on the surface of the carrier. This technique has the advantage of producing catalysts with shallow metal concentration profiles near the surface of the catalyst particles, which decreases pore-diffusion resistance.

Ion exchange is a very effective method for dispersing metals, oxides, and cations on carriers. However, only carriers that have cation-exchange capacities can be used. The ion-exchange procedure is often used to prepare metal supported on aluminas and molecular sieves (i.e., zeolites, metallosilicates, etc.). Metal-loaded zeolite catalysts are easy to prepare using this technique because of their unusually high cation-exchange capacity. Catalysts prepared by this procedure initially result in highly dispersed metal cations. Reduction can lead to highly dispersed metal particles. Further oxidation results in highly dispersed oxide phases.

To carry out the exchange procedure, the carrier must possess negatively charged ions to which exchangeable cations are bonded. The cation initially bonded to the surface (H^+, NH_4^+, Na^+) is ion exchanged with the desired cation, maintaining electrical neutrality during the procedure. The exchange is carried out by mixing the carrier with the desired cation salt in a dilute aqueous solution for 1 to 24 h at temperatures up to 100 °C (210 °F). The exchanged carrier is then collected by filtration and washed with excess water before further processing.

Sometimes, a single ion-exchange procedure is not sufficient to obtain the desired level of metal loading. Multiple ion-exchange procedures with optional drying and calcining steps in between can then be conducted.

Precipitation. Amorphous and crystalline metal oxide and mixed metal oxide catalysts can be prepared using a variety of precipitation techniques. Examples of these unsupported oxide catalysts include coprecipitated $NiO \cdot Al_2O_3$ for steam

reforming to produce hydrogen, $CuO \cdot ZnO \cdot Al_2O_3$ for methanol synthesis, and $SiO_2 \cdot Al_2O_3$ for fluid catalytic cracking (FCC) of heavy oils to lower-molecular-weight fuels.

In a typical procedure, an aqueous solution of one or more metal salts contacts a basic solution, such as an aqueous alkali, ammonium hydroxide, or ammonium carbonate, to cause the precipitation of insoluble metal hydroxides or carbonates. The catalyst is then collected by filtration and washed repeatedly, prior to drying. Catalysts prepared by this method are often calcined at temperatures that exceed 300 °C (570 °F) after drying in order to decompose metal oxide precursors, such as hydroxides, and form the desired oxides. Temperatures that are even higher are used to form crystalline mixed oxides, such as perovskites or spinels. Catalysts that are prepared using these procedures sometimes need to be crushed into powder form prior to use, as in slurry-phase processes.

The precipitation method used to prepare metal oxide catalysts is also used to prepare some standard catalyst carrier materials, such as Al_2O_3, TiO_2, and SiO_2. Their preparation is discussed in detail below.

Preparation of Common Carriers Used in Supported Catalysts

Catalyst carriers are usually high-surface-area inorganic materials with complex pore structures, into which catalytic materials such as palladium, platinum, cobalt, chromium oxide, and vanadium pentoxide are deposited using the methods described above. At one time, it was thought that catalyst carriers only served to provide inert high surface areas with suitable strength and durability, on which catalytic substances could be dispersed, thus maximizing the number of active sites. However, it is now widely recognized that the carrier often plays a critical role in the performance of the catalyst, in terms of activity, selectivity, and durability.

The selection of the appropriate carrier is the first and most important step in designing a supported metal or metal oxide catalyst. Parameters such as surface area, porosity, thermal stability, acidity, and the inherent activity of the carrier itself are all critical to the carrier selection process. Because reactants and product must diffuse within the carrier, the size of its pores is critical for optimum transport. Carrier materials can be categorized as:

- Active carriers, such as alumina, silica-alumina, zeolites, titanium oxide, and carbon in powder or particulate form
- Inert carriers, such as silica, in powder or particulate form
- Structural supports, such as the monoliths upon which catalyzed carriers are deposited

The most important catalyst supports for experimental and industrial use are high-surface-area inorganic oxides and carbon. Their characteristics and preparations are described briefly below. Structural supports are described in the section "Catalyst Powder Processing" in this article.

Alumina (Al_2O_3) is one of the most important commercial carrier materials used in industrial applications. It is a component of many environmental catalysts, including automobile catalytic converters and catalysts for the oxidation of volatile organic compounds. It is also used in petroleum catalysts, for hydrodesulfurization and reforming, and in chemical catalysts, for hydrogenation, isomerization, and oxidation reactions.

Aluminas with high surface areas (100-600 m^2/g, or 2-14 ft^2/lb) are generally prepared by the thermal decomposition of well-crystallized hydroxides or precipitated colloidal gels. The high surface area of alumina is due to a network of $Al(OH)_x$ species (particles of 2 to 5 nm, or 0.08 to 0.2 μin.) bonded together to form polymer-type chains. Precipitation can be performed by the acidification of aluminate, the neutralization of aluminum salts, or the hydrolysis of alcoholate.

The phase of alumina that is formed strongly depends on the pH used in the precipitation step and the thermal history of the resulting solid support. For example, precipitation at a pH of 11, followed by drying, forms aluminum trihydrate, known as Bayerit, whereas precipitation at a pH of 9, followed by drying, forms pseudo-Boehmit, the monohydrate crystal (AlO·OH). The gamma phase of alumina, obtained by calcining at 350 to 600 °C (660 to 1110 °F), is the most widely used. Treatment at temperatures above approximately 800 °C (1470 °F) results in the conversion to lower-surface-area phases of alumina.

Silica (SiO_2). The preparation of different silicas has been reviewed in great detail in the literature (Ref 1). Silica is often used in polymerization catalysts, such as 0.1% chromium oxide impregnated on silica, for the formation of polyethylene.

Most silicas used in catalysis are synthetic. Preparation conditions have a dramatic influence on the properties of the silica that is formed. Variations of pH, rate of precipitation, aging of the precipitate, and drying and calcination conditions can lead to silicas with controlled porosities and surface areas.

Silica gel can be prepared by the polymerization of silicic acid or the aggregation of colloidal silica. Alkaline solutions of silicates (pH of 12) can be neutralized with acid, resulting in the formation of polymeric silicic acid, which precipitates as a hydrogel. When chains of silicic acid polymerize, they form a high-surface-area network with interconnecting pores of varying sizes. After controlled drying and calcination, silicas with high surface areas (200 to 600 m^2/g, or 5 to 14 ft^2/lb) can be obtained.

Zeolites are highly crystalline silicoaluminates with well-defined pore structures comprising tetrahedral silicon and aluminum oxide units. They have pore diameters of 0.3 to 1.0 nm (0.01 to 0.04 in.) and surface areas of 300 to 700 m^2/g (7 to 17 ft^2/lb), both of which primarily depend on the type of zeolite. Zeolites have a three-dimensional framework structure with this empirical formula:

$$M_{x/n}^{+n}\ [(AlO_2)_x\ (SiO_2)_y]\cdot wH_2O$$

where *w* is the number of water molecules associated with the zeolite and the bracketed term is the zeolite framework and the crystallographic unit cell. The cation *M* with valence *n* is present to balance the negative charge on the lattice created by the substitution of Si^{+4} by Al^{+3} in the framework structure. Silicon/aluminum ratios vary with the type of zeolite and the preparation conditions.

Zeolites are generally synthesized by a hydrothermal process. Sodium hydroxide is commonly added to sodium silicate and sodium aluminate, causing gelation to occur (Ref 2). The freshly coprecipitated silica/alumina gel is allowed to age at 25 to 200 °C (75 to 390 °F) to cause crystallization. The zeolite is collected by filtration, and then washed, dried, and calcined. The conditions of aging (temperature and pressure), pH, and silicon/aluminum ratio are some of the important factors determining the type of zeolite that is prepared.

Zeolites are of great interest catalytically, primarily because of their high activity and unusual selectivity in a variety of acid-catalyzed reactions. They are also interesting as catalyst carriers for metals, metal cations, and oxides. They are used in the petroleum industry in fluid catalytic cracking (acidic *Y* zeolite) and isomerization catalysts (platinum/mordenite), and for the methanol-to-gasoline process (ZSM-5). Most important, catalytically, are the zeolites from the faujasite group (*X* and *Y* zeolite), as well as chabazite, erionite, offretite, mordenite, and the pentasil zeolites ZSM-5 and ZSM-11.

Titanium oxide (TiO_2), or titania, is currently used as a catalyst carrier for the selective catalytic reduction of nitrogen oxide (NO_x, or NO + NO_2) using ammonia in stationary source applications. It has two crystal structures, anatase and rutile. The anatase form is more important catalytically, because of its high surface area (25 to 100 m^2/g, or 0.06 to 2 ft^2/lb). The rutile structure has a much lower surface area (<10 m^2/g, or 0.2 ft^2/lb). Titania in the anatase form is prepared by precipitation from boiling titanium (IV) sulfate solution. The rutile form can be prepared directly from the precipitation of a chloride solution or by calcination of the anatase phase at 600 °C (1110 °F) for several hours.

Carbon exists in several morphological forms, such as charcoals, carbon blacks, graphite, and molecular sieve structures. Many carbons occur naturally from wood, peat, nuts, shells, and other organic matter. Charcoal, known for its adsorptive properties, is prepared by the pyrolysis of organic polymers. Charcoals are highly porous with surface areas of approximately 1000 m^2/g (25 ft^2/lb). Carbon blacks are prepared by the controlled pyrolysis of hydrocarbons. The nature of the precursor hydrocarbon and the pyrolysis conditions determine the surface area, pore structure, and surface chemistry of the carbon black.

Carbon carriers have been used extensively for precious metals, transition metals, and alkali and alkaline earth metals. Carbon-supported catalysts (platinum, palladium, and nickel on carbon) are used in a variety of catalytic processes, such as alkylation, hydroalkylation, and hydrogenation.

Other inorganic oxides that are sometimes, but not commonly, used as catalyst carriers include zirconia, rare-earth oxides, alkaline earth oxides, chromia, niobia, tin oxide, and zinc oxide. These are often prepared simply by precipitation of the corresponding metal salts (nitrates or sulfates), followed by washing and calcination. Zirconia can be prepared with a fairly high surface area (approximately 150 m^2/g, or 5 ft^2/lb), and therefore is finding use in more catalyst applications.

Many of the mixed metal oxide catalysts described in the section "Precipitation" can also serve as potential catalyst support materials.

References cited in this section

1. R.K. Iler, *Chemistry of Silica,* John Wiley and Sons, 1979

2. D.W. Breck, *Zeolites Molecular Sieves, Structure, Chemistry, and Uses,* John Wiley & Sons, 1974, p 245

Catalyst Powder Processing

The form of the catalyst used for a specific reaction depends on the type of reactor being used. Powder catalysts are usually used for slurry-phase processes, whereas tablets or extruded catalysts are used in fixed-bed reactors, and microsphere catalysts (50 to 120 μm, or 2 to 5 mils) are used in fluidized bed reactors. Catalyzed honeycombs or monoliths are used in numerous environmental applications. Therefore, catalyst powders are often converted into a suitable form (particulates or washcoats for honeycombs) for a specific reactor design. In general, powder processing techniques are made easier by using powders having well-defined particle sizes in order to yield catalyst products that are homogeneous and have attrition resistance.

In the tableting process, the powder is firmly pressed into a die and shaped into small cylinders, rings, or beads. Powders composed of deformable particles acquire reasonable cohesion upon tableting. Plastifying agents (talc, graphite, stearic acid, etc.) are sometimes added to powders to prevent them from sticking to the sides of dies and stamps.

In the beading or granulation process, individual particles of different sizes are rotated under a spray of liquid to form larger, more homogeneously sized particles. The operation is done in a horizontal rotating cylinder or pan with a rotation axis of approximately 45° inclined. The particles roll over one another to give almost perfectly spherical particles (0.5 to 20 mm, or 0.02 to 0.8 in.).

In the paste extrusion process, catalyst powders are converted into a paste that is used to form larger particles. The paste is moved through a drilled plate and made into cylinders with diameters of 1 to 10 mm (0.04 to 0.4 in.). The paste must have enough plasticity to give granules with sufficient cohesion. The rheological properties of the paste can be adapted by adding volatile materials (acids, stearates, methyl cellulose, or polymers) or other materials that will not influence the activity of the catalyst (colloidal alumina, silica, clays, etc.).

Spray drying, a simultaneous drying and shaping procedure, is a widely used technique to produce spherical materials. A suspension or slurry that contains about 20 to 60% solids is sprayed in hot gases (100 to 400 °C, or 210 to 750 °F). The tiny drops that form are dried very quickly, which results in almost perfectly shaped microspheres. This process is used to make catalysts for fluid catalytic cracking (FCC). The average life of an FCC catalyst during use is about 6 mo, during which it experiences temperatures as high as 750 °C (1380 °F). Therefore, a highly attrition resistant and thermally stable catalyst is necessary. Several binders have been developed that can be added to the slurry to substantially increase the hardness of FCC microspheres.

Catalyzed honeycomb or monolith structures with parallel channels are utilized in high-flow-rate processes where pressure drops must be minimized. They have been used in numerous environmental applications, including automobile catalytic converters and abatement systems for volatile organic compounds and selective catalytic reduction. In general, honeycombs provide good mechanical strength and resistance to thermal shock. However, because they have low surface areas, a catalyzed carrier (washcoat) must be deposited on their channels. The most widely used monolith is made from cordierite ($2MgO\cdot 2Al_2O_3\cdot 5SiO_2$). Some metallic materials also are being used.

The finished catalyst is prepared by dipping the honeycomb into an aqueous slurry containing catalyzed carriers that will adhere to the walls of each channel. Excess slurry is then blown from the channels to avoid plugging. The washcoated honeycomb is then dried and calcined (300 to 600 °C, or 570 to 1110 °F) to fix the catalyzed washcoat securely to the honeycomb walls and to decompose precursor compounds (Fig. 1).

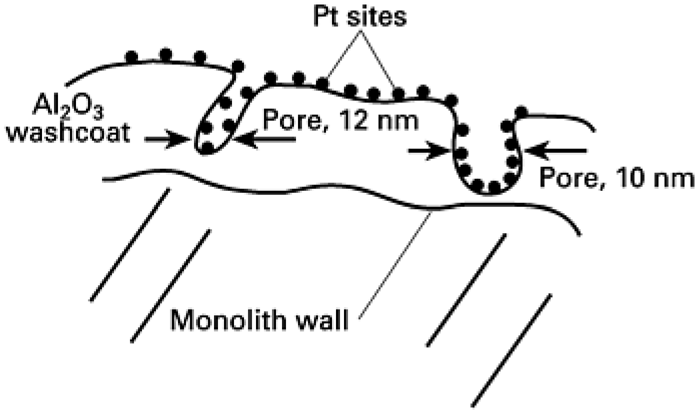

Fig. 1 Impregnated catalyst washcoated on a substrate honeycomb

The rheology of the catalyst slurry is determined by its solids content (25 to 60%), the pH, and the particle size of the catalyst (preferably, 10 to 25 μm, or 0.4 to 1 mil). Sometimes the addition of binders, such as alumina or silica sols, is required to improve adhesion onto the monolithic support. The honeycomb has some porosity, which ensures adhesion of the catalyzed washcoat.

Protective Coatings for Carbon-Carbon Composites

James R. Strife, United Technologies Research Center; James E. Sheehan, MSNW, Inc.

Introduction

CARBON-CARBON is a unique composite material in which a nonstructural carbonaceous matrix is reinforced by carbon fibers to create a heat-resistant structural material. The carbon fibers are generally employed as woven fabric in two-dimensional laminates, or as multidimensional preforms created by textile processing of multifilament tows (Ref 1, 2). Composite densification is typically accomplished using phenolic resins in a preforming process, followed by liquid impregnation, vapor phase carbon infiltration, or combinations of the two to achieve pore filling (Ref 3, 4, 5, 6, 7, 8, 9, 10). High-temperature pyrolysis is used to convert liquid impregnants to carbon while vapor phase infiltration is conducted in reduced-pressure reactors where flowing hydrocarbon gas infiltrates the composite and is thermally decomposed to deposit carbon. The result is a low-density (1.5 to 1.9 gm/cm^3) composite that derives its mechanical performance from the carbon fiber reinforcement.

Because carbon fibers tend to increase in strength with increasing temperature (Ref 11), carbon-carbon composites retain their tensile strength at extreme temperatures. Carbon-carbon composites provide unmatched specific stiffness and strength at temperatures from 1200 to 2200 °C (2192 to 3992 °F). At temperatures below 1000 °C (1832 °F), carbon-carbon composites exhibit specific strength equivalent to that of the most advanced superalloys (Ref 12). As a result of their carbon constituents and weakly bonded reinforced matrix, carbon-carbon composites also have superior thermal shock, toughness, ablation, and high-speed friction properties. These properties have led engineers to apply carbon-carbon in reentry bodies, rocket nozzles, and exit cones for strategic missiles, and in brake discs for military aircraft (Ref 8, 9, 10, 13). Recently a commercial aerospace application, brake discs for transport aircraft, has become prominent (Ref 14).

Coating technology for carbon-carbon has been driven primarily by the aerospace and defense industries, in applications where the composite is exposed to high-temperature oxidizing environments. Advanced applications include hot-section components for limited-life missile engines, exhaust components for fighter aircraft, hypersonic vehicle fuselage and wing components, and structures for space defense satellites (Ref 13). The most notable application of coated carbon-carbon is for the nose cap and wing leading edges of the Shuttle Orbiter vehicle (Ref 15, 16, 17). Over 40 successful missions have been flown, demonstrating the flight worthiness of coated carbon-carbon in reentry applications.

References

1. L.E. McAllister and W.L. Lachman, in *Handbook of Composites,* A. Kelly and S.T. Mileiko, Ed., North-Holland, 1983, p 111
2. F.K. Ko, in *Carbon-Carbon Materials and Composites,* J.D. Buckley and D.D. Edie, Ed., Noyes, 1993, p 71
3. H.O. Pierson and M.L. Lieberman, in *Carbon,* Vol 13, 1975, p 159
4. J.H. Cranmer, I.G. Plotzker, L.H. Peebles, and D.R. Uhlmann, in *Carbon,* Vol 21, 1983, p 201
5. M.A. Forrest and H. Marsh, in *J. Mater. Sci.,* Vol 18, 1983, p 973
6. G.S. Rellick, D.J. Chang, and R.J. Zaldivar, in *J. Mater. Res.,* Vol 7, 1992, p 2798
7. N. Murdie, C.P. Ju, J. Don, and M.A. Wright, in *Carbon-Carbon Materials and Composites,* J.D. Buckley and D.D. Edie, Ed., Noyes, 1993, p 105
8. E. Fitzer, A. Gkogkidis, and M. Heine, in *High Temp.-High Press.,* Vol 16, 1984, p 363
9. E. Fitzer and A. Gkogkisdis, in *Petroleum-Derived Carbons,* J.D. Bacha, J.W. Newman, and J.L. White, Ed., American Chemical Society, 1986, p 346
10. R.L. Burns, in *Carbon-Carbon Materials and Composites,* J.D. Buckley and D.D. Edie, Ed., Noyes, 1993, p 197
11. C.R. Rowe and D.L. Lowe, in *Extended Abstracts of the 13th Biennial Conference on Carbon,* American Carbon Society, July 1977, p 170
12. J.R. Strife and J.E. Sheehan, in *Ceramic Bulletin,* Vol 67 (No. 2), 1988, p 369
13. L. Rubin, in *Carbon-Carbon Materials and Composites,* J.D. Buckley and D.D. Edie, Ed., Noyes, 1993, p 267
14. S. Awasthi and J.L. Wood, in *Adv. Ceram. Mater.,* Vol 3, 1988, p 449
15. H.G. Maahs, C.W. Ohlhorst, D.M. Barrett, P.O. Ransone, and J.W. Sawyer, in *Materials Stability and Environmental Degradation,* MRS Symp. Proc., Vol 125, A. Barkatt, E.D. Verink, and L.R. Smith, Ed., Materials Research Society, 1988, p 15
16. R.C. Dickinson, in *Materials Stability and Environmental Degradation,* MRS Symp. Proc., Vol 125, A. Barkatt, E.D. Verink, and L.R. Smith, Ed., Materials Research Society, 1988, p 3
17. D.M. Curry, E.H. Yuen, D.C. Chao, and C.N. Webster, in *Damage and Oxidation Protection in High Temperature Composites,* Vol 1, G.K. Haritos and O.O. Ochoa, Ed., ASME, 1991, p 47

Fundamentals of Protecting Carbon-Carbon

Historical Development of Protecting Carbon Bodies. Many of the constituents and approaches for protecting carbon-carbon have grown from early research work aimed at protecting synthetic graphite bodies. Sixty years ago, a patent was issued to the National Carbon Co. (Ref 18) for a coating method to render carbon articles oxidation resistant at high temperatures. Coating systems composed of an inner layer of SiC and outer glazes based on B_2O_3, P_2O_5, and SiO_2 were described. This work demonstrated the utility of glassy materials as coating constituents to enhance oxidation resistance. Work on JTA graphite for reentry applications (Ref 19, 20, 21) was particularly significant. In these materials, refractory compounds containing boron, silicon, zirconium, and hafnium were used as additions to impart oxidation resistance. Oxidation resulted in formation of a borate glass coating that was protective for several hours up to 1700 °C (3092 °F). Enhancement of oxidation resistance through additions of boron to the body of carbon materials was an important contribution of this work.

The investigation by Chown and coworkers of refractory carbides for protecting graphite (Ref 22) was an important early contribution to coating technology. Their results showed that chemical vapor deposition (CVD) of SiC could provide reliable protection for long periods of time at temperatures below 1700 °C (3092 °F). Experiments with a variety of refractory carbides and boride coatings formed by reaction sintering demonstrated that protection for short times up to 2200 °C (3992 °F) could be achieved with sintered ZrC and ZrB_2 coatings.

Coatings based on the use of iridium (Ref 23, 24) were investigated in the 1960s to protect graphite up to temperatures as high as 2100 °C (3812 °F). This concept relied on the very low carbon diffusivity and oxygen permeability of iridium as a solid oxygen barrier. While some success was achieved, significant problems associated with volatile oxide formation, adherence, and the high thermal expansion of iridium limited the usefulness of this technology.

Carbon-carbon was thrust into the forefront as a high-temperature materials research topic by the requirement for a reusable, lightweight thermal protection system for the Shuttle Orbiter (Ref 25, 26, 27, 28). The oxidation-protected carbon-carbon presently used for the shuttle nose cap and wing leading edge is based on a substrate containing low-strength, low-elastic-modulus rayon precursor fibers. The coating system is composed of a SiC coating, formed by conversion of the carbon-carbon in a pack process, and an outer silicate glaze coating filled with SiC powder (Ref 25, 26, 27). The process also involves sealing cracks in the coating system with silicon ethoxide (Ref 28). The SiC conversion layer is over 1 mm (0.025 in.) thick.

Throughout the 1980s, a significant level of research activity focused on the protection of high-performance carbon-carbon that used heat-stabilized polyacrylonitrile (PAN) or pitch-based fibers. These composites have higher strength, higher elastic moduli, and lower thermal expansion coefficients than the rayon-based materials. Applications have focused on using high-performance carbon-carbon in structural-weight-critical roles requiring substrates and coatings of minimum thickness. For example, coating thicknesses normally are targeted to be 0.2 to 0.4 mm (0.005 to 0.010 in.). These physical factors, coupled with the significant increase in coating-substrate thermal mismatch stresses, have proved to be significant barriers to acceptable performance and broader use of carbon-carbon composites.

Carbon-Carbon Constituents and Microstructure. Applications requiring coatings typically use carbon fibers in laminated woven cloth or three-dimensional woven reinforcements. The fibers used are derived from rayon, PAN, or petroleum pitch and have a wide range of properties. For example, the elastic modulus along the fiber axis ranges from approximately 41.4 GPa (6 Msi) for rayon fibers to 414 GPa (60 Msi) for heat-stabilized PAN to 690 GPa (100 Msi) for pitch fibers. The axial fiber expansion coefficients become lower as the fiber modulus increases.

The characteristics of the matrix vary, depending on the method of densification. Generally, the matrix microstructure spans a range from being glasslike, with small, randomly oriented crystallites of turbostratic carbon, to having strongly oriented and highly graphitized large crystallites. Weak interfaces usually exist between the fibers and matrix, because strong covalent atomic bonding prevents the carbon constituents from sintering, even at very high temperatures. Because the mechanical properties of the matrix are substantially inferior to those of the fibers, the fibers generally control the mechanical performance and expansion characteristics of the composites. A rayon-fabric-reinforced laminated construction typically exhibits the following in-plane properties: a tensile strength of 51.7 MPa (7.5 ksi), a tensile elastic modulus of 13.8 GPa (2 Msi), and a thermal expansion coefficient of 2.4×10^{-6} °C^{-1} (1.3×10^{-6} °F^{-1}). Laminated constructions that have high-performance fibers exhibit the following typical in-plane properties: a tensile strength of 276 MPa (40 ksi), a tensile elastic modulus of 90 GPa (13 Msi), and a thermal expansion coefficient of 1.4×10^{-6} °C^{-1} (0.8×10^{-6} °F^{-1}).

Matrix Inhibition. Carbon begins to oxidize at measurable rates at approximately 371 °C (700 °F). Carbon-carbon composites exhibit high internal surface areas due to the porous nature of the structure (typical levels of interconnected porosity are 10 to 15%). Adding inhibitor phases to the matrix has become an important facet of an overall oxidation protection system, because inhibitors allow some control of oxidation that can occur through defects in coatings. Inhibitors can also prevent catastrophic oxidation failure due to coating spallation at high temperatures.

Additions of boron, boron compounds, and phosphorus compounds have been effective in protecting carbon bodies (Ref 29, 30, 31, 32, 33, 34) by true chemical inhibition and formation of internal and external glass layers that act as diffusion barriers. The practice of making boron additions to carbon-carbon for improved oxidation resistance was first disclosed in a 1978 patent (Ref 35). Since that time, many improvements and variations on this theme have been reported (Ref 36, 37, 38, 39, 40, 41, 42, 43, 44, 45).

Internal chemical modifications can be made either by mixing the carbonaceous and nonoxide inhibitor powders and consolidating the constituents to form the carbon body, or by impregnating the porous body with liquids that contain the inhibitors, usually in oxide form. Boron and many nonoxide boron compounds are quite refractory, so the powder mixing and carbon processing route has often been used (Ref 32, 33, 34). In composite fabrication, submicron refractory compound additives are normally carried within impregnating resins and are dispersed through the fiber tows as well as between the fabric plies.

Coating Selection Principles. The most critical component of any coating architecture is the primary oxygen barrier. The oxygen barrier prevents oxygen ingress to the underlying composite by providing a physical permeation barrier and, in some cases, by gettering oxygen in the process. The critical parameters that guide the selection of the oxygen barrier are its oxidation characteristics, thermal expansion coefficient, and inherent oxygen permeability. A material that forms an adherent, low-permeability oxide scale is preferred as an oxygen barrier because it oxidizes slowly and has the potential to self-heal. An Arrenius plot of rate constants for oxidation of refractory materials typically considered for

coating applications (Ref 46, 47) is presented in Fig. 1. Scale growth as a function of time can be estimated from Fig. 1 using the relationship $x^2 = Kt$, where x is the scale thickness, K is the parabolic rate constant, and t is time in hours. The silicon-base ceramics exhibit substantially lower oxide growth kinetics than the aluminum-, hafnium-, or zirconium-base ceramics. Time and temperature of service will dictate material selection and coating thickness. However, from the standpoint of forming thin protective scales in thermal cycles with peak temperatures in the range of 1400 to 1700 °C (2552 to 3092 °F), only Si_3N_4 and SiC exhibit sufficiently low rate constants for oxide growth over extended time periods.

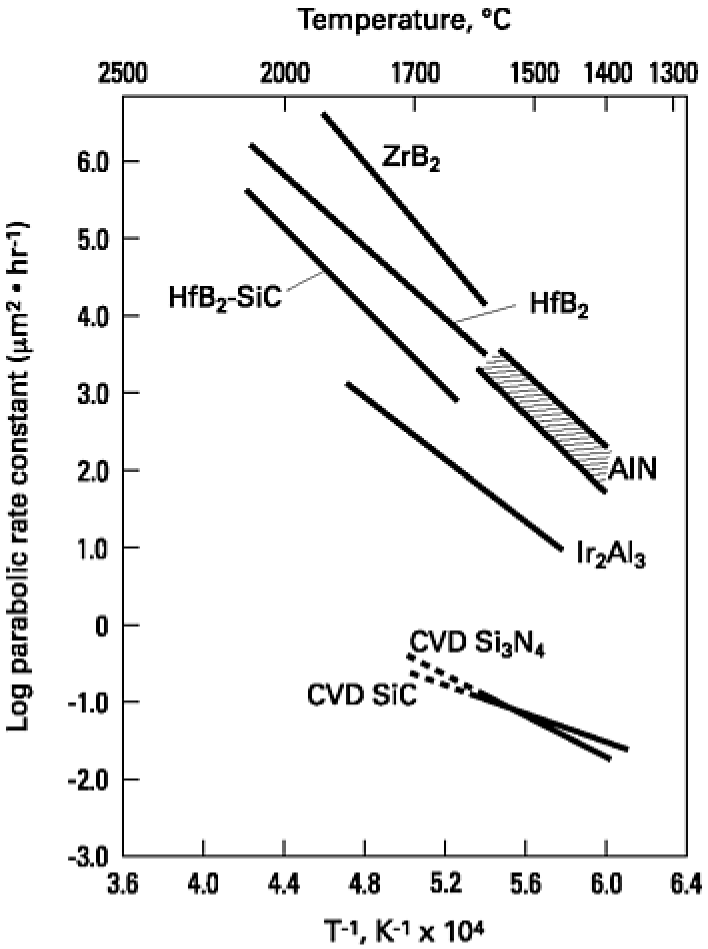

Fig. 1 Oxidation kinetics of refractory materials. CVD, chemical vapor deposition

Figure 2 compares the thermal expansion behavior of refractory coating candidates with that measured for high-performance, fabric-reinforced carbon-carbon (Ref 12, 46, 47). The expansion of carbon-carbon in the in-plane directions is substantially lower than for any of the refractory ceramics. This expansion difference, coupled with the high modulus of the refractory materials, results in significant thermal mismatch stresses when they are employed as coatings. An estimate of the thermal mismatch stresses when the coating thickness is small relative to the carbon-carbon substrate thickness can be calculated using the relationship

$$s_c = \frac{E(a_{c-}a_s)\Delta T}{1-v}$$

where σ_c is the stress in the coating, E is the coating elastic modulus, u is the Poisson ratio of the coating, α_s is the thermal expansion coefficient of carbon-carbon, α_c is the thermal expansion coefficient of the coating, and ΔT is the difference between the deposition temperature and the selected temperature for stress calculation.

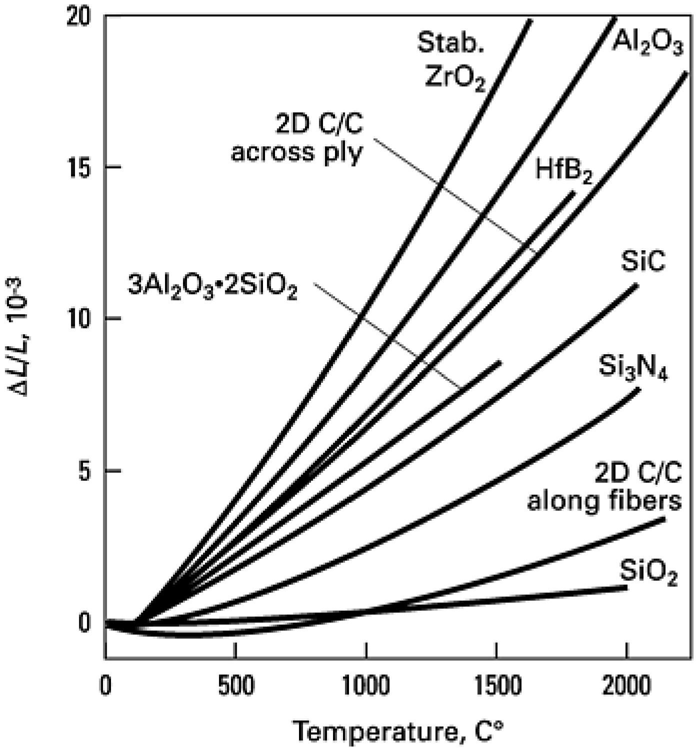

Fig. 2 Thermal expansion characteristics of ceramics and carbon-carbon laminates. C/C, carbon-carbon laminate; *L,* specimen length

The properties of refractory materials that have been used in deposition studies are summarized in Table 1. Figure 3 presents the thermal stresses calculated as a function of temperature when these coatings were deposited onto high-performance two-dimensional carbon-carbon laminates. For the refractory ceramics, silicon nitride provides the lowest thermal mismatch stresses of any of the ceramic coating candidates. These stresses are still high enough to cause cracking, however. Therefore, it is usually found that deposited ceramic coatings exhibit microcracking and that the crack pattern depends on the coating thickness and deposition temperature. Iridium metal deposited by electron-beam physical vapor deposition techniques can have low thermal mismatch stresses upon cooling. However, such a coating must then be able to withstand extremely high compressive stresses upon heating. In previously reported work (Ref 47), it has been shown that iridium-base coatings deposited by this technique onto high-performance carbon-carbon fail by compressive spalling at elevated temperatures.

Table 1 Properties of refractory materials deposited on carbon-carbon composites

Materials	Deposition process	Deposition temperature, °C	Bulk properties		
			Modulus Msi	Poisson's ratio	CTE (20-1900 °C), ppm/°C
SiC	CVD	1050	65	0.19	5.2
TiC	CVD	1000	65	0.19	9.5

AlN	CVD	1250	50	0.3	6.1
Si_3N_4	CVD	1420	46	0.3	3.6
Ir	Sputtering	250	76	0.3	7.9
HfO_2	EBPVD	1000	20	0.25	10.6

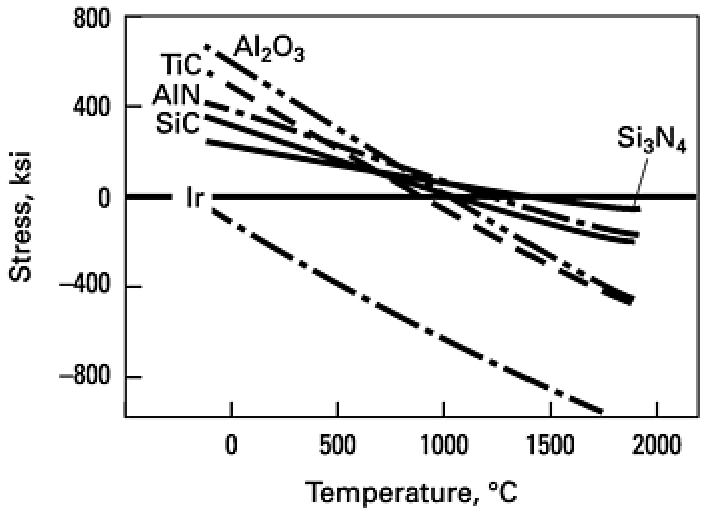

Fig. 3 Calculated thermal stresses for thin coatings on high-performance carbon-carbon laminates. Ratio of substrate thickness to coating thickness = 20

References cited in this section

12. J.R. Strife and J.E. Sheehan, in *Ceramic Bulletin,* Vol 67 (No. 2), 1988, p 369
18. H.V. Johnson, "Oxidation Resisting Carbon Article," U.S. Patent 1,948,382, 20 Feb 1934
19. K.J. Zeitsch, in *Modern Ceramics,* J.E. Hove and W.C. Riley, Ed., John Wiley, 1967, p 314
20. S.A. Bortz, in *Ceramics in Severe Environments,* W.W. Kriegel and H. Palmour, Ed., Plenum, 1971, p 49
21. E.M. Goldstein, E.W. Carter, and S. Klutz, in *Carbon,* Vol 4, 1966, p 273
22. J. Chown, R.F. Deacon, N. Singer, and A.E.S. White, in *Special Ceramics,* P. Popper, Ed., Academic Press, 1963, p 81
23. J.M. Criscione, R.A. Mercuri, E.P. Schram, A.W. Smith, and H.F. Volk, "High Temperature Protective Coatings for Graphite," ML-TDR-64-173, Part II, Materials Laboratory, Wright-Patterson Air Force Base, Oct 1974
24. *High Temperature Oxidation Resistant Coatings,* National Academy of Sciences and Engineering, 1970, p 112
25. D.C. Rogers, D.M. Shuford, and J.I. Mueller, in *Proceedings of the Seventh National SAMPE Technical Conference,* Society of Aerospace Material and Process Engineers, 1975, p 319
26. D.C. Rogers, R.O. Scott, and D.M. Shuford, in *Proceedings of the Eighth National SAMPE Technical Conference,* Society of Aerospace Material and Process Engineers, 1976, p 308
27. Surface Seal for Carbon Parts, *NASA Technical Briefs,* Vol 6 (No. 2), MSC-18898, 1981

28. D.M. Shuford, "Enhancement Coating and Process for Carbonaceous Substrates," U.S. Patent 4,471,023, 11 Sept 1984
29. M.J. Lakewood and S.A. Taylor, "Oxidation-Resistant Graphite Article and Method," U.S. Patent 3,065,088, 20 Nov 1962
30. E.M. Goldstein, E.W. Carter, and S. Klutz, in *Carbon,* Vol 4, 1966, p 273
31. W.E. Parker and J.F. Rakszawski, "Oxidation Resistant Carbonaceous Bodies and Method for Making," U.S. Patent 3,261,697, 19 July 1966
32. R.E. Woodley, in *Carbon,* Vol 6, 1968, p 617
33. H.H. Strater, "Oxidation Resistant Carbon," U.S. Patent 3,510,347, 5 May 1970
34. K.J. Zeitsch, in *Modern Ceramics,* J.E. Hove and W.C. Riley, Ed., John-Wiley, 1967, p 314
35. L.C. Ehrenreich, "Reinforced Carbon and Graphite Articles," U.S. Patent 4,119,189, 10 Oct 1978
36. T. Vasilos, "Self-Healing Oxidation-Resistant Carbon Structure," U.S. Patent 4,599,256, 8 July 1986
37. P.E. Gray, "Oxidation Inhibited Carbon-Carbon Composites," U.S. Patent 4,795,677, 3 Jan 1989
38. D.W. McKee, in *Carbon,* Vol 25, 1987, p 551
39. J.F. Rakszawski and W.E. Parker, in *Carbon,* Vol 2, 1964, p 53
40. D.W. McKee, C.L. Spiro, and E.J. Lamby, in *Carbon,* Vol 22, 1984, p 507
41. R.C. Shaffer, "Coating for Fibrous Carbon Materials in Boron Containing Composites," U.S. Patent 4,164,601, 14 Aug 1979
42. R.C. Shaffer and W.L. Tarasen, "Carbon Fabrics Sequentially Resin Coated with (1) A Metal-Containing Composition and (2)A Boron-Containing Composition Are Laminated and Carbonized," U.S. Patent 4,321,298, 23 March 1982
43. I. Jawed and D.C. Nagle, Oxidation Protection in Carbon-Carbon Composites, *Mat. Res. Bull.,* Vol 21, 1986, p 1391
44. D.W. McKee, in *Carbon,* Vol 24, 1986, p 737
45. J.E. Sheehan and H.D. Batha, "C-C Composite Matrix Inhibition," paper presented at the 16th National Technical Conference, Society of Aerospace Material and Process Engineers, Oct 1984
46. J.R. Strife, in *Damage and Oxidation Protection in High Temperature Composites,* G.K. Haritos and O.O. Ochoa, Ed., American Society of Mechanical Engineers, 1991, p 121
47. J.R. Strife, in *Proceedings of the Sixth Annual Conference on Materials Technology,* M. Genisio, Ed., Southern Illinois University at Carbondale, 1990, p 166

Preferred Coating Approaches

Coating approaches are dictated by both application requirements and fundamental behavior. Generally speaking, SiC-base and Si_3N_4-base coatings have found broad use at temperatures below 1700 °C (3092 °F) because of minimum thermal mismatch stresses and low oxide-scale growth kinetics. In the higher temperature range, 1700 to 2200 °C (3092 to 3992 °F), refractory carbides and borides have been used for short time periods. Coating deposition techniques that have been used include pack cementation, CVD, and slurry processes. Coating architectures are normally built using combinations of these techniques. In the following sections, typical coating architectures are discussed in accordance with the process used to deposit the primary oxygen barrier.

Pack Cementation. The coating system used on the Shuttle Orbiter vehicle is the preeminent example of the use of a pack process to create an oxidation protection system for carbon-carbon (Ref 17). In this process, the carbon-carbon part is packed in a retort with a dry pack mixture of alumina, silicon, and silicon carbide. The retort is placed in a furnace, and under argon atmosphere a stepped time-temperature cycle is used to activate conversion of the carbon-carbon surface to SiC. Peak process temperature is approximately 1760 °C (3200 °F). This creates a porous SiC surface nominally 1.0 to 1.5 mm in thickness. Multiple impregnation and curing with an acid-activated tetraethoxysilicate liquid produces SiO_2 coating of the porous surfaces. A surface sealant consisting of a mixture of a commercial alkali silicate bonding liquid filled with SiC powder is then applied.

This system was designed to provide protection during multiple reentry cycles where surface temperatures of 1538 °C (2800 °F) are anticipated. The success of the shuttle missions and further testing (Ref 15, 16, 17) has proven this to be an

effective approach for low-performance rayon-based composites. Attempts to use similar coatings modified with boron (Ref 48, 49) for other aerospace applications requiring high-performance carbon-carbon have met with only limited success.

Chemical Vapor Deposition. Attempts to expand carbon-carbon use to turbine engine hot-section and exhaust components fostered the need for protective coatings that could be applied as thin layers over the structural components without compromising mechanical performance. The coating architectures developed have been dependent on the application lifetime as well as on dynamic or static structural requirements. The CVD coatings are normally applied in multiple cycles to ensure even deposition rates over curved surfaces. A substrate pretreatment is normally used to enhance adherence. Silicon nitride overlay coatings have been shown to be effective for limited-life (<20 h) cycles where heating above the deposition temperature occurs rapidly and peak temperatures reach 1760 °C (3200 °F) (Ref 46, 47, 50). These coatings have employed a thin reaction layer of SiC (formed in a pack process, of the order of 5 μm) to serve as a reaction barrier and to enhance adherence. The Si_3N_4 has been applied in thicknesses ranging from 125 to 250 μm (0.005 to 0.010 in.) in a multiple-step CVD process.

Other applications require that carbon-carbon withstand hundreds of hours of exposure to peak temperatures in the range of 1400 to 1500 °C (2552 to 2732 °F) and undergo thermal cycling to temperatures in the range of 600 to 1200 °C (1112 to 2192 °F). In these extended-life applications, a boron-rich inner layer is used to provide a source of glassy phase to seal microcracks in the outer coatings. Elemental boron, boron carbide, and combinations of boron compounds mixed with silicon carbide or silicon are inner layer approaches. These layers are deposited in thicknesses normally in the range of 25 to 50 μm (0.001 to 0.002 in.) using CVD, conversion of the carbon surface, and slurry coating (Ref 51, 52, 53). Depositing SiC or Si_3N_4 by CVD is the preferred method to provide hard, erosion-resistant surfaces that cover the boronated inner layers and inhibit vaporization of borate glass sealants (Ref 54, 55). Overlay thicknesses in the range of 200 to 300 μm (0.008 to 0.012 in.) are normally deposited in a multiple-step process. A typical coating architecture on an inhibited composite is shown schematically in Fig. 4.

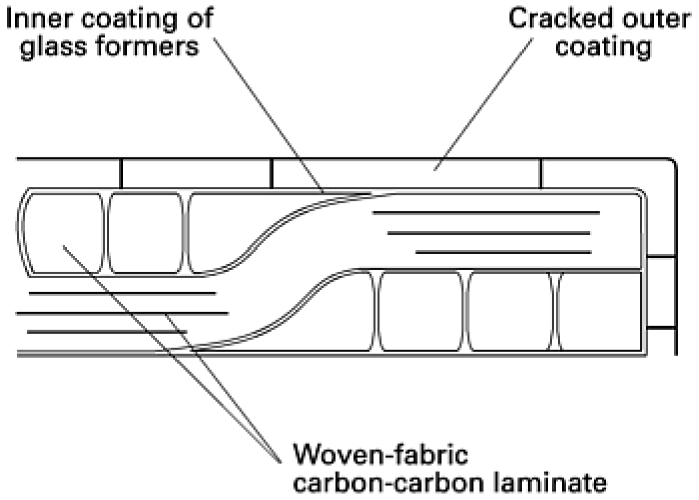

Fig. 4 Schematic of coating architecture used to protect carbon-carbon for extended-life applications

Silicate glazes are frequently applied to fill the microcrack network existing in SiC and Si_3N_4 coatings. Although the glaze is applied externally and is susceptible to vaporization and physical removal, it has been shown to improve cyclic oxidation lifetimes. Glaze overcoats are normally applied as aqueous sols incorporating boron and silicon that can be painted, sprayed, or dip coated. Typical processing involves air drying and firing above 1038 °C (1900 °F) in an argon atmosphere (Ref 54). The glaze can be periodically replenished.

Slurry coatings are produced by dispersing appropriate ceramic or metal powders in a liquid vehicle to make the slurry, applying the slurry as a paint to the component surface, evaporating or gelling the liquid to harden the coating, and then heating to a high temperature to stabilize and densify the coating. Slurries are applied by brushing, spraying, or dipping. The liquids can be water or volatile organics with organic binders in solution, inorganic or organic sols or solutions that form oxides, or thermosetting preceramic polymers or polymer solutions (Ref 56, 57).

Hardening produces a coating that is composed of the powder particles bound together and bonded to the substrate by the solid that is precipitated or condensed from the liquid. Heating to a high temperature decomposes the binder phase to form carbon or a ceramic. The shrinkage associated with binder decomposition and incomplete solid state sintering of the powder particles will result in a cracked, porous, and often weakly bonded coating unless a flowable and wetting liquid is formed by one of the constituents. This can be a glass, molten metal, or ceramic melt.

Coatings meant to provide oxidation protection for graphite and carbon-carbon composite articles at temperatures below 1000 °C (1832 °F) often contain large amounts of boron in the form of elemental boron, B_4C, BN, metal borides, or B_2O_3 (Ref 58, 59). Employing B_2O_3 glass provides a wetting liquid at low temperatures on initial heating, and the nonoxides rapidly oxidize in use to produce the same result. Coatings composed mostly of refractory oxide particles bound together with small amounts of borate glass have shown utility at temperatures in the range of 1200 to 1500 °C (2192 to 2732 °F) in configurations where evaporation of the B_2O_3 is inhibited (Ref 38). In making such coatings the boron can be present in the powder constituents, the liquid vehicle, or both. Water or alcohol solutions of boric acid and liquid boron alkoxides are often used (Ref 38, 44). Solutions of preceramic boron polymers are also a possibility (Ref 60, 61).

Slurry coatings meant for higher temperatures, in which borates are replaced by glassy alkali silicates or aluminum phosphate, are prominent (Ref 28, 48). The use of siloxane fluids as preceramic polymers has also been disclosed (Ref 62). Converting the carbon surface to SiC is often recommended as a pretreatment to ensure the adherence of glassy borate, silicate, and phosphate coatings (Ref 28, 48).

The bonding and densification of slurry coatings with molten metal and melted ceramic phases has been used to produce protective layers with intermediate to very high temperature capabilities. Dense, very adherent coatings capable of extreme-temperature service can be made from paints containing fine refractory boride particles (Ref 22). The coatings are fully stabilized by heating the borides in contact with the carbon surface to temperatures over 2000 °C (3632 °F) in an inert environment to form a boride-carbon eutectic liquid. Coatings made by melting certain combinations of metal powders and reacting these with the carbon surface to form refractory carbides (Ref 63) are protective to 1800 °C (3272 °F). Recent work of this type (Ref 64) using a mixture of silicon, hafnium, and chromium powders reacted with the carbon surface at 1450 °C (2642 °F) has produced carbide coatings that provide excellent oxidation protection for short times at 1200 °C (2192 °F).

References cited in this section

15. H.G. Maahs, C.W. Ohlhorst, D.M. Barrett, P.O. Ransone, and J.W. Sawyer, in *Materials Stability and Environmental Degradation*, MRS Symp. Proc., Vol 125, A. Barkatt, E.D. Verink, and L.R. Smith, Ed., Materials Research Society, 1988, p 15
16. R.C. Dickinson, in *Materials Stability and Environmental Degradation,* MRS Symp. Proc., Vol 125, A. Barkatt, E.D. Verink, and L.R. Smith, Ed., Materials Research Society, 1988, p 3
17. D.M. Curry, E.H. Yuen, D.C. Chao, and C.N. Webster, in *Damage and Oxidation Protection in High Temperature Composites,* Vol 1, G.K. Haritos and O.O. Ochoa, Ed., ASME, 1991, p 47
22. J. Chown, R.F. Deacon, N. Singer, and A.E.S. White, in *Special Ceramics,* P. Popper, Ed., Academic Press, 1963, p 81
28. D.M. Shuford, "Enhancement Coating and Process for Carbonaceous Substrates," U.S. Patent 4,471,023, 11 Sept 1984
38. D.W. McKee, in *Carbon,* Vol 25, 1987, p 551
44. D.W. McKee, in *Carbon,* Vol 24, 1986, p 737
46. J.R. Strife, in *Damage and Oxidation Protection in High Temperature Composites,* G.K. Haritos and O.O. Ochoa, Ed., American Society of Mechanical Engineers, 1991, p 121
47. J.R. Strife, in *Proceedings of the Sixth Annual Conference on Materials Technology,* M. Genisio, Ed., Southern Illinois University at Carbondale, 1990, p 166
48. D.M. Shuford, "Composition and Method for Forming a Protective Coating on Carbon-Carbon Substrates," U.S. Patent 4,465,777, 14 Aug 1984
49. T.E. Schmid, "Oxidation Resistant Carbon/Carbon Composites for Turbine Engine Aft Sections," AFWAL-TR-82-4159, Materials Laboratory, Wright-Patterson Air Force Base, Oct 1982

50. J.R. Strife, "Development of High Temperature Oxidation Protection for Carbon-Carbon Composites," NADC Report 91013-60, Naval Air Development Center, Warminster, PA, 1990
51. D.M. Shuford, "Composition and Method for Forming a Protective Coating on Carbon-Carbon Substrates," U.S. Patent 4,465,888, 14 Aug 1984
52. R.A. Holzl, "Self Protecting Carbon Bodies and Method for Making Same," U.S. Patent 4,515,860, 7 May 1985
53. D.A. Eitman, "Refractory Composite Articles," U.S. Patent 4,735,850, 5 April 1988
54. H. Dietrich, in *Mater. Eng.,* Aug 1991, p 34
55. J.E. Sheehan, in *Carbon-Carbon Materials and Composites,* J.D. Buckley and D.D. Edie, Ed., Noyes, 1993, p 2
56. C.W. Turner, Sol-Gel Process-Principles and Applications, Ceram. Bull., Vol 70, 1991, p 1487
57. R.W. Rice, in *Ceram. Bull.,* Vol 62, 1983, p 889
58. N.A. Hooton and N.E. Jannasch, "Coating for Protecting a Carbon Substrate in a Moist Oxidation Environment," U.S. Patent 3,914,508, 21 Oct 1975
59. G.R. Marin, "Oxidation Resistant Carbonaceous Bodies and Method of Producing Same," U.S. Patent 3,936,574, 3 Feb 1976
60. W.S. Coblenz, G.H. Wiseman, P.B. Davis, and R.W. Rice, Emergent Process Methods for High-Technology Ceramics, *Mater. Sci. Res.,* Vol 17, 1984
61. L.G. Sneddon, K. Su, P.J. Fazen, A.T. Lynch, E.E. Remsen, and J.S. Beck, in *Inorganic and Organometallic Oligomers and Polymers,* Kluwer Academic Publishers, 1991
62. M.S. Misra, "Coating for Graphite Electrodes," U.S. Patent 4,418,097, 29 Nov 1983
63. A.J. Valtschev and T. Nikolova, "Protecting Carbon Materials from Oxidation," U.S. Patent 3,348,929, 24 Oct 1967
64. H.S. Hu, A. Joshi, and J.S. Lee, *J. Vac. Sci.,* Vol A9, 1991, p 1535

Practical Limitations of Coatings

As mentioned above, carbon-carbon composites can be used as structural materials to at least 2200 °C (3992 °F). At the time of this writing, viable coating concepts to match this capability have not been consistently demonstrated, especially for times greater than a few hours. SiC and Si_3N_4 are limited thermodynamically to temperatures of approximately 1800 to 1815 °C (3272 to 3300 °F). At higher temperatures, the SiO_2 layers that form and protect these materials are disrupted by CO and N_2 interfacial pressures that become greater than 10^{-1} MPa (1 atm), causing the coatings to erode by uncontrolled oxidation (Ref 12, 47). Use of more refractory materials such as HfC or HfB_2 is limited by the very rapid oxidation rates pointed out in Fig. 1. Rapid conversion of these films to high-expansion oxides leads to severe spallation in thermal cycles. Thus, above approximately 1760 °C (3200 °F), coating lifetimes are currently limited to a few hours.

For the range of applications where coating architectures incorporating borate sealant glasses are used, coating use temperatures are limited to approximately 1500 to 1550 °C (2732 to 2822 °F). When B_2O_3 contacts carbon at atmospheric pressure, the CO reaction product pressure will exceed 10^{-1} MPa (1 atm) at approximately 1575 °C (2867 °F). Borate glasses also cause dissolution of the protective SiO_2 scale forming on SiC or Si_3N_4, leading to more rapid corrosion because of the high oxygen permeability of the mixed glass. Experience in test cycles with peak temperatures about 1400 °C (2552 °F) has shown that accelerated dissolution of coatings along microcrack boundaries eventually causes gross oxidation of boron-base inner layers, leading to massive dissolution of the silicon-base overlays.

Moisture sensitivity of borate glasses (Ref 65) can be a major limitation. Hydrolysis at low temperatures in moist air converts adherent B_2O_3-containing layers into loosely bonded boric acid particulate. Under long-term exposure, sealant glasses forming beneath the hard overlays undergo moisture attack that leads to spallation. Subsequent heating cycles that rapidly release moisture can cause catastrophic failure. Finally, high-temperature exposure to moist environments makes borate glass susceptible to vaporization by the formation of HBO_2 (Ref 44).

References cited in this section

12. J.R. Strife and J.E. Sheehan, in *Ceramic Bulletin,* Vol 67 (No. 2), 1988, p 369
44. D.W. McKee, in *Carbon,* Vol 24, 1986, p 737
47. J.R. Strife, in *Proceedings of the Sixth Annual Conference on Materials Technology,* M. Genisio, Ed., Southern Illinois University at Carbondale, 1990, p 166
65. P.B. Adams and D.L. Evans, in *Mater. Sci. Res.,* Vol 12, 1978, p 525

Plasma Surface Engineering of Plastics

Om S. Kolluri, AIRCO Coating Technology

Introduction

THE NATURE of the surface of the materials used in a product increasingly determines its success in almost every industry. This is true whether one is dealing with surface cleanliness, bonding of different components, biocompatibility, or mechanical performance of the part under conditions of use. Designers must often select specially formulated and expensive polymeric materials to ensure satisfactory performance, even though these materials often require surface preparation. In some cases, entire design concepts must be abandoned due to the prohibitive cost of the required polymer or the inability of available materials to deliver the desired performance attribute. The alternative to this scenario is to choose the material for its bulk properties and modify the surface of the material to achieve the desired performance attributes. In most cases the final step in the process is the application of a coating that offers the desired performance.

Conventional Methods. Historically, surface engineering methods have included mechanical abrasion, solvent wiping to remove surface contamination, solvent swelling, wet chemical etching, and the application of specialized coatings. Application of functional coatings has invariably required surface preparation to achieve an adequate bond between the substrate surface and the coating of choice. Each of these surface engineering methods has limitations, thus providing a strong driving force for the development of alternative surface preparation methods. Many of the common methods mentioned are accompanied by safety and environmental risks, increased risk of part damage, and expensive pollution and disposal problems.

Abrasion only increases the surface area of the part prior to adhesive bonding, and it is thus of limited utility. It often does not reach hidden areas of complex part geometries, and it is operator sensitive, dirty, and difficult to do on small or delicate parts.

Solvent cleaning is useful for removing gross contamination. In ultraclean applications, solvent cleaning merely replaces one contaminant with another. Solvent surface treatment is beneficial in cases where swelling of the polymer substrate can improve adhesion of coatings without adversely affecting the mechanical properties of the substrate. The equipment required is inexpensive, and the process works reasonably well in many cases. The major drawbacks of this technology are the environmental and process hazards associated with the use of large quantities of chemicals. Any savings in equipment cost is usually offset by the increased cost of environmental controls. Solvent-based surface treatment has limited utility when a distinct change in the chemical nature of the substrate surface is desired.

Acid etching is more effective than solvent-based methods, but it can easily result in overtreated and damaged parts, in addition to serious hazard and disposal problems. For example, other than plasma treatment, the most effective method for improving the bonding of materials to fluoropolymers has been to etch the surface with a material commonly referred to as *sodium etch.* The process consists of brief immersion of the component to be bonded in a solution of sodium naphthalene in tetrahydrofuran or another suitable solvent. Although sodium etch is quite effective in treating fluoropolymers, concerns with operator safety and the problems of disposal have caused many users to seek alternatives.

Energetic Processes. Flame, ultraviolet (UV), and corona surface treatment have often been suggested as alternatives to wet chemical methods. Of these three methods, flame treatment and corona surface treatment have been adopted on a larger scale. In flame treatment, the surface to be modified is passed through a flame generated by combustion of hydrocarbon gases. In the case of corona treatment, the surface to be modified is exposed to a point discharge across a pair of electrodes. The discharge acts to ionize the gas present in the gap, which subsequently introduces changes in the chemistry of the surface. Flame and corona, although useful in oxidizing the surfaces of plastics, have limited utility in many applications. In addition, the transitory nature of these modifications prevents their widespread use in many applications.

Limitations. Corona treatment is limited by the materials and part configurations that are responsive to this method of surface preparation. Complex shapes cannot easily be treated, because the treatment quality is a function of the distance of the part from the electrode. Thus, small-diameter holes and surfaces that are difficult to access in complex parts prove particularly troublesome. The result is an uneven surface treatment at best. Because corona discharge surface treatments are typically conducted in ambient air, the process is subject to change from day to day as the environment changes in the location where such treatment is being conducted. Finally, the high-voltage discharge often results in thermal damage to sensitive materials such as thin-wall plastics and film.

Flame treatment suffers from many of the limitations of corona treatment: difficulty in reaching recessed areas and evenly treating complex shapes. Thermal damage from overtreatment is another common problem with flame treatment.

Cold gas plasma technology is rapidly becoming the preferred industrial process for many applications requiring surface chemical modification. Plasma surface treatment, which is conducted in a vacuum environment, affords a wide latitude of possibilities in chemically changing the surface of a plastic to suit a particular application. Three mechanisms contribute to improvement in the adhesion of two components and the adhesion of coatings:

- Removal of surface contaminants and weakly bound polymer layers
- Enhancement of wettability through incorporation of polar groups that facilitate spontaneous spreading of adhesive or matrix resin
- Formation of functional groups on the surface that permit covalent bonding

When specialized surface characteristics are desired, coatings with unique chemical and physical characteristics can be deposited by plasma polymerization. Examples include antiscratch or antifog coatings, lubricious coatings, biocompatible coatings, and chemical and vapor barrier coatings. Because plasma treatment is a process of surface modification, the bulk properties of the material are retained. The nature of the process also allows precise control of the process parameters and ensures repeatability of the process in industrial applications. Finally, several studies have demonstrated that these surface modifications can be achieved with minimal impact on the environment.

Plasma Processing Equipment

Most, if not all, plasma equipment consists of similar components, but the design of the reactor chamber, the distribution of power, the excitation frequency, and the gas dynamics can all be critical parameters influencing the efficiency and properties of plasma reactions. An extensive amount of work has been published that shows a direct correlation between excitation frequency and plasma reactivity. Manufacturers of plasma equipment employing radio-frequency (RF) excitation use either low frequencies (i.e., less than 400 kHz) or the higher frequencies 13.56 or 27.12 MHz as specified by the Federal Communications Commission. For applications involving the treatment of plastics, 13.56 MHz is the preferred frequency.

Also important is whether the material being treated is in a primary or a secondary plasma. Older equipment using large cylindrical barrels typically comprises secondary plasma systems (Fig. 1a). The plasma is created either between closely spaced, paired electrodes, which may function as shelves, or in the annulus between the outer wall of the vessel and a ring electrode, when employed. Treatment of materials placed within the working volume depends on the diffusion of active species created in the primary plasma (i.e., within the RF field). Diffusion of these active species is very dependent on pressure; the higher the pressure, the shorter the mean free path. The mean free path is the distance that active species can probably travel before undergoing collisions that deactivate radicals or neutralize ions. Therefore, when using a secondary plasma, the concentration of active species varies either across the diameter of a barrel system or between electrode pairs, as the case may be. Thus, by the physical laws of nature, the treatment within the working volume of a secondary plasma system cannot be uniform.

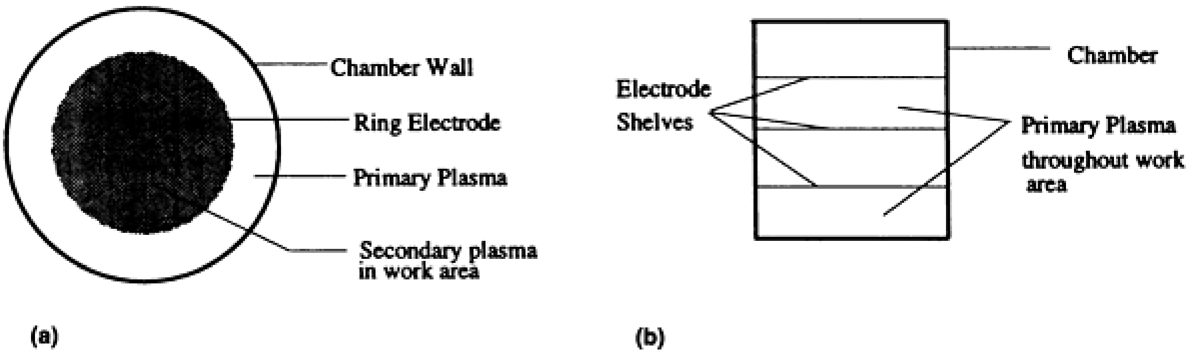

Fig. 1 Schematic of plasma processing equipment. (a) Barrel-type reactor, typical of secondary plasma systems. (b) Primary plasma reactor

By contrast, when working within the RF field, or primary plasma, the gas is constantly being excited. Thus, polymeric articles being treated are immersed in a constant concentration of active species. Further, because diffusion is not a mechanistic limitation, significantly higher operating pressures may be used. This allows a higher process gas flow rate, ensuring that out-gassing species from the polymer are sufficiently dilute, providing the full benefits of the desired process gas. In addition, the primary plasma is rich in UV radiation, which is often an important initiation step in polymer reactions. Ultraviolet radiation is line of sight, so uniform treatment of multiple parts can be obtained only when working within the primary plasma. Otherwise, any part in the shadow of another will receive different radiation, and therefore the effectiveness of the treatment will vary.

The types of reactors used for the deposition of plasma polymers have been varied. Glass and/or quartz reactors or aluminum chambers with metal parallel-plate electrodes seem to predominate in the literature, although several investigators have used inductively or capacitively coupled systems with external electrodes. High rates of deposition are found in the glow area, with the rate of deposition decreasing as one moves farther away from the glow discharge region. Consequently, primary plasma systems that use a 13.56 MHz RF source are favored. The RF excitation used by various equipment manufacturers can be as low as 2 to 4 kHz, or it can be the more typical 13.56 MHz (high frequency). Microwave plasma systems have also been used for the deposition of plasma polymers. Previous studies have shown that the densities of films deposited by low-frequency systems are significantly lower than those of films deposited by either the high-frequency or microwave plasma systems. The choice of equipment used for plasma polymerization and deposition is thus dictated by the rate of deposition desired, the film properties that can be obtained by the various systems, and practical considerations such as the size of the parts to be treated and the processing rates that are feasible in any given system.

Plasma Technology

Overview of Plasma Treatment

There are many definitions of the term *plasma*, according to the various disciplines with which it is involved. It has often been referred to as "the fourth state of matter," the generation of plasma being analogous to the transitions that occur when energy supplied to a material causes solids to melt and liquids to become gases. Sufficient additional energy supplied to a gas creates a plasma. In the case of cold gas plasma, typical of that used in this work, the process is excitation of a gas at reduced pressure by RF energy. Typically, a plasma is composed of a large concentration of highly excited atomic, molecular, ionic, and radical species. On an atomic scale, plasma generation cannot be construed as a room-temperature equilibrium process, because the bulk of the material remains near room temperature. The plasma contains free electrons as well as other metastable particles that break covalent chemical bonds upon collision with the surfaces of polymers placed in the plasma environment, thus creating free radicals on the polymer surface (Ref 1). The free radicals then undergo additional reactions, depending on the gases present in the plasma or subsequent exposure to gases in the atmosphere. The result is that these gas radical reactions form a surface that is potentially very different from that of the starting bulk polymer. Because the process is conducted in a reactor under very controlled conditions, the end result is very reproducible.

Plasma processing is not one process, but rather a "field of opportunities" that can be classified into three overlapping categories: plasma surface modification, plasma-induced grafting, and plasma film deposition. These processes are described in more detail in the section "Plasma Processes" in this article.

Plasma surface modification (plasma activation) is the alteration of surface characteristics by the substitution of chemical groups or moieties for groups normally present on the polymer chain being modified. The assumed mechanism is free-radical creation and coupling of these free radicals with active species from the plasma environment. Depending on the process gas selected, a large variety of chemical groups can be incorporated into the surface: hydroxyl, carbonyl, carboxylic, amino, or peroxyl groups. Most important, the insertion or substitution of these groups in the polymer chain is under the control of the operator. In this manner, the surface energies and the surface chemical reactivity of plastics can be altered completely without affecting their bulk properties.

Plasma-induced grafting is another method by which plastic surfaces can be modified. If a noble gas is employed to generate a plasma, a multitude of free radicals are created along the polymer backbone. If an unsaturated monomer such as allyl alcohol is introduced into the reaction chamber after the plasma is extinguished, but prior to the introduction of air, it will add to the free radical, yielding a grafted polymer. The range of functional and reactive sites that can be incorporated onto a surface is increased significantly with this technique. This process differs from activation in that instead of functional modification of the surface polymer chains, material is added to the polymer backbone.

Plasma film deposition (plasma polymerization) uses gases or vapors that fractionate and undergo polymerization under the influence of RF energy. For example, methane (CH_4) under the influence of plasma will deposit as a polyhydrocarbon that has a density approaching 1.6 g/cm^3. Any material that can be introduced into the process chamber is a potential candidate as a feed material for plasma polymerization. The properties of materials polymerized in this manner are very different from those of polymers obtained via conventional polymerization methods. These properties include a high degree of cross-linking and the ability to form pinhole-free films that adhere tenaciously to various substrates.

Plasma Process Applications

The particular plasma process used in a given application is dictated by the desired end result. For example, when contamination removal is the primary goal, the process of choice is plasma surface modification. When the goal is to improve the adhesion of two materials, the most commonly used process is surface modification, with plasma-induced grafting offering an attractive alternative. The particular process used is application-specific rather than industry-specific. For example, cleaning processes are used in many industries, such as aerospace, electronics, packaging, and medical products.

All plasma processes have a common thread in that the surface change is accomplished by an ionized gas. As a result of this common basis, it is easy to accomplish several objectives in a single system. For example, surface cleaning and the application of protective coatings is always accomplished in a single reactor with a multiple-step process, instead of using two separate process areas as is common with conventional technology.

Figure 2 illustrates the components of a typical plasma surface treatment system. As described above, the chamber is evacuated to a specified pressure using a mechanical vacuum pump, and gas is introduced into the chamber through flowmeters. During normal operation, gas is continuously introduced into the chamber, and the unreacted species and byproducts are continuously evacuated. The chamber thus operates in a steady state. Application of RF energy to the electrodes ionizes the gas in the reactor. A capacitance matching network tunes the chamber impedance to a constant load.

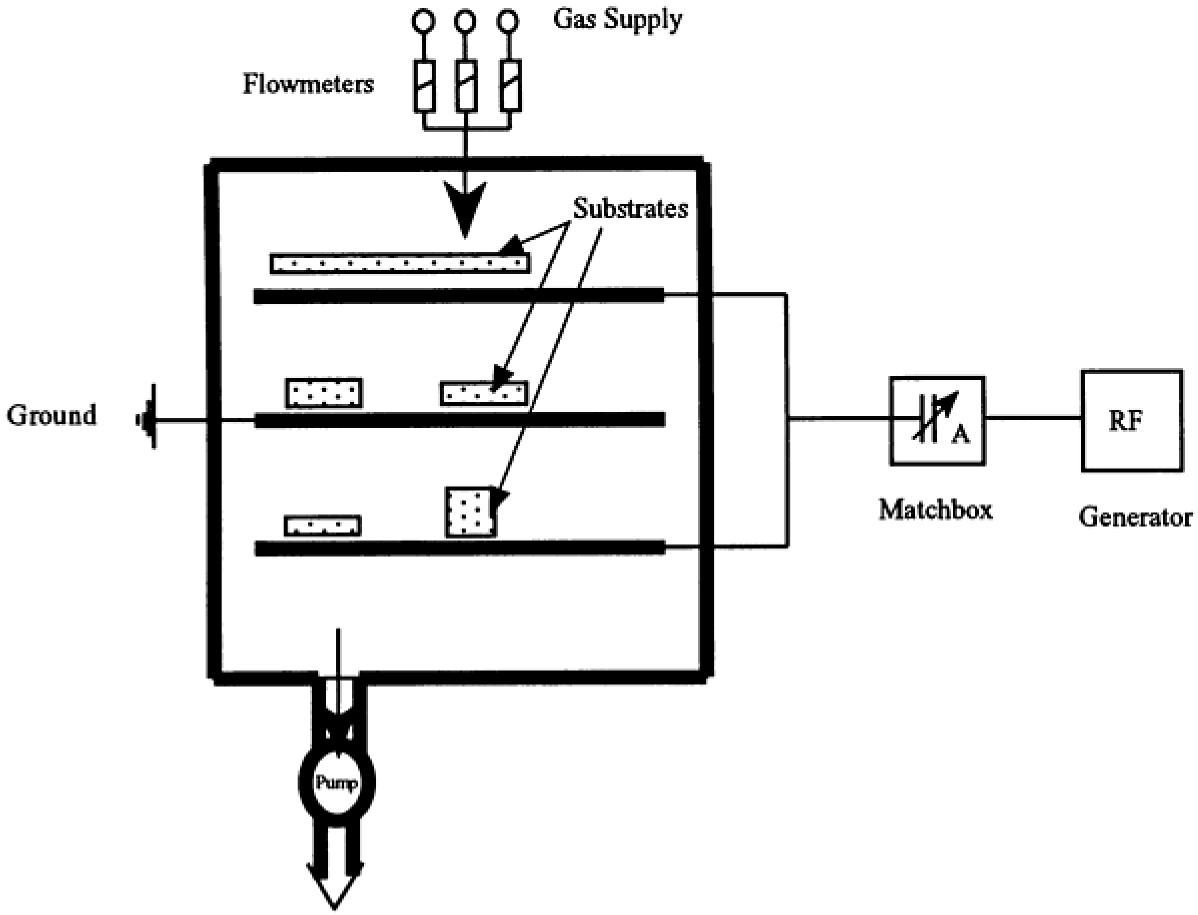

Fig. 2 Typical plasma surface treatment system

All commercial reactor systems consist of similar components, but there are variations in design parameters, such as power coupling efficiency and the gas-handling capacity of the vacuum pump. For this reason, it is difficult to translate process conditions from one system design to another. Nonetheless, Table 1 shows suggested starting process conditions for various materials and adhesive systems.

Table 1 Typical plasma surface treatment conditions

Substrate	Adhesive system/ paint system	Process gas	Operating pressure, torr	Radio-frequency power,W	Process time, min
Polypropylene	Urethane	Oxygen	0.400	200	1.0
Nylon	Epoxy	Ammonia	0.200	400	3.0
Polyphenylenesulfide	Epoxy	Nitrous oxide	0.150	300	0.5
Polytetrafluoroethylene	Epoxy	Ammonia	0.100	550	1.5
Polyethylene	Epoxy	O_2/CF_4	0.200	300	1.5

Adhesion performance for a specific system can be optimized by designing experiments in which the RF power, gas, process pressure, and process time are varied. In the case of plasma-induced grafting and plasma polymerization, process conditions are highly dependent on reactor geometry and reactor design. The experimenter should refer to appropriate references for guidance about starting process conditions.

Plasma Discharge Reactions and Surface Interactions

Although any gas can be ionized using RF excitation, a gas such as O_2, N_2, He, Ar, NH_3, N_2O, CO_2, CF_4, and air, or some combination of these gases, is commonly used in most plasma processes. One of the more commonly used plasma processes is surface treatment in an oxygen plasma, which is aggressive in its reactivity and forms numerous components. Within an oxygen plasma O^+, O^-, O_2^+, O_2^-, O, O_3, ionized ozone, metastably excited O_2, and free electrons are generally observed. The ionization of oxygen into the various species found in an oxygen plasma can be represented by the following reaction scheme:

$$O_2 + e \rightarrow O_2^- \rightarrow O + O^-$$
$$e + O \rightarrow O^+ + 2e$$
$$e + O_2 \rightarrow O_2^+ + 2e$$
$$e + 2O_2 \rightarrow O_2^- + O_2^- + O \rightarrow O_3 + e$$

These reactions represent a small sampling of those that occur in an oxygen glow discharge. As the components formed during the ionization recombine, they release energy and photons, emitting a faint blue glow and much UV radiation. The photons in the UV region have enough energy to break the carbon-carbon and carbon-hydrogen bonds in the materials on the surface that are exposed to the plasma. In the case of contaminants, the net effect appears to be degradative, such that lower-molecular-weight materials are created. These materials are subsequently removed by the vacuum, and in this manner the surface that has been exposed to a plasma is cleaned. Lower-molecular-weight polymer fractions that comprise the weak boundary layers on the surface are also removed in this manner.

Once the contaminants have been removed, the virgin polymer surface is exposed to the plasma environment. The electrons, ions, and free radicals in the plasma act on this exposed polymer, creating free radicals in the molecular chains on the surface (Ref 1, 2, 3). The free radicals that are created on the polymer surface by this process can then react with the various molecular and active species present in the plasma environment. In a low-pressure oxygen plasma, the following oxidation reaction scheme has been suggested:

$$RH + O\bullet \rightarrow R\bullet + \bullet OH$$
$$R\bullet + O_2 \rightarrow RO_2.$$
$$RO_2. + R'H \rightarrow RO_2H + R'\bullet$$
$$RO_2\bullet + R'\bullet \rightarrow RO_2R'$$

Here RO_2H and RO_2R' indicate the formation of acids and esters. Not indicated in the above reaction scheme are the possible formation of alcohols, ethers, peroxides, and hydroperoxides.

Thus, besides the reactions resulting from the bombardment of the surface by photons, ions, and neutral particles, all of the active species in the plasma react with the polymer surface. The byproducts that consist of CO_2, H_2O, and low-molecular-weight hydrocarbons are readily removed by the vacuum system. The use of co-reactants can modify the surface chemistry obtained with a single gas chemistry or accelerate the reaction kinetics. For example, in an oxygen plasma, the breaking of the carbon-carbon and carbon-hydrogen bonds is the rate-limiting step. When tetrafluoromethane is introduced as co-reactant, the O_2-CF_4 plasma yields excited forms of O, OF, CO, CF_3, CO_2, and F. Fluorine or fluorine-containing species are more effective in breaking the carbon-carbon and carbon-hydrogen bonds, so the reaction rate is accelerated. These examples illustrate how plasma technology can be used as a "limitless box" to accomplish the desired surface engineering objectives.

Contamination Removal

Vapor degreasing or sonication in organic solvents is the most common form of contaminant removal. However, the Montreal protocol on ozone-depleting chemicals has mandated the replacement of chlorofluorocarbon-based cleaning

solutions, and use of many of the traditional solvents is also being restricted due to environmental concerns. The alternatives, including water-based systems, have proven to be less effective than expected. Plasma cleaning is now being looked upon as an effective alternative and is beginning to find increasing use (Ref 4, 5, 6, 7, 8).

Ablation is the key process by which contaminants are removed from the surface of materials placed in a plasma (see the description in the previous section about how carbon-carbon and carbon-hydrogen bonds are broken). The choice of gas used for cleaning applications depends on both the contaminant and the substrate to be cleaned. Contaminants that are difficult to remove, such as silicone oils, require aggressive chemistries containing tetrafluoromethane or sulfuroushexafluoride. When delicate materials are to be cleaned, a less aggressive chemistry such as that offered by the noble gases, argon or helium, is commonly used.

Plasma Surface Modification (Plasma Activation)

Plasma treatment using commonly available gases (air, oxygen, nitrogen, and the others described above) is often referred to as *plasma surface modification.* The distinguishing factor is the absence of reactive gases, such as unsaturated hydrocarbons or saturated hydrocarbons, or any other materials that would result in the deposition of a film on the substrate. In many industries, surface chemical interactions play a central role in the functional performance of the product. For example, the interaction between the surface and a specialized coating is important in the successful performance of the coating. Another example is that in the biomedical industry, one encounters interactions between the surface and proteins or chemical reagents in applications involving cell culture or diagnostic devices (Ref 9, 10, 11, 12). A similar phenomenon exists in adhesive bonding when two dissimilar surfaces are joined. Adhesive bonding represents a large percentage of the applications requiring surface modification, so it will be used to illustrate this process, but the basic principles are equally valid for other applications.

The strength of an adhesive joint is influenced by several factors (Ref 13, 14, 15). Removal of contaminants and process aids provides a means for the adhesive to interlock with the substrate surface rather than with a boundary layer that is merely resting on the surface. In addition, increasing the surface energy of the substrate above the surface tension of the adhesive makes it possible for the adhesive to wet the entire surface of the polymer substrate. The increase in the apparent surface area of contact increases the strength of the adhesive bond (Fig. 3).

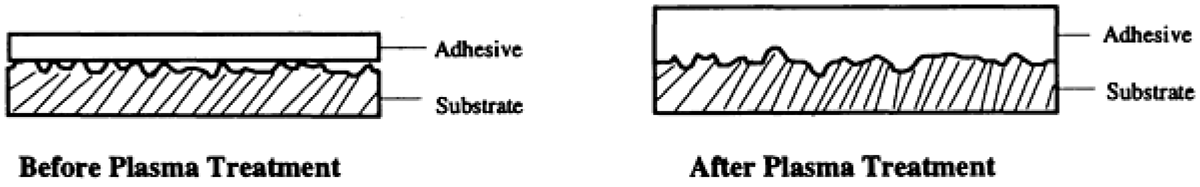

Fig. 3 Schematic of ablation, or microroughening, of the surface layer of a polymer substrate by plasma surface modification. Microroughening increases the area of contact between an adhesive and a substrate to strengthen the bond.

Ablation of the surface layers of the exposed polymer can result in a microroughened surface that increases the area of contact between the adhesive and the substrate. Adhesion strength is further enhanced by modification of the surface chemistry in a manner that facilitates covalent bonding between the adhesive and the substrate surface. These changes are accomplished by competing molecular reactions that take place on the surface of a polymer substrate in a plasma. Ablation of the surface layers of the polymer can also take place in a plasma and occur through a similar mechanism. If the substrate consists of a blend or alloy of materials that react differently in a plasma, differential ablation of these components can be used to create a microroughened surface.

Substitution of atoms in the polymer molecule with chemical groups from the plasma is often referred to as *activation.* The surface energy of the polymer placed in a plasma can be increased very rapidly by plasma-induced oxidation, nitration, hydrolization, or amination. The higher surface energy of the polymer surface increases its wettability, which describes the ability of a liquid to spread over and penetrate the surface. The resulting increase in apparent bonded surface area increases the strength of the bond. The process of activation can also be used to replace surface polymer groups with those that facilitate covalent bonding between the polymer substrate and the adhesive.

The use of plasma surface treatment to improve adhesion is well known (Ref 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30), and several literature sources provide an in-depth discussion of the nature of gas plasmas and their chemistries (Ref 1, 16, 18, 21, 22, 23). The gases most commonly employed for surface modification are O_2, N_2, He, Ar, NH_3, N_2O, CO_2, CF_4, and air or some combination of these gases. The first step of the process is contaminant removal by chain scission, and several reports documenting the efficacy of plasma surface cleaning in improving adhesion have been published (Ref 1, 24, 26). Once the contaminants have been removed, the virgin polymer surface is exposed to the plasma environment. The electrons, ions, and free radicals in the plasma act on this exposed polymer, creating free radicals in the molecular chains on the surface (Ref 1, 2, 3). The free radicals that are created on the polymer surface by this process can then react with the various molecular and active species present in the plasma environment.

The permanent nature of these changes on the polymer surface have been confirmed by spectroscopy and documented in several studies (Ref 31, 32, 33, 34). The use of other gases permits the incorporation of other functional groups on the polymer surface. Examples include the use of ammonia, nitrogen, and oxides of nitrogen plasmas that are used to incorporate nitrogen in the surface and create nitrogen-base functional groups such as primary and secondary amines (Ref 35, 36).

One result of modification of the polymer surface is an increase in the surface energy of the polymer and an attendant improvement in surface wetting. As stated above, adequate wetting of the surface by the adhesive contributes to the improvement in bond strength by increasing the apparent area of contact over which the load is distributed. Published studies suggest that this improvement in wetting contributes directly to the observed improvement in the strength of the adhesive bond (Ref 37, 38, 39). As stated above (Fig. 3), another factor that contributes to improved adhesion is an increase in surface area of the polymer surface through microroughening (ablation of the polymer surface through exposure to a plasma). This is particularly the case when the plasma is highly reactive, as when oxygen is used as one of the gas components that is being ionized. The nature of the gas being ionized to create the plasma is not the only factor that determines the extent of ablative etching; the nature of the polymer that is exposed to the plasma also plays a key role. Studies have shown that etching through ablation of surface polymer layers does occur in polymers such as polyethylene, polyethylene terephthalate, and nylon 66 (Ref 22, 40), whereas polyaramid materials such as Kevlar appear to be resistant to microroughening through ablation of the polymer chains (Ref 41).

Evidence presented in several studies indicates that the strength of the adhesive bond depends on the particular functional group that has been created on the surface of the polymer. Some of these studies draw a direct correlation between the nature of the chemical groups on the surface, the nature of the adhesive used, and the observed improvement in adhesion (Ref 22, 39, 42). Other studies relate the improvements to effects of hydrogen bonding and specific surface chemical interactions that do not necessarily result in covalent bonding between the polymer surface and the adhesive (Ref 43). Sometimes it is left to the reader to deduce the conclusions from the adhesion data presented, along with data describing the nature of the surface chemistry (Ref 44, 45).

As these examples illustrate, the selection of the process gas determines how the plasma will alter the polymer. Very aggressive plasmas can be created from relatively benign gases. Oxidation by fluorine free radicals that are generated when tetrafluoromethane is included as one of the gases is as effective as oxidation by the strongest mineral acid solution. The primary difference is that the byproducts of the plasma process do not require special handling, because the active species recombine to their original stable and nonreactive form outside the RF field. In all cases, profound and permanent changes in the chemical nature of the polymer surface are implemented. The stability of these surface changes is a function of the materials themselves and the storage conditions used (Ref 46). For instance, plasticizers that can migrate to the surface, or contaminants in the storage area that can be attracted to these high-energy surfaces, will negate the effects of the chemical changes that have been created on the surface of these materials. Contact angle measurements and electron spectroscopy of plasma-treated surfaces have confirmed the permanent nature of plasma surface modification of polymers. For example, plasma-modified fluorinated ethylene propylene (FEP) was shown to retain its surface chemical characteristics over an 18-month observation period (Ref 47). Similar phenomena have been observed by other investigators for other materials, such as polyethylene and polystyrene (Ref 48). These changes ultimately lead to significant improvements in adhesion strength, as Table 2 suggests.

Table 2 Lap shear strength of untreated and plasma-treated surfaces

Material	Plasma chemistry	Adhesive	Bond strength, MPa	Failure mode	Reference

Vectra A625	Control	Epoxy	6.47	Adhesive	19
	Oxygen plasma	Scotchweld 2216 (3M)	11.02	Cohesive	
	Ammonia plasma	Scotchweld 2216 (3M)	8.55	Cohesive	
Noryl 731	Control	Epoxy	4.25	Adhesive	19
	Oxygen plasma	Scotchweld 2216 (3M)	10.24	Adhesive	
	Ammonia plasma	Scotchweld 2216 (3M)	12.40	Cohesive	
Ultem 1000	Control	Epoxy	1.28	Adhesive	19
	Oxygen plasma	Scotchweld 2216 (3M)	13.37	Cohesive	
	Ammonia plasma	Scotchweld 2216 (3M)	14.18	Cohesive	
Rynite 530/935	Control	Epoxy	4.71	Adhesive	27
	Plasma treatment A	Epoxy	40.51	Cohesive	
	Plasma treatment B	Epoxy	41.83	Cohesive	
Tefzel	Control	Epoxy	0.07	. . .	23
	Ammonia plasma	Uniset D276	1.39	. . .	
	O_2/SF_6 plasma	Uniset D276	2.02	. . .	

Plasma-Induced Grafting

As effective as plasma surface modification might be, the extent to which the surfaces of polymers can be modified is limited. Plasma-induced grafting is another method by which chemical functional groups can be incorporated. In this process, free radicals are generated on the surface of a polymer through the use of an inert gas plasma. Because of the nonreactive nature of the inert gas plasma, surface chemical modification of the polymer does not occur. However, if a polymer surface that has been treated in this fashion is exposed to vapors of unsaturated monomers, the monomers get attached to the surface. A variety of vinyl monomers are available, and the possibilities for incorporating many different chemical functional groups are endless. Unlike surface modification, this is a two-step process, which adds a degree of complexity. Few studies have appeared in the open literature; the majority of such processes are being used in proprietary applications (Ref 49, 50, 51).

Plasma Film Deposition (Plasma Polymerization)

Compared to the processes described above, plasma film deposition is an entirely new avenue for bonding dissimilar materials. For example, films deposited from a methane plasma have been shown to dramatically improve the adhesion

properties of many materials when tested in both the dry and wet states (Ref 49). The process of plasma film deposition is often called *plasma polymerization*, although the process that takes place is not polymerization in the classical sense.

Gases in plasma may undergo polymerization, usually through a free radical initiation process. When a gas is ionized by RF energy, the resulting plasma contains free electrons as well as other metastable particles. When the process gas mixture used consists wholly or in part of hydrocarbon gases, the hydrocarbon molecule is fractured into free radical fragments, which become the sites at which the polymerization process is initiated. As the molecular weight of the plasma-polymerized product increases, the product is deposited onto the substrate placed within the plasma chamber. The fragmentation of the feed gas in the plasma generates free radical species for initiating the polymerization process, so gases that have zero functionality, such as methane (CH_4), can be used to form plasma polymers. In addition to methane, plasma polymers have been formed from other hydrocarbon gases such as ethylene or propylene, fluorocarbon monomers such as tetrafluoroethylene, and organosilicon compounds such as hexamethyldisiloxane (HMDSO) or vinyltrimethylsilane. Due to the complex nature of the fragmentation process, the resulting polymer structure is unlike any that can be deduced from conventional polymerization mechanisms (Ref 52). The physics of plasma polymerization has been described in depth elsewhere in sufficient detail for the interested reader (Ref 49, 53, 54).

The conditions used during glow discharge polymerization determine not only the structure of the resulting film but also the rate at which these films are deposited onto the target substrate materials (Ref 49, 55, 56). The degree to which the monomer is fragmented depends on the amount of energy supplied per unit weight of monomer that is allowed to flow through the reactor. When sufficient energy is supplied to break all the bonds of the monomer molecule, the recombination or polymerization process becomes atomic in nature. In addition, the structure of the plasma polymers can be varied by changing the reaction conditions, including the use of co-monomers or the introduction of oxygen, nitrogen, or ammonia into the reaction chamber during the polymerization process. Studies have correlated the power input, the type of monomer used, and the monomer flow rate to the density and type of active species in the plasma, and these factors in turn determine the rate of deposition and the film structure (Ref 56, 57). Table 3 shows typical deposition rates for some common plasma-polymerized films.

Table 3 Deposition rates for various compounds

Compound	**Deposition rate (D), $10^8 \times$ gm/cm^2/min**	**D/D_0**
Hexamethyldisiloxane	$233 = D_0$	1.00
Acrylic acid	28	0.12
Styrene	173	0.74
Tetramethyldisiloxane	191	0.82
Divinyltetramethyldisiloxane	641	2.75
Ethylene	42	0.18
Benzene	110	0.47

Source: Ref 49

Plasma of ammonia, mixtures of hydrogen and nitrogen, and oxides of nitrogen have been used to incorporate nitrogen atoms in the surface layers of the polymer (Ref 35, 36), but the level of nitrogen incorporation has been less than 10 at.% (Ref 36). In contrast, films deposited from allyl amine have shown to contain up to 25 at.% nitrogen, as measured by spectroscopic methods (Ref 58). Despite this high nitrogen content, however, Ref 58 reports a lower-than-expected

concentration of amino groups. Other studies have shown concentrations of up to 2 molecules/nm^2 of reactive amine groups on the surface of films deposited from allyl amine onto FEP substrates. These surface concentrations were determined by derivatization of the amine groups with fluoroscein isothiocyanate and subsequent detection of the fluoroscein chromophore by optical spectroscopy (Ref 59). Electron spectroscopy does not always allow precise determination of functional sites, so the earlier data may reflect limitations of the analytical methods used.

In a similar vein, hydroxyl and carboxylic acid functionalities can be incorporated by plasma polymerizing acrylic acid (Ref 60) or allyl alcohol (Ref 58). Another technique commonly employed to incorporate specific atomic species is the use of co-reactants along with the primary monomer. In one such example, ammonia or acrylonitrile was used as the co-reactant during the deposition of films from a methane plasma (Ref 61). Two additional techniques for modifying plasma-deposited films are plasma surface modification of the deposited film in a second process step and wet chemical reaction methods. As an example, carbonyls formed during the plasma deposition of films from N-vinylpyrrolidone were reacted with lithium aluminum hydride and sodium borohydride to convert these carbonyls to hydroxyl groups (Ref 62).

The use of plasma-deposited films for adhesion enhancement is not limited to polymeric substrates. Such films have also been deposited onto inorganic materials, such as mica (Ref 60), and metal substrates, such as aluminum and steel, in an effort to improve adhesion of these materials to polymers (Ref 49).

Plasma film deposition technology has become a significant tool in achieving performance attributes beyond simple adhesion improvement. The diverse applications include biocompatibility, permeation control of films, corrosion resistance of metal surfaces, and hard coats or abrasion-resistant coatings for plastic substrates. Plasma-polymerized films have been successfully used for developing gas separation membranes and as barrier coatings for packaging applications. Such coatings are typically deposited from the plasma polymerization of siloxane monomers (Ref 63, 64, 65, 66). As shown in Table 4, plasma-deposited films offer barrier properties that are significantly better than those obtained by films deposited by evaporative methods.

Table 4 Oxygen transmission rates of evaporated and plasma-deposited SiO_x coatings on polyethylene terephthalate

Process	**Material**	**Thickness, Å**	**O_2 rate, cc/m^2/day**	**H_2O rate, g/m^2/day**
Resistance evaporation	SiO	600	2.2	2.5
Electron-beam evaporation	SiO	600	3.0	2.0
Plasma-enhanced chemical vapor deposition	SiO_2	200	1.0	1.0

Source: Ref 64

Table 5 compares the physical properties and permeation characteristics of plasma-deposited films with those of a silicone rubber membrane for use in gas separation. The membranes prepared from HMDSO are similar to silicone rubber but of a higher density, and they appear to offer better selectivity. Note that the structure of the plasma-deposited film significantly influences the permeation properties, as evidenced by the differences between HMDSO films and hydroxymethyldisilazane films. Other applications include optical coatings (Ref 67), abrasion-resistant coatings (Ref 68, 69), and coatings that act as semiconducting films (Ref 70). As shown in Table 6, plasma-deposited coatings offer a 300% improvement in the abrasion resistance of polycarbonate substrates compared with that of uncoated plastic.

Table 5 Physical properties and permaselectivity of plasma-polymerized (PP) films

Parameter	**PP HMDSO, 0.5 μm**	**PP HMDSN, 0.5 μm**	**Silicone rubber, 1.0 μm**

Film density, g · cm^{-3}	1.40	1.35	1.05
C, H, N content, mass %	32.5, 8.3, 0.0	32.0, 8.5, 7.2	32.0, 8.1, 0.0
N_2 permeation coefficient[(a)]	1.3×10^{-15}	0.27×10^{-15}	3.5×10^{-15}
Separation Factor			
CH_4/N_2	2.7	1.2	2.4
C_4H_{10}/N_2	21.0	9.8	7.8
CO_2/N_2	8.1	3.9	5.4
He/N_2	2.8	2.3	2.8
O_2/N_2	2.4	0.7	2.4

HMDSO, hexamethyldisiloxane. HMDSN, hydroxymethyldisilazane.

Source: Ref 63

(a) The N_2 permeation coefficient is calculated as [m^3, STP (m)/(m^2(s)(Pa)] where STP is standard temperature and pressure.

Table 6 Haze resulting form abrasion of polycarbonate substrates

Sample	Haze, %	Notes
Uncoated polycarbonate	5.2 ± 0.8	Average haze for ten samples
Coated polycarbonate	4.1 ± 0.5	Average haze for three samples
Coated and oxygen-treated polycarbonate	2.5 ± 0.2	Average haze for six samples
Uncoated and unabraded polycarbonate	2.3 ± 0.1	Average haze for ten samples
Coated and unabraded polycarbonate	2.2 ± 0.1	Average haze for three samples

Source: Ref 69

Biomedical applications of plasma-polymerized films are primarily devoted to biocompatible coatings (Ref 71, 72, 73, 74). The interaction between plastics and body fluids such as human blood and proteins is complex and not well understood. Because plastic materials offer an opportunity to develop and design lifesaving devices and prosthetics, the

focus in these applications has been biocompatibility for both short-term use and long-term implants. Several literature sources offer excellent summaries of these applications (Ref 74).

References cited in this section

1. H.V. Boenig, *Plasma Science and Technology,* Cornell University Press, 1982
2. N. Morosoff, B. Crist, M. Bumgarner, T. Hsu, and H.K. Yasuda, Free Radicals Resulting from Plasma Polymerization and Plasma Treatment, *Symposium on Plasma Chemistry of Polymers,* M. Shen, Ed., Marcel Dekker, 1976
3. G.W. Pitt, J.E. Lakenan, D.M. Fogg, and B.A. Strong, Enhanced Interfacial Adhesion of Fibers to Thermoplastic: Comparison of Polyaramid and Glass, *SAMPE Quarterly,* Oct 1991
4. W.E. Hansen and M. Hozbor, "Gas Plasma Cleaning for Electrical Product Manufacture," paper presented at International Coil Winding Association Conference, 1991
5. O.S. Kolluri, "Surface Cleaning with Plasma--An Environmentally Safe Alternative," Technical Note, Himont Plasma Science, 1990
6. J. Fessman and H. Grünwald, Plasma Treatment for Cleaning Metal Parts, *Proceedings of the Third International Conference on Plasma Surface Engineering,* Garmisch-Partenkirchen, Germany, Oct 1992
7. M.A. Hozbor, W.P. Hansen, and M. McPherson, Plasma Cleaning of Metal Surfaces: An Alternative to CFCs, *Precision Cleaning,* March 1994
8. M.A. Hozbor and A.C. Greene, "Plasma Cleaning and Drying: Alternatives to Conventional Technologies," paper submitted to Precision Cleaning Conference, May 1994, Witter Publishing
9. I.H. Loh, Plasma Surface Modifications for Biomedical Applications, *Spectrum,* April 1991
10. C.P. Sharma et al., Introduction of Surface Functional Groups onto Biomaterials by Glow Discharge, *Biomaterials Applications,* Vol 2, 1987, p 205-218
11. G. Joseph et al., Platelet Adhesion to Surfaces Treated with Glow Discharge and Albumin, *Biomaterials Research,* Vol 20, 1986, p 677-682
12. D. Klee et al., Modification of Polyurethane for Endothelial Cell Seeding, *Makromol. Chem. Makromol. Symp.,* Vol 19, 1988, p 179-187
13. L.E. Rantz, Proper Surface Preparation: Bonding's Critical First Step, *Adhesives Age,* May 1987
14. J.W. Prane, Some Insight into Why Adhesives Adhere, *Adhesives Age,* June 1989
15. E.M. Petrie, Adhesively Bonding Plastics: Meeting an Industry Challenge, *Adhesives Age,* May 1989
16. P.W. Rose and E. Liston, Gas Plasma Technology and Surface Treatment of Polymers Prior to Adhesive Bonding, *Proceedings of the SPE 43rd ANTEC,* Society of Plastics Engineers, 1985
17. M. Londshien and W. Michaeli, "Plasma Treatment--A Technology to Improve Adhesion," paper presented at Society of Plastics Engineers ANTEC, 1991
18. S.L. Kaplan and P.W. Rose, Plasma Surface Treatment of Plastics, *Technical Papers,* Vol 34, Society of Plastics Engineers, April 1988
19. S.L. Kaplan and P.W. Rose, Plasma Treatment Upgrades Adhesion in Plastic Parts, *Plastics Engineering,* Vol 44 (No. 5), May 1988
20. S.L. Kaplan, P.W. Rose, H.X. Nguyen, and H.W. Chang, Gas Plasma Treatment of Spectra ô Fiber, *SAMPE Quarterly,* Vol 19 (No. 4), July 1988
21. H.X. Nguyen, G. Riahi, G. Wood, and A. Poursartip, Optimization of Polyethylene Fiber Reinforced Composites Using a Plasma Surface Treatment, *Proceedings of the 33rd International SAMPE Symposium,* Society of Aerospace Material and Process Engineers, 1988
22. O.S. Kolluri, S.L. Kaplan, and P.W. Rose, "Gas Plasma and the Treatment of Advanced Fibers," paper presented at Advanced Polymer Composites '88 RETEC, Society of Plastics Engineers, 1988
23. G.P. Hansen, R.A. Rushing, R.W. Warren, S.L. Kaplan, and O.S. Kolluri, "Achieving Optimum Bond Strength with Plasma Treatment," Technical Paper AD89-537, Society of Manufacturing Engineers, 1989

24. L.C. Jackson, Improving Adhesion by Gas Plasma Contaminant Removal, *Adhesives Age,* Sept 1978
25. W. Yang and N. Sung, Adhesion Promotion through Plasma Treatment in Thermoplastic/Rubber Systems, *Polymeric Materials Science and Engineering,* Vol 62, 1990
26. R.L. Bersin, How to Obtain Strong Adhesive Bonds via Plasma Treatment, *Adhesives Age,* March 1972
27. S. Sangiuolo and W.E. Hansen, "Plasma Surface Treatment for Automotive Coil Applications--A Case Study," paper presented at International Coil Winding Association Conference, 1990
28. H. Shonhorn, F.W. Ryan, and R.H. Hansen, Surface Treatment of Polypropylene for Adhesive Bonding, *Journal of Adhesion,* Vol 2, April 1970
29. H. Schonhorn and R.H. Hansen, Surface Treatment of Polymers for Adhesive Bonding, *Journal of Applied Polymer Science,* Vol 11, 1967
30. J. Osterndorf, R. Rosty, and M.J. Bodnar, Adhesive Bond Strength and Durability Studies Using Three Different Engineering Plastics and Various Surface Preparations, *SAMPE Journal,* Vol 25 (No. 4), July/Aug 1989
31. L.J. Gerenser, XPS Studies of Plasma Modified Polymer Surfaces, *Polymeric Materials Science and Engineering,* Vol 62, 1990
32. T.G. Vargo, J.A. Gardella, and L. Salvati, Multitechnique Surface Spectroscopic Studies of Plasma Modified Polymers--Part III: H_2O and O_2/H_2O Plasma Modified Poly (methyl methacrylate)s, *Journal of Polymer Science, Part A: Polymer Chemistry,* Vol 27, 1989
33. D.J.D. Moyer and J.P. Wightman, Characterization of Surface Pretreatments of Carbon Fiber-Polyimide Matrix Composites, *Surface and Interface Analysis,* Vol 14, 1989
34. J.E. Klemberg-Sapieha, L. Martinu, E. Sacher, and M.R. Wertheimer, "Plasma Surface Interactions in the Treatment of Polymers," paper presented at Society of Plastics Engineers ANTEC, 1991
35. J.R. Hollahan, B.B. Stafford, R.D. Falb, and S.T. Payne, Attachment of Amino Groups to Polymer Surfaces by RF Plasmas, *Journal of Applied Polymer Science,* Vol 13, 1969
36. N. Inagaki, S. Tasaka, J. Ohkubo, and H. Kawai, Hydrophilic Surface Modification by Plasma of Nitrogen Oxides, *Polymeric Materials Science and Engineering,* Vol 62, 1990
37. E. Liston, The Relationship between Water Wettability and Adhesion Bonding, *Polymeric Materials Science and Engineering,* Vol 62, 1990
38. S.P. Wesson and R.E. Allred, Surface Energetics of Plasma Treated Carbon Fiber Reinforcements, *Proceedings of the American Chemical Society Division of Polymeric Materials: Science and Engineering,* 1988
39. S. Mujin, H. Baorong, W. Yisheng, T. Ying, H. Weiqiu, and D. Youxian, The Surface of Carbon Fibers Continuously Treated by Cold Plasma, *Composite Science and Technology,* 1989
40. T. Yasuda, T. Okuno, M. Miyama, and H.K. Yasuda, Relationship between the Crystallinity and the Plasma Etching Characteristics of PET and Nylon 66, *Polymeric Materials Science and Engineering,* Vol 62, 1990
41. R.E. Allred, E.W. Merrill, and D.K. Roylance, Surface Chemistry and Bonding of Plasma-Aminated Polyaramid Filaments, *Proceedings of the American Chemical Society Symposium on Composites,* 1983
42. G. Dagli and N.H. Sung, Surface Modification of Graphite Blocks and Fibers by Plasma Polymerization, *Polymeric Materials Science and Engineering,* 1987
43. I. Iyengar and D.E. Erickson, Role of Adhesive-Substrate Compatibility in Adhesion, *Journal of Applied Polymer Science,* Vol 2, 1967
44. S. Nowak, H.P. Haerri, and L. Schlapbach, Surface Characterization and Adhesion of Plasma Treated Polypropylene, *Polymeric Materials Science and Engineering,* Vol 62, 1990
45. G.M. Porta, D.F. Foust, M.C. Burrell, and B.R. Karas, "The Physical and Chemical Aspects of Adhesion: Vacuum Metallization of Polyetherimide," paper presented at Society of Plastics Engineers ANTEC, 1991
46. H.S. Munro and D.I. McBriar, The Aging of Oxygen Plasma Treated Polymers, *Polymeric Materials Science and Engineering,* Vol 56, 1987
47. C.B. Hu and D.D. Solomon, Long Term Stability of Plasma Treated FEP--Evaluated by Surface and Bulk Properties, *Polymer Reprints,*Vol 28 (No. 2), 1981

48. Unpublished data, Himont Plasma Science
49. H. Yasuda, *Plasma Polymerization,* Academic Press, 1985
50. B. Das, Cold Plasma Activation of Continuously Moving Fiberglass Strand, *SAMPE Journal,* Vol 28 (No. 2), March/April 1992
51. K. Fujimoto, H. Inoue, and Y. Ikada, Protein Adsorption and Platelet Adhesion onto Polyurethane Grafted with Methoxy-poly(ethyleneglycol) Methacrylate by Plasma Technique, *Journal of Biomaterial Research,* Vol 27, 1993
52. P.W. Rose, O.S. Kolluri, and R.D. Cormia, "Continuous Plasma Polymerization onto Carbon Fiber," paper presented at 34th International SAMPE Symposium, May 1989
53. D.C. Schram, G.M.W. Kroesen, and J.J. Buelens, The Physics of Plasma Polymer Deposition, *Polymeric Materials Science and Engineering,* Vol 62, 1990
54. N. Morosoff, *An Introduction to Plasma Polymerization, Plasma Deposition, Treatment, and Etching of Polymers,* R. d'Agostino, Ed., Academic Press, 1990
55. R. d'Agostino, F. Fracassi, and F. Illuzi, The Influence of Plasma Parameters on Polymerization Kinetics and the Structure of Deposited Films, *Polymeric Materials Science and Engineering,* Vol 62, 1990
56. G. Smolinsky and M.J. Vasile, A Correlation of the Chemistry with the Polymerization Rate in an RF Discharge of Methane, *Symposium on Plasma Chemistry of Polymers,* M. Shen, Ed., Marcel Dekker, Inc.,1976
57. K. Yanagihara, M. Kimura, K. Numata, and M. Niinomi, A Hard Carbon Coating by CH_4/CF_4 Plasma Polymerization, *Polymeric Materials Science and Engineering,* Vol 56, 1987
58. W.R. Gombotz and A.S. Hoffman, Functionalization of Polymeric Films by Plasma Polymerization of Ally Alcohol and Ally Amine, *Polymeric Materials Science and Engineering,* Vol 56, 1987
59. H.J. Griesser and R.C. Chatelier, Characterization of Plasma Polymer Films from Amines and Other Polar Monomers, *Polymeric Materials Science and Engineering,* Vol 62, 1990
60. D.L. Cho, P.M. Claesson, C.G. Gölander, and K.S. Johansson, Structure and Surface Properties of Plasma Polymerized Acrylic Acid Layers, *Polymeric Materials Science and Engineering,* Vol 62, 1990
61. R.A. Engelman and H.K. Yasuda, Nitrogen and Oxygen Incorporation into Glow Discharge Polymers, *Polymeric Materials Science and Engineering,* Vol 62, 1990
62. R.E. Marchant, D. Yu, X. Li, and M.J. Danilich, Functionalized Plasma Polymers by Chemical Derivatization, *Polymeric Materials Science and Engineering,* Vol 62, 1990
63. J. Weichart and J. Müller, Plasma Polymerization of Silicon Organic Membranes for Gas Separation, *Proceedings of the Third International Conference on Plasma Surface Engineering,* Garmisch-Partenkirchen, Germany, Oct 1992
64. J.T. Felts, Transparent Barrier Coatings Update: Flexible Substrates, *Proceedings of the Society of Vacuum Coaters 36th Annual Technical Conference,* 1993
65. E. Sacher, J.E. Klember-Sepieha, H.P. Schreibner, and M.R. Wertheimer, Moisture Barrier Properties of Plasma Polymerized Hexamethyldisiloxane, *J. Appl. Poly. Sci.,* Vol 38, 1984
66. J. Sakata and M. Yamamoto, Application of Plasma Polymerized Films to Gas Separation Membranes, *J. Appl. Poly. Sci.,* Vol 42, 1988
67. H.U. Poll, J. Meichsner, M. Arzt, M. Freidrich, R. Rochotzki, and E. Kreybig, Optical Properties of Plasma Polymer Films, *Proceedings of the Third International Conference on Plasma Surface Engineering,* Garmisch-Partenkirchen, Germany, Oct 1992
68. C. Benndorf, J.T. Harnack, and U. Fell, Deposition of Me-C:H Coatings from Metal Organic Precursors Using a Plasma Activated RF Process, *Proceedings of the Third International Conference on Plasma Surface Engineering,* Garmisch-Partenkirchen, Germany, Oct 1992
69. T. Wydeven, Plasma Polymerized Coatings for Polycarbonate: Single Layer, Abrasion Resistant, and Antireflection, *Applied Optics,* Vol 16 (No. 3), March 1977
70. A. Kruse, A. Baalman, W. Budden, V. Schlett, and M. Hennecke, Thin Conductive Coatings Formed by Plasma Polymerization of 2-Iodothiophene, *Proceedings of the Third International Conference on Plasma*

Surface Engineering, Garmisch-Partenkirchen, Germany, Oct 1992

71. A.S. Chawla and R. Siphehia, Characterization of Plasma Polymerized Silicone Coatings Useful as Biomaterials, *J. Biomed. Mat. Res.,* Vol 18, 1984, p 537
72. B. Lassen, C.-G. Gölander, A. Johansson, and H. Elwing, Some Model Surfaces Made by RF Plasma Aimed for the Study of Biocompatibility, *Clinical Materials,*Vol 11, 1992
73. C.-G. Gölander, B. Lassen, K. Nilsson-Ekdahl, and U.R. Nilsson, RF-Plasma Modified Polystyrene Surfaces for Studying Complement Activation, *J. Biomater. Sci. Polymer Edn.,* Vol 4 (No. 1), 1992
74. B.D. Ratner, A. Chilkoti, and G.P. Lopez, Plasma Deposition and Treatment for Biomaterial Applications, *Plasma Deposition, Treatment, and Etching of Polymers,* R. d'Agostino, Ed., Academic Press, 1990

Surface Engineering of Carbide, Cermet, and Ceramic Cutting Tools

A.T. Santhanam and D.T. Quinto, Kennametal Inc.

Introduction

RAPID TECHNOLOGICAL DEVELOPMENT has produced global competition in manufacturing, and the incentive to improve productivity has never been greater. This article discusses the expanding role of surface engineering in increasing the manufacturing productivity of carbide, cermet, and ceramic cutting tool materials used in machining operations.

Acknowledgements

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Tool Material Classes

The classes of tool materials currently in use for machining operations are high-speed tool steels, carbides, cermets, ceramics, polycrystalline cubic boron nitrides (CBN), and polycrystalline diamonds (PCD). The different materials vary greatly in wear resistance and toughness. Figure 1 shows schematically their relative application ranges in terms of machining speeds and feed rates. Higher machining speeds require tool materials with greater wear resistance, whereas higher feed rates require tools with increased toughness. High-speed tool steels are the toughest materials; however, their relatively low wear resistance limits their application to low-speed machining. (Cleaning, finishing, and coating of tool steels are discussed in the article "Surface Engineering of Specialty Steels" in this Volume.) At the other end of the spectrum, superhard materials such as CBN and PCD are highly wear resistant and can be employed at high speeds. There is, however, a tradeoff between wear resistance and toughness that can limit the application of these superhard tools to lighter feed rates.

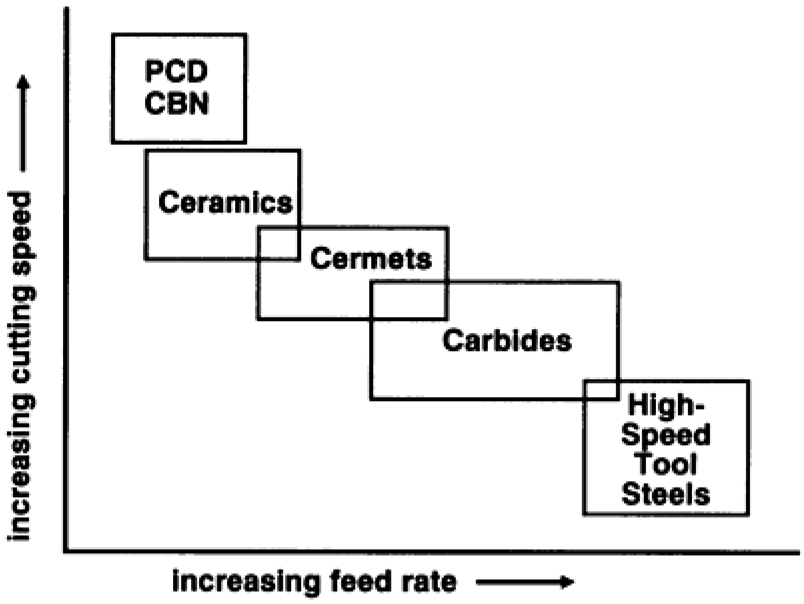


Fig. 1 Relative machining application ranges of cutting tool materials

In between the two extremes of high-speed tool steels and superhard materials are carbides, cermets, and ceramic tool materials, which are used over a wide range of speeds and feed rates to suit the diverse machining needs of the automotive, aerospace, and other manufacturing industries. Tables 1, 2, and 3 list the representative properties of carbide, cermet, and ceramic tool materials, respectively. In the past two decades, surface modification technologies have significantly expanded tool application ranges, particularly for carbides, and have dramatically improved manufacturing productivity.

Table 1 Typical properties of cemented carbides

Nominal composition, wt%	Grain size	Hardness, HRA	Density, g/cm^3	Transverse rupture strength, MPa	Compressive strength, MPa	Young's modulus, GPa	Relative abrasion resistance[a]	Coefficient of thermal expansion[b], µm/m · K	Thermal conductivity, W/m · K	Palmquist toughness[c], kg/mm
94WC-6Co	Fine	92.5-93.1	15.0	1790	5930	614	100	5.9	108	80
94WC-6Co	Medium	91.7-92.2	15.0	2000	5450	648	58	5.4	100	90
90WC-10Co	Fine	90.7-91.3	14.6	3100	5170	620	22	6.0	80	120
72WC-8TiC-11.5TaC-8.5Co	Medium	90.7-91.5	12.6	1720	5170	558	13	6.8	50	123

Source: Ref 44

(a) Based on a value of 100 for the most abrasion-resistant material.

(b) Room temperature to 1000 °C (1832 °F).

(c) Slope of load, *P*, vs. total crack length, $\sum_i l_i$, in a *P* vs. $\sum_i l_i$ plot obtained in indentation tests.

Table 2 Typical properties of cermets

Composition	Vickers hardness, kg/mm^2	Modulus of rupture, MPa	Fracture toughness K_{Ic}, MPa $\sqrt{m}$	Young's modulus, GPa
(Ti,Mo/W)CN	1650	1500	8.5	450

(Ti,Mo/W,Nb,Ta)CN	1500	1800	10.0	410

Table 3 Typical properties of ceramics

Composition	Transverse rupture strength, MPa	Young's modulus, GPa	Fracture toughness K_{Ic}, MPa $\sqrt{m}$	Coefficient of thermal expansion, μ/m · K
Al_2O_3	400	390	4.0	8.2
Al_2O_3-TiC	700	420	4.5	8.3
Sialon[(a)]	760	300	6.0	3.2

Source: Ref 8

(a) Values specific to Kyon 2000 (Kennametal Sialon Grade).

Cemented carbides belong to a class of hard, wear-resistant, refractory materials in which the hard carbides of Group IVB-VIB metals are bound together or cemented by a ductile metal binder, usually cobalt or nickel. The first cemented carbide was produced in the 1920s and consisted of tungsten carbide (WC) with a cobalt binder (Ref 1). A remarkable feature of cemented carbides is that they can be tailored to provide different combinations of abrasion resistance and toughness by controlling the amount of cobalt and WC grain size.

Over the years, the basic WC-Co material has been modified to produce a variety of cemented carbides containing WC-TiC, WC-TiC-TaC, WC-TiC-(Ta,Nb)C, and other solid-solution cubic carbides that cover a wide range of applications, including metalcutting, mining, construction, rock drilling, metal forming, structural components, and wear parts. The commercially significant alloys for machining contain 5 to 12 wt% Co and up to 15 wt% cubic carbides. Carbide grain sizes from 0.5 to 5 μm are commonly used.

Cermets. The technical definition is that a cermet is a composite of a ceramic material with a metallic binder. Although WC-Co tools also fit this definition, in the North American machining industry the term *cermets* is applied more specifically to TiC-based tools that contain mainly nickel as a binder. Cermet tools have lower density than WC tools but are heavier than ceramic inserts of equal size. The first cutting tool in this family, a TiC-Ni alloy, was commercialized as early as the 1930s, but it could not compete with the inherently stronger WC-Co-based tools. Additions of molybdenum to TiC-Ni alloys in 1960 brought cermets closer in performance to WC-Co-based tools in finish machining of steels.

Titanium carbonitride cermets based on Ti(C,N)-Ni-Mo were introduced in 1970, followed by (Ti,Mo)(C,N)-based compositions that provided a balance of wear resistance and toughness due to their finer microstructures (Ref 2). Continued development in this area has now resulted in complex cermets having a variety of additives, such as Mo_2C, TaC, NbC, ZrC, HfC, WC, VC, Cr_3C_2, and aluminum (Ref 3). Various mixes of these additives impart different combinations of wear resistance, thermal shock resistance, and toughness, and they allow tools to be tailored for a wide range of machining applications. The newer cermets are used in semifinishing and finishing of carbon and alloy steels, stainless steels, ductile irons, free-machining aluminum and other nonferrous alloys, and some high-temperature alloys. The metal removal operations may include turning, boring, milling, threading, and grooving.

Ceramic tools are inherently more stable than carbide tools at high temperatures (high cutting speeds) but are less fracture resistant; hence, recent developments have been focused on improving their fracture toughness. There are basically two classes of ceramic cutting tools: Al_2O_3 ceramics and tools based on silicon nitride (Si_3N_4) and solid solutions of aluminum and oxygen in silicon nitride (Sialons).

Al_2O_3 Ceramics. The white Al_2O_3-based ceramics may contain low levels of zirconia (ZrO_2) as a sintering aid and are used for machining cast iron. Higher levels are used in tools to machine steels. The ZrO_2 improves fracture toughness by a transformation toughening or crack deflection mechanism (Ref 4, 5), but it decreases the thermal conductivity and hardness of the tool.

Additions of up to 30 vol% TiC to Al_2O_3 make the inserts black and improve the thermal conductivity, hardness, and toughness of the tools without seriously degrading their chemical stability. Al_2O_3-TiC ceramics are employed on a wide range of workpiece materials, including cast iron, steel, and nickel-base superalloys.

SiC-whisker-reinforced Al_2O_3 ceramics, developed in the early 1980s (Ref 6), offer better toughness than white ceramics due to crack deflection by the dispersed SiC whiskers in the microstructure (Ref 7). The whiskers also increase hardness and improve thermal shock resistance by increasing thermal conductivity and reducing the thermal expansion coefficient. The major application of these tool materials is high-speed/high-feed machining of nickel-base superalloys. These ceramics can be used on cast irons but are rarely used on steels because of the poor chemical stability of SiC.

Si_3N_4/Sialon ceramics were introduced in the early 1980s. Their whisker-like grain structure makes them tougher than the white Al_2O_3 ceramics, and they also possess excellent hot hardness and thermal shock resistance. These characteristics permit them to be used at high speeds and feed rates and in interrupted cutting of nickel-base superalloys and cast irons (Ref 8, 9). However, the lower chemical stability of Si_3N_4/Sialon tool materials (compared to Al_2O_3 ceramics) prohibits their application in most steel machining.

Superhard Materials. As discussed earlier, superhard materials are extremely wear resistant. CBN is the tool of choice for machining hard steels (i.e., steels with hardnesses greater than 50 HRC). PCD, on the other hand, cannot be used for steel machining because of diamond's solubility in iron and the catalytic effect of iron, which causes graphitization of the diamond. The primary application of PCD tools is in the very-high-speed machining of aluminum-silicon alloys, composites, and other nonmetallic workpieces.

References cited in this section

1. K. Schroeter, U.S. Patent 1,549,615, 1925
2. E. Rudy, S. Worcester, and W. Elkington, in *High Temp. High Press.,* Vol 6 (No. 4), 1974, p 447-454
3. H. Doi, Science of Hard Materials, *Proceedings of the 2nd International Conference on the Science of Hard Materials* (Rhodes), Sept 23-28, 1984, Ser. No. 75, Adam Hilger Ltd., 1986, p 489-523
4. N. Claussen, in *Mater. Sci. Eng.,* Vol 71, 1985, p 23-38
5. F.F. Lange, in *J. Mater. Sci.,* Vol 17 (No. 1), 1982, p 225-234
6. G.C. Wei and P.F. Becher, in *Am. Ceram. Soc. Bull.,* Vol 64 (No. 2), 1985, p 298-304
7. K.T. Faber and A.G. Evans, in *Acta Metall.,* Vol 31 (No. 4), 1983, p 565-576
8. B. North and R.D. Baker, in *Int. J. Refractory Hard Metals,* Vol 3 (No. 1), 1984, p 46-51
9. C.W. Beeghly and A.F. Shuster, in *Proceedings of the Society of Carbide and Tool Engineers Conference on Advances in Tool Materials For Use in High Speed Machining* (Scottsdale, AZ), Feb 1987, ASM International, p 91-99
44. A.T. Santhanam, P. Tierney, and J.L. Hunt, Cemented Carbides, *Properties and Selection: Nonferrous Alloys and Special-Purpose Materials,* Vol 2, *ASM Handbook,* ASM International, 1990, p 950-977

Tool Failure Mechanisms

Machining of metals is a complex process. The cutting tool environment features high localized temperatures (~1000 °C, or 1830 °F) and high stresses (~700 MPa, or 100 ksi). The tool may experience repeated impact loads during interrupted cuts, and the workpiece chips may chemically interact with the tool material. The response of a tool material to the above conditions dictates its performance. High temperatures and stresses can cause blunting from the plastic deformation of the tool tip, and high stresses alone may lead to catastrophic fracture. In addition, the useful life of cutting tools may be limited by a variety of wear processes, such as crater wear, flank wear or abrasive wear, builtup edge, depth-of-cut notching, and thermal cracks (Fig. 2). The origin of the various tool failure mechanisms is now well understood (Ref 10).

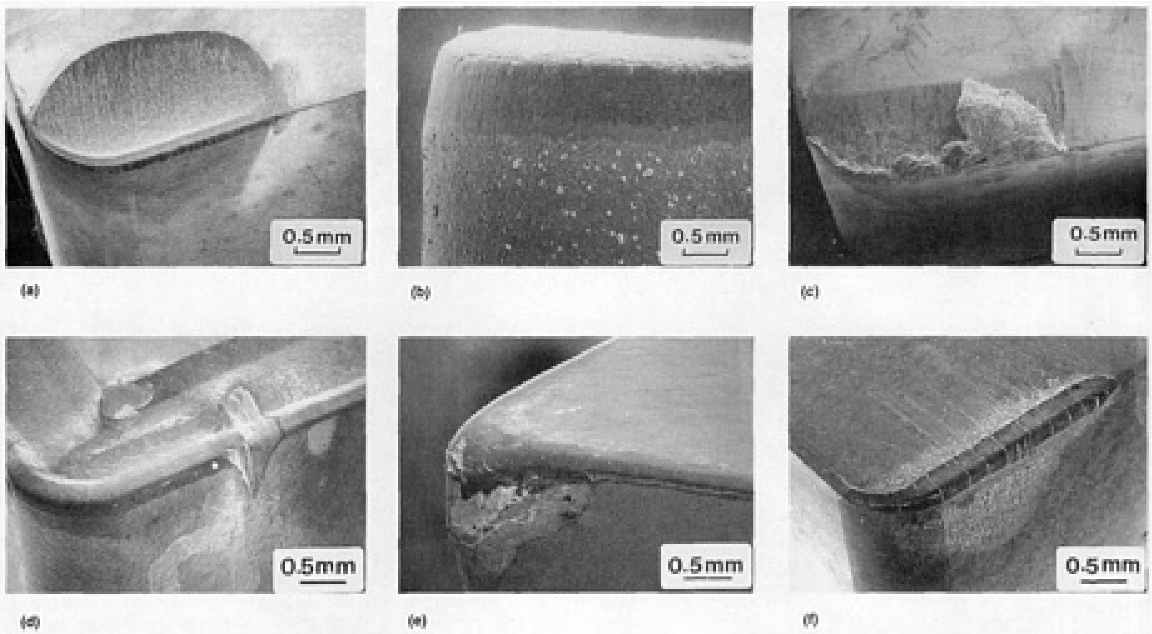


Fig. 2 Tool wear mechanisms. (a) Crater wear on a cemented carbide tool produced during the machining of plain carbon steel. (b) Abrasive wear on the flank face of a cemented carbide tool produced during the machining of gray cast iron. (c) Builtup edge produced during low-speed machining of a nickel-base alloy. (d) Depth-of-cut notching on a carbide tool produced during the machining of a nickel-base superalloy. (e) Carbide insert showing nose wear (tool-tip blunting) due to insufficient deformation resistance of the tool. (f) Thermal and mechanical cracks in a carbide insert after interrupted cutting of low-alloy steel

Crater wear (Fig. 2a), observed on the rake face of cutting tools, generally occurs during machining of relatively soft steels and ductile irons at high speeds. It is primarily caused by a chemical interaction between the rake face of a metalcutting insert and the hot metal chip flowing over the tool. This interaction may involve diffusion or dissolution of the tool material into the chip. Adhesion of tool material and chip follows, with consequent microfracture of the tool underneath the adhered material.

Flank wear (Fig. 2b), on the other hand, is observed on the flank or clearance face of a metalcutting insert and is caused by abrasion of the flank face by the hard constituents of the workpiece. This failure mechanism is commonly observed during machining of cast irons and steels where the abrasive particles are mainly Fe_3C and nonmetallic inclusions.

Builtup edge (Fig. 2c) refers to welding of the workpiece material to the tool tip. It typically occurs when soft low-carbon steels and nonferrous materials are machined at low speeds and light feed rates. This may result in attrition wear if small fragments of tool material are carried away as the builtup edge breaks off.

Depth-of-cut notching (Fig. 2d) occurs at the depth-of-cut line and is often attributed to the chemical reaction (oxidation) of the tool material with the atmosphere (Ref 11) or to abrasion by the hard, sawtooth outer edge of the chip (Ref 12). Notching is a problem with workpieces that tend to work harden and generate high tool-tip temperatures, such as austenitic stainless steels and nickel-base superalloys. Depth-of-cut notching can lead to tool fracture. Aside from selection of a tool material that is relatively chemically inert and possesses high fracture toughness, notching can be minimized by applying optimized geometries, such as chamfered edges and round insert styles, that spread the depth of cut over a wider area of the cutting edge.

Nose wear (Fig. 2e), or tool-tip blunting, results from insufficient deformation resistance of a tool material in a given machining application.

Thermal cracks (Fig. 2f) develop when the repeated heating and cooling associated with interrupted cutting, such as milling, create temperature gradients at the cutting edge. With prolonged interrupted cutting, lateral cracks may appear

parallel to the cutting edge. The thermal and lateral cracks may join together and cause small fragments of tool material to break away.

Fracture is the least desirable mode of tool failure because it is unpredictable and catastrophic. The preferred mode is flank wear, because it progresses gradually and can be easily monitored for tool-changing protocol. Most tool material development work is focused on minimizing flank wear and preventing unwanted tool failure modes such as catastrophic fracture, gross plastic deformation, builtup edge, crater wear, and depth-of-cut notching.

References cited in this section

10. V.C. Venkatesh and M. Sachitanandam, in *Annals CIRP,* Vol 29, 1980, p 19-22
11. E.M. Trent, *Metalcutting,* 3rd ed., Butterworth-Heinemann Ltd., 1991
12. M. Lee, J.G. Horne, and D. Tabor, in *Wear of Materials,* K.C. Ludema, W.A. Glaeser, and S.K. Rhee, Ed., American Society of Mechanical Engineers, 1979, p 460-469

Applicable Methods for Surface Engineering of Cutting Tools

A major breakthrough in controlling cutting tool wear came in the 1960s with the advent of protective hard coatings for cemented carbide inserts. This mode of surface modification increased tool life on steels and cast irons by a factor of at least two to three (Ref 13). Coatings also permitted the use of higher cutting speeds, boosting machining productivity.

The precursor to the development of coated carbide tools occurred in the mid-1960s, when laminated inserts consisting of a base of WC-Co alloy with a sintered layer of high TiC were produced. Although metalcutting productivity increased, thermal stresses during machining often caused the laminate to spall during use.

Chemical Vapor Deposited Coatings. Further development of laminated tools was superseded in 1969 by the application of a thin (~5 μm) layer of hard TiC coating to the cemented carbide tool by chemical vapor deposition (CVD) (Ref 13). In the CVD coating process, the tools are heated in a sealed reactor to about 1000 °C (1830 °F) with gaseous hydrogen at atmospheric or lower pressure; volatile compounds are added to the hydrogen to supply the metallic and nonmetallic constituents of the coating.

In TiC deposition, a reaction often occurs in which titanium combines with carbon from the cemented carbide substrate. The resulting surface decarburization leads to the formation of a brittle eta phase and to associated substrate microporosity at the coating-substrate interface. The early coated tools were particularly notorious in this regard and showed inconsistent performance during interrupted cuts (Ref 14). Such performance inconsistencies have now been largely eliminated by a number of metallurgical and processing innovations that have resulted in coatings with greater thickness uniformity, more adherence, and more consistent morphology and microstructure with minimum interfacial eta phase and associated porosity (Ref 15). Additional information is available in the article "Chemical Vapor Deposition of Nonsemiconductor Materials" in this Volume.

Multilayer CVD Coatings. During the 1970s, CVD coatings evolved from single-layer TiC coatings to multilayer hard coatings comprising various combinations of TiC, TiCN, TiN, HfN, and Al_2O_3 (Fig. 3). Multilayer coatings, through a combination of properties, suppress crater wear, flank wear, and builtup edge and extend the range of application. A variation of the multilayer coating employs multiple alternating layers. Figure 3(e) shows a coating with alternating layers of Al_2O_3 and TiN that is particularly effective in high-speed machining of steels and cast irons (Ref 16).

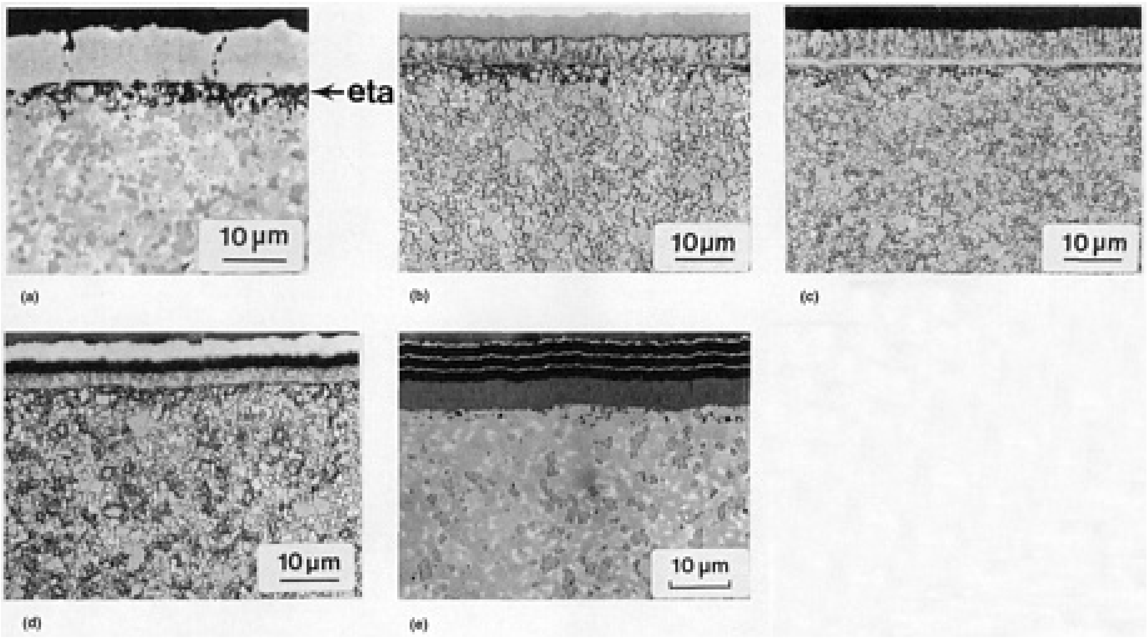


Fig. 3 Chemical vapor deposition coatings. (a) Cemented carbide insert with TiC coating. Note eta phase at the coating-substrate interface. (b) 73WC-19(Ti,Ta,Nb)C-8Co alloy with a TiC/TiCN/TiN coating about 10 μm thick. (c) 85WC-9(Ti,Ta,Nb)C-6Co alloy with a TiC/Al_2O_3 coating about 9 μm thick. (d) 85WC-9(Ti,Ta,Nb)C-6Co with a TiC/Al_2O_3/TiN coating about 10 μm thick. (e) TiCN coating supporting multiple alternating coating layers of Al_2O_3 and TiN

The high temperatures employed during CVD coating generally ensure good bonding between the substrate and the coating. The thermal expansion coefficients of the coating materials (TiC, TiCN, TiN, and Al_2O_3) are higher than those of the WC-Co-based substrates, so CVD coatings are in residual tension at room temperature. In certain cases, the stresses may be relieved by transverse cracks that form in the coating. These cracks do not affect coating adhesion, but they may initiate tool fracture in interrupted cutting operations in which the cutting edge is subjected to fatigue-type loading. Residual tensile stresses are most severe at tool corners. To minimize their effect, and also to minimize the formation of eta phase, which tends to develop to a greater extent at sharp tool edges, CVD-coated tools are honed before coating.

Tailored Substrates for CVD-Coated Tools. Although the early CVD-coated tools substantially improved metalcutting productivity, they were prone to catastrophic fracture when applied at high feed rates or in intermittent cutting operations. One solution to this problem is to improve the fracture toughness of the substrate by increasing its cobalt content. Unfortunately, this approach decreases deformation resistance, which can result in tool-tip blunting.

A major breakthrough in resolving the conflict between fracture toughness and deformation resistance occurred in the late 1970s, when a TiC/TiCN/TiN-coated tool was developed with a peripheral cobalt-enriched zone, 10 to 30 μm thick (Fig. 4a), that provided superior edge strength while maintaining the deformation resistance of the bulk of the coated tool (Ref 17). This development permitted users to make heavy interrupted machining cuts such as those encountered in scaled forgings and castings at lower speeds. Further advancements in the cobalt enrichment concept (Fig. 4b) have expanded the application range of this type of tool to higher speeds (Ref 18).

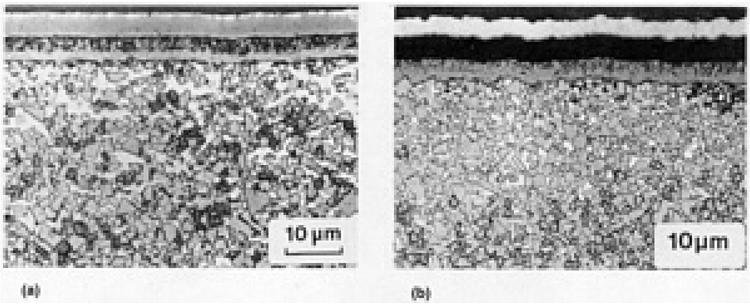


Fig. 4 Multilayer chemical vapor deposition coatings on cobalt-enriched substrates. (a) 86WC-8(Ti,Ta,Nb)C-6Co alloy with cobalt-enriched periphery and a TiC/TiCN/TiN coating. (b) Second-generation cobalt-enriched cemented carbide tool with TiC/Al_2O_3/TiN coating

Medium-Temperature CVD Coatings. In the mid-1980s a new CVD process for depositing TiCN was commercialized. Using a mixture of $TiCl_4$, H_2, and an organic C/N compound such as acetonitrile, it was shown that TiCN can be deposited at moderate temperatures (700 to 900 °C, or 1300 to 1650 °F) at faster deposition rates than in the conventional CVD process (Ref 19). The reduced process temperature and the faster deposition rate minimize the formation of the embrittling eta phase at the coating-substrate interface (Fig. 5) and lessen the thermally induced tensile cracks that are common to higher-temperature CVD coatings (Ref 20).

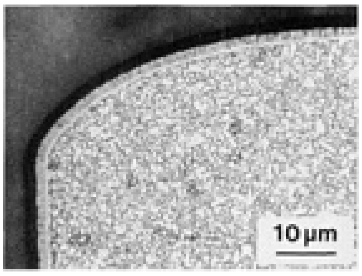


Fig. 5 Medium-temperature chemical vapor deposition TiCN/Al_2O_3 coating on a cemented carbide substrate

Physical Vapor Deposited Coatings. In the 1980s, physical vapor deposition (PVD) emerged as a commercially viable process for applying hard TiN coatings to cemented carbide tools. In this process the coating is deposited in a vacuum by condensation from a flux of neutral or ionized atoms where the metal species are derived from a variety of sources, including electron-beam evaporation, magnetron sputtering, and arc evaporation (Ref 21, 22). In the ion plating variation of the basic PVD process, the flux of atoms and ions is activated by an electrical glow discharge plasma, and the charged species are accelerated toward the substrate by applying a negative bias potential on the substrate. For hard coatings, the evaporated or sputtered metal or cation species (titanium, hafnium, zirconium, etc.) are evaporated or sputtered and are made to react with the gaseous species (N_2, NH_3, CH_4, etc.) introduced into the vacuum chamber. Because PVD coatings are produced at low pressures (10^{-3} to 10^{-2} torr), the atoms and molecules have long mean free paths and undergo fewer collisions, making PVD a line-of-sight deposition technique. This necessitates moving the tool fixtures during the PVD deposition to ensure uniformly thick coatings on both the rake and flank faces of tool inserts.

A number of factors make the PVD process attractive for use with cemented carbide tools:

- Lower deposition temperature (<500 °C, or 930 °F) prevents eta-phase formation and produces crack-free coatings with finer grain sizes.
- The coatings are smooth and thus generate less frictional heat during machining.
- Depending on the deposition technique, compressive residual stresses, which are beneficial in resisting crack propagation, may be introduced into the coating (Ref 23).
- PVD coating preserves the transverse rupture strength of the carbide substrate, whereas the CVD

process generally reduces the transverse rupture strength by as much as 30% (Ref 24, 25).

- PVD coatings can be applied uniformly over sharp cutting edges (Fig. 6a). A sharp edge is desirable in a cutting tool because it leads to lower cutting forces, reduced tool-tip temperatures, and finer workpiece surface finishes.

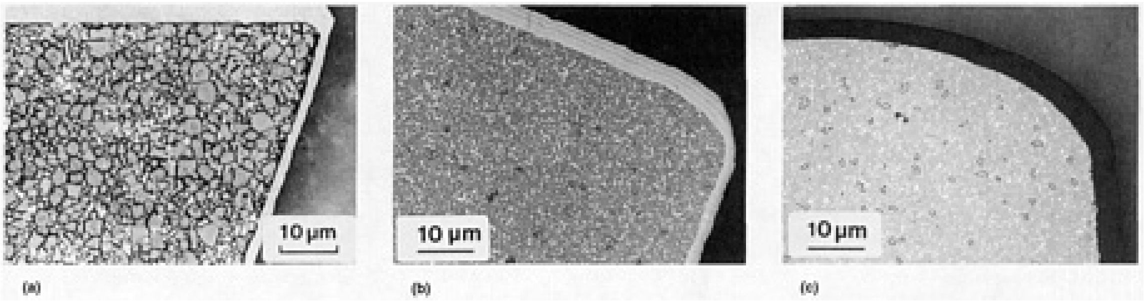


Fig. 6 Physical vapor deposition coatings on cemented carbide substrates. (a) TiN. (b) TiCN. (c) TiAlN

In the last three years, newer compositions such as TiCN (Fig. 6b), TiAlN (Fig. 6c), TiZrN, and CrN have been commercialized using the PVD process. PVD Al_2O_3 coatings, however, are not yet commercially available.

Additional information about PVD coatings is available in the articles "Growth and Growth-Related Properties of Films Formed by Physical Vapor Deposition Processes" and "Vacuum Deposition, Reactive Evaporation, and Gas Evaporation" in this Volume.

Plasma-Assisted CVD Coatings. The high deposition temperatures (~1000 °C, or 1830 °F) of CVD coatings can degrade the strength of the cemented carbide substrate. On the other hand, the PVD coating process, which takes place at lower temperatures (~500 °C, or 930 °F), has a line-of-sight disadvantage. A compromise between the two techniques is the plasma-assisted CVD coating process, which offers a combination of moderate deposition temperature (~600 °C, or 1110 °F) and good thickness uniformity without the need to rotate the tools during the coating process.

In the traditional CVD process, thermal energy activates the chemical reaction that forms the hard coating compounds. In plasma-assisted CVD, lower-temperature activation is enabled by the energetic particles in a plasma, typically an argon discharge. Both direct-current and radio-frequency power supplies are used to deposit the conducting (TiN and TiC) and insulating (Al_2O_3) coatings (Ref 26). Use of plasma-assisted CVD for hard coatings on cemented carbide substrates is not yet widespread, probably due in part to the process economics relative to the competing CVD and PVD methods. Additional information is available in the article "Plasma-Enhanced Chemical Vapor Deposition" in this Volume.

CVD/PVD Coatings. A recent development in carbide cutting tool coatings combines an outer PVD TiN layer with inner CVD TiN/TiCN layers on a tough cobalt-enriched substrate for interrupted cutting applications such as milling (Fig. 7). The inner CVD layers provide excellent adhesion and wear resistance, and the outer PVD layer offers a hard, fine-grain, crack-free, smooth surface endowed with compressive residual stress. The synergistic effects of this combination contribute to excellent tool performance in milling of steel components at relatively high speeds (Ref 27).

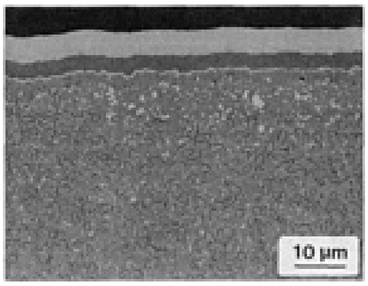


Fig. 7 Combination of a chemical vapor deposition TiN-TiCN coating and a physical vapor deposition TiN coating on a cobalt-enriched cemented carbide insert

Diamond Coatings. The most recent addition to the development of hard coatings is the low-pressure synthesis of diamond films by carbonaceous gas decomposition in the presence of hydrogen ions. This process is an alternative to the high-pressure, high-temperature synthesis of bulk diamond, which is used to fabricate PCD tips that are brazed onto WC-Co substrates. These PCD-tipped inserts are relatively expensive, but they provide a 20- to 100-fold increase in tool life over uncoated WC-Co inserts in the machining of highly abrasive nonferrous alloys (e.g., aluminum-silicon).

The progress in thin-film diamond coating research has been significant in the last few years. The outstanding problem to date has been unsatisfactory adhesion of the diamond coating to the carbide substrate, partly due to an inherently large mismatch in the coefficients of thermal expansion. Although a ceramic substrate such as silicon nitride presents a better match with diamond, WC-Co-based substrates are more economical when good diamond coating adhesion is obtained. Diamond-coated carbide inserts with good coating adhesion are now being introduced commercially. Recent data from field tests indicate that such diamond-coated inserts can approach the performance of the PCD counterparts (Ref 28). Additionally, diamond-coated inserts will eventually feature chipbreaker designs that are difficult to fabricate in PCD inserts. Research continues regarding the control of diamond grain morphology (Fig. 8) as it relates to the final workpiece surface finish.

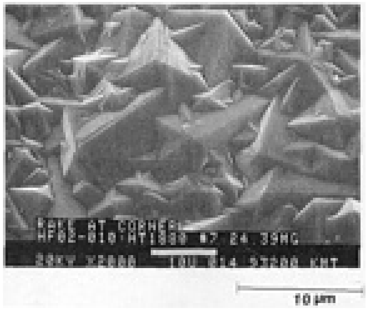


Fig. 8 Diamond coating on a cemented carbide insert

Ion implantation is a surface modification process that consists of injecting energetic ions into the surface layers of a material. It has been applied to carbide wear products and end mills with limited success (Ref 29). Its main drawback is that the implantation depth and subsurface region disordered by knock-on collisions are no deeper than tenths of a micron. This is much too thin compared to hard coatings that are typically 5 to 10 μm. Ion implantation has therefore not been successfully applied in machining applications. Additional information about this process is available in the article "Ion Implantation" in this Volume.

References cited in this section

13. C.S. Ekmar, German Patent 2,007,427, Feb 1969
14. W. Schintlmeister, O. Pacher, K. Pfaffinger, and T. Raine, in *J. Electrochem. Soc.,* Vol 123, 1976, p 924-929
15. V.K. Sarin and J.N. Lindstrom, in *J. Electrochem. Soc.,* Vol 126, 1979, p 1281-1287
16. W.A. Bryant, F.B. Battaglia, B.K. Downey, and K.E. Undercoffer, in *Proceedings of the 12th International Plansee Seminar,* Metallwerk Plansee GmbH, 1989, p 187-210
17. B.J. Nemeth, A.T. Santhanam, and G.P. Grab, in *Proceedings of the 10th International Plansee Seminar,* Metallwerk Plansee GmbH, 1981, p 613-627
18. A.T. Santhanam, G.P. Grab, G.A. Rolka, and P. Tierney, An Advanced Cobalt-Enriched Grade Designed to

Enhance Productivity, *High Productivity Machining--Materials and Processes,* American Society for Metals, 1985, p 113-121

19. M. Bonetti-Lang, R. Bonetti, H.E. Hintermann, and D. Lohmann, in *Int. J. Refractory Hard Metals,* Vol 1, 1982, p 161-165
20. R.S. Bonetti, H. Wiprachtiger, and E. Mohn, in *Metal Powder Report,* Vol 45, 1990, p 837-840
21. R.F. Bunshah, Ed., *Deposition Technologies for Films and Coatings: Developments and Applications,* Noyes Publications, 1982
22. W.D. Sproul, *Cutting Tool Engineering,* CTE Publications, Inc., 1994, p 52-57
23. D.T. Quinto, A.T. Santhanam, and P.C. Jindal, in *Mater. Sci. Eng.,* Vol A105/106, 1988, p 443-452
24. K. Kamachi, T. Ito, and T. Yamamoto, in *Surf. J. Int.,* Vol 1, 1986, p 82-86
25. G.J. Wolfe, C.J. Petrosky, and D.T. Quinto, in *J. Vac. Sci. Technol.,* Vol A4 (No. 6), 1986, p 2747-2754
26. U. Konig, R. Tabersky, and H. Vanden Berg, in *Surf. Coat. Technol.,* Vol 50, 1991, p 57-62
27. A.T. Santhanam, R.V. Godse, G.P. Grab, D.T. Quinto, K.E. Undercoffer, and P.C. Jindal, U.S. Patent 5,250,367, 5 Oct 1993
28. A. Inspektor, C.E. Bauer, and E.J. Oles, paper presented at Internat. Conf. Met. Coatings and Thin Films '94 (San Diego, CA), 25-29 April 1994, to be published in *Surf. Coat. Technol.*
29. J.R. Treglio, A. Tian, and A.J. Perry, in *Surf. Coat. Technol.,* Vol 62, 1993, p 438-442

Properties of Hard Coatings

The successful application of hard coatings on cutting tool substrates is due to the combination of physical and mechanical properties of the coating. From a functional standpoint, chemical stability, hot hardness, and good adhesion to the substrate are essential; optimum coating thickness, fine microstructures, and compressive residual stresses can further enhance their performance.

Chemical Stability. The criterion for chemical inertness is either a high negative standard free energy of formation of the coating material or low solubility in the workpiece material at temperatures encountered during machining. As can be seen in Fig. 9 and Table 4, CVD Al_2O_3 coatings singularly meet these requirements for machining of irons and steels. However, amorphous PVD Al_2O_3 coatings are unstable and are not as satisfactory as the crystalline Al_2O_3 obtained in CVD. PVD TiAlN coatings are also chemically stable and offer the potential for high-speed machining of steels. Diamond-coated tools are suitable for machining nonferrous alloys containing abrasive second-phase particles (e.g., aluminum-silicon alloys) as well as for machining nonmetallic materials that do not react with carbon (e.g., metal-matrix composites and fiber-reinforced plastics).

Table 4 Properties of chemical vapor deposited coating materials

Material	Room-temperature microhardness kg/mm^2	Coefficient of thermal expansion µm/·K	Thermal conductivity at 1000 K, W/m·K	Relative dissolution rates into iron at:	
				500 °C (932 °F)	1100 °C (2030 °F)
TiC	2800-3200	7.7	38	1.0	1.0
TiN	2000-2200	9.4	25	1.8×10^{-3}	2.2×10^{-1}
HfN	1700	6.9	10	3.8×10^{-5}	2.5×10^{-2}
Al_2O_3	2100-2300	8.4	7.5	8.9×10^{-11}	4.1×10^{-5}

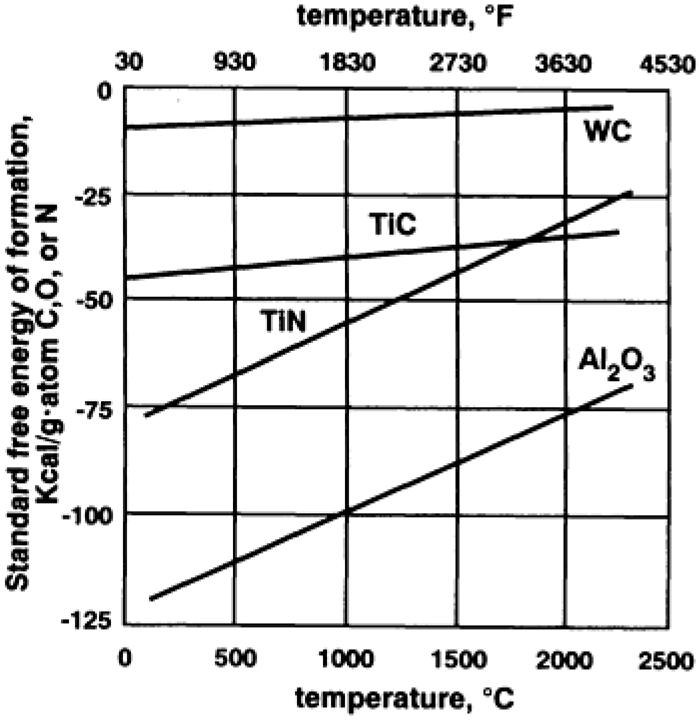


Fig. 9 Variation in the standard free energy of formation of WC, TiN, TiC, and Al_2O_3 with temperature. This parameter gives an indication of the extent to which these materials will undergo diffusion wear.

Hot Hardness. The importance of coating material hardness in resisting abrasive wear has been well documented (Ref 30). High coating hardness is also believed to be beneficial in resisting the abrasive wear component of crater wear (Ref 31). The relevant hardness corresponds to the high temperatures characteristic of those prevalent during machining. Figure 10 shows Vickers microhardness as a function of test temperature for Al_2O_3, TiN, and TiC. Although TiC has high room-temperature hardness, it loses hardness rapidly with temperature. Al_2O_3, on the other hand, has lower room-temperature hardness but retains its hardness to higher temperatures. The data thus suggest that TiC coatings would be more effective at lower speeds, whereas Al_2O_3 coatings, by virtue of high hot hardness and chemical stability, would be most effective for high-speed machining. These concepts have been validated in the machining of 1045 steel and gray cast iron (Ref 32).

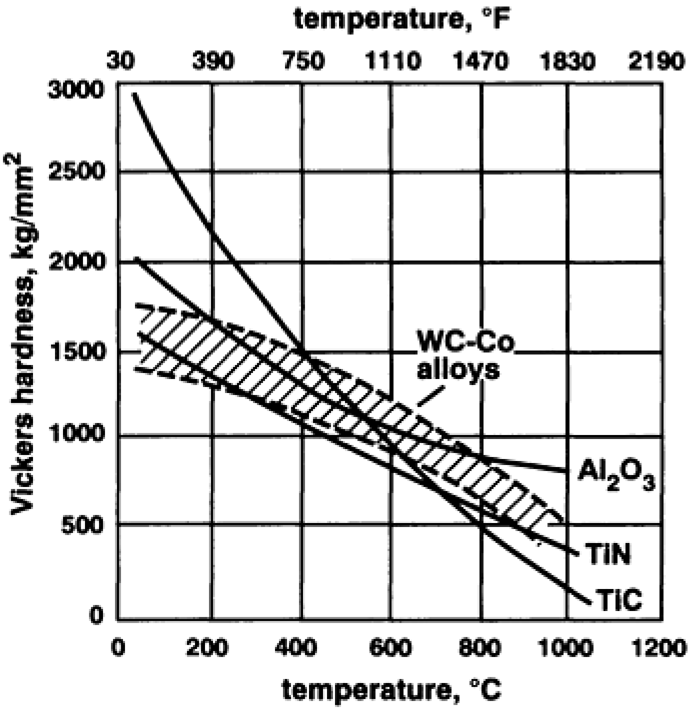


Fig. 10 Temperature dependence of hardness of TiC, Al_2O_3, and TiN. The range of hardness of WC-Co alloys is also shown.

Microstructure. The microstructure of hard coatings controls their mechanical properties and metalcutting performance. A generalized Hall-Petch relationship between grain size of the coating and microhardness has been shown to hold true for CVD and PVD coatings (Ref 33). The higher measured microhardness of PVD TiN relative to that of CVD TiN has been attributed not only to the finer grain sizes obtained in the PVD process but to the presence of compressive residual stresses (Ref 33). Compressive residual stress developed during ion bombardment in certain PVD processes retards crack propagation and thus produces a fracture toughness advantage for PVD-coated tools.

Grain boundary voids developed during columnar growth of some PVD coatings do not allow retention of residual stresses and lead to lower hardness (Ref 34). Likewise, CVD coarse-grain alpha-Al_2O_3, which grows with intergranular voids, is not expected to be as hard as the void-free, fine-grain kappa-Al_2O_3. Alternating multilayers of CVD kappa-Al_2O_3, which have fine grain sizes due to periodic interruption of growth, are harder than Al_2O_3 that has been allowed to grow as a single, thick coating (Ref 17). However, transformation from the metastable kappa phase to the stable alpha phase at high temperatures (~1050 °C, or 1920 °F) may induce stresses and a subsequent decrease in coating adhesion.

Coating morphology can also affect surface roughness, which in turn may increase the frictional forces and generate heat at the chip-tool interface. It is known that the relatively smoother PVD TiN-coated carbide tools decrease cutting forces and produce better workpiece surface finishes than CVD-coated tools (Ref 25). In contrast, rough surface morphology is still an issue in diamond coatings (Ref 28).

Adhesion. Good coating adhesion to the substrate is a necessary condition for satisfactory performance of the coated tool. It has been shown that varying levels of measured adhesion directly relate to tool life, other variables being constant (Ref 33).

During the high-temperature CVD process, initial coating nucleation on the carbide substrate occurs under conditions that allow interdiffusion of coating and substrate atoms at the interface. In plasma-assisted PVD processes, energetic ion bombardment creates lattice defects that enhance diffusion of coating species at the interface, even at lower deposition temperatures.

It is necessary to choose compatible coating-substrate combinations that accommodate film growth stresses and thermal mismatch stresses at the interface. As noted earlier, coating phase transformations can also induce stresses that may affect

adhesion. Substrate surface contaminants prior to coating, particularly in the PVD process, can have detrimental effects on coating adhesion and should be minimized. The use of a thin titanium interlayer to remove residual oxide contaminants, as well as to accommodate interfacial stress, is now common in industrial PVD TiN deposition (Ref 35). Current PVD technology provides well-adhered coatings that are as effective as CVD coatings in demanding applications.

Coating Thickness. To achieve maximum metalcutting productivity, the thickness of the modified surface layer has to be optimized. If the modified tool surface region is too thin, the effect persists for a negligibly short time during cutting. If the coating is too thick, the layer acts as a bulk material and the advantage of an engineered composite may be lost. It is established that functional tool coatings should be at least 2 μm thick and that they may be as thick as 20 μm. Coatings deposited by CVD are typically 10 μm thick, while PVD coatings are usually less than 5 μm thick. As mentioned above, ion implantation, which affects no more than 0.1 μm of surface depth, has been found to be ineffective.

References cited in this section

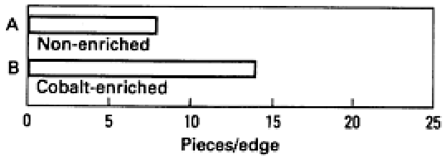
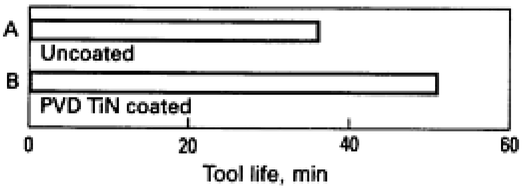
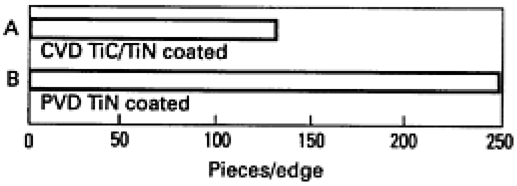
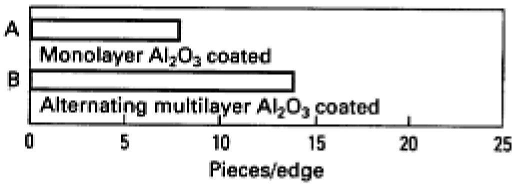
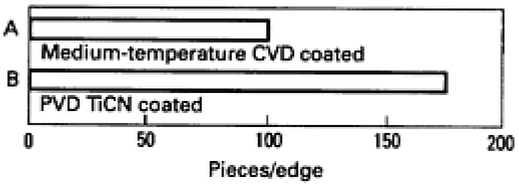
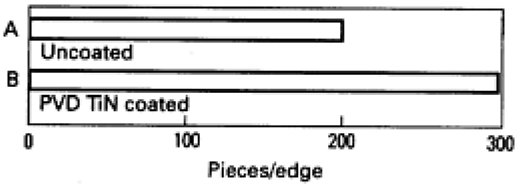
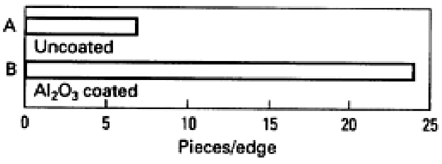
17. B.J. Nemeth, A.T. Santhanam, and G.P. Grab, in *Proceedings of the 10th International Plansee Seminar,* Metallwerk Plansee GmbH, 1981, p 613-627
25. G.J. Wolfe, C.J. Petrosky, and D.T. Quinto, in *J. Vac. Sci. Technol.,* Vol A4 (No. 6), 1986, p 2747-2754
28. A. Inspektor, C.E. Bauer, and E.J. Oles, paper presented at Internat. Conf. Met. Coatings and Thin Films '94 (San Diego, CA), 25-29 April 1994, to be published in *Surf. Coat. Technol.*
30. B.M. Kramer, in *J. Vac. Sci. Technol.,* Vol A4, 1986, p 2870-2873
31. P.K. Mehrotra and D.T. Quinto, in *Metal Powder Reports,* Vol 41, 1986, p 891-898
32. T.E. Hale, paper presented at the International Machine Tool Show Technical Conference, National Machine Tools Builders Association, 1982
33. D. T. Quinto, in *J. Vac. Sci. Technol.,* Vol A6, 1988, p 2149-2157
34. P.J. Burnett and D.S. Rickerby, in *Surf. Eng.,* Vol 3 (No. 1), 1987, p 69-76
35. S.J. Bull, P.R. Chalker, C.F. Ayres, and D.S. Rickerby, in *Mater. Sci. Eng.,* Vol A139, 1991, p 71-78
46. R. Porat, in *Proceedings of the 8th International Conference on CVD,* J.M. Blocher, Ed., Electrochemical Society, 1981, p 533
47. B.N. Kramer and P.K. Judd, in *J. Vac. Sci. Technol.,* Vol A3 (No. 6), 1985, p 2439-2444

Application of Coated Tools

The advent and evolution of various coating technologies has produced a wide array of coated carbide tools with broad application ranges. At the same time, specialized areas of application exist where specific coatings and/or substrates offer outstanding performance. Typical applications for each category of coated metalcutting tools are highlighted below. Table 5 gives a few examples of machining productivity enhancements that are due to surface modification of carbide, cermet, and ceramic tool materials.

Table 5 Effect of surface treatments on the performance of cemented carbide, cermet, and ceramic tool materials

Operation	Work material	Cutting speed		Feed rate	Depth of cut		ISO No. (ANSI No.)	Results
		m/min	sfm		mm	in.		
Cemented carbide tool materials								

Turning[(a)]	4137H steel forging	73-98	240-320	0.76 mm/rev (0.03 in./rev)	4.6-19	0.2-0.7	TNMG 330924 (TNMG 666)	
Face milling	1020 steel	152	500	0.18 mm/tooth (0.007 in./tooth)	. . .	. . .	SPGN 120308 (SPG 422)	
Camshaft milling	5150 steel	274	900	0.18 mm/tooth (0.007 in./tooth)	. . .	. . .	SPGN 190412 (SPG 633)	
Facing	Ductile iron	174	570	0.50 mm/rev (0.02 in./rev)	9.38	0.4	CNMG 190612 (CNMG 643)	
Face milling	1020 steel	330	1080	0.20 mm/tooth (0.008 in./tooth)	3.75	0.15	SEHW 1204AFTN (SEHW 43AGT)	
Cermet tool mateial								
Turning and facing	430F stainless steel	197	640	0.15 mm/rev (0.006 in./rev)	1.0	0.04	VNMG 160408 (VNMG 332)	
Ceramic tool mateial								
Turning and facing	Gray cast iron brake drum	550	1800	0.63 mm/rev (0.025 in./rev)	3.75-5.0	0.15-0.2	RNGN 120400T (RNG 43T)	

(a) CVD TiC/TiCN/TiN coated tool

CVD-Coated Tools. Normal-temperature (~1000 °C, or 1830 °F) CVD-coated cemented carbides make up over 80% of all coated carbide metalcutting tools in use. These tools are employed in a variety of metalcutting applications, including turning, boring, parting, threading, grooving, and milling. They are used in machining carbon, alloy, and stainless steels and gray and ductile cast irons, covering a very wide range of speeds and feeds.

CVD-Coated Tools with Cobalt-Enriched Substrates. Multilayer CVD-coated tools with specially tailored cobalt-enriched substrates combine the wear resistance of the hard coatings with an edge-toughened substrate. These tools can therefore handle medium to heavy roughing to semifinishing operations on cast irons and high-temperature alloys, as well as stainless, low-carbon, and alloy steels. The broad application range of cobalt-enriched tools enables them to cover a large percentage of the metalcutting operations of a plant, allowing the user to stock fewer grades.

Medium-Temperature CVD and Plasma-Assisted CVD Coated Tools. The microstructures of tools coated by medium-temperature CVD and plasma-assisted CVD are characterized by a negligible amount of eta phase at the coating-substrate interface. This permits them to be used in all applications where normal-temperature CVD tools are applied, in addition to those operations that involve interrupted cuts (Ref 26, 36).

CVD/PVD-coated tools benefit from the synergistic effects of wear-resistant inner CVD layers combined with a smooth, fine-grain, crack-free outer PVD layer featuring compressive residual stresses. CVD/PVD-coated tools are therefore suited for interrupted cutting operations such as milling of low- and medium-carbon steels and alloy steels (Ref 27). The full potential of CVD/PVD coatings on cemented carbide tools has yet to be determined.

PVD-Coated Tools. The PVD coating process offers unique advantages, including the ability to apply a fine-grain, smooth, low-friction, and crack-free coating over sharp edges. When deposited by the ion plating method, PVD coatings also feature compressive residual stresses. These characteristics make PVD-coated tools particularly useful in threading, grooving, parting, finish-turning, and milling operations. Typical workpiece materials include low-carbon and alloy steels, hardened steels, stainless steels, and high-temperature nickel-base alloys.

Diamond-Coated Tools. Diamond coatings, with their extremely high hardness, can provide excellent productivity in the machining of nonferrous alloys containing abrasive second-phase particles, such as aluminum-silicon alloys, and in the machining of composite nonmetallic materials that do not have a chemical reactivity problem with carbon. Initial applications of the diamond-coated tools will be similar to those where PCD tools are applied (Ref 37), with the former providing further flexibility in the use of molded chipbreakers, and in rough cuts where surface finish requirement is not stringent.

References cited in this section

26. U. Konig, R. Tabersky, and H. Vanden Berg, in *Surf. Coat. Technol.,* Vol 50, 1991, p 57-62
27. A.T. Santhanam, R.V. Godse, G.P. Grab, D.T. Quinto, K.E. Undercoffer, and P.C. Jindal, U.S. Patent 5,250,367, 5 Oct 1993
36. E. Kubel, in *Surf. Coat. Technol.,* Vol 49, 1991, p 268-274
37. B. Lux, in *Proceedings of the 12th International Plansee Seminar,* Vol 3, H. Bildstein and H.M. Ortner, Ed., Metallwerk Plansee GmbH, 1989, p 615

Coatings for Ceramic and Cermet Inserts

Coatings for ceramic and cermet tool materials have not received the extensive development efforts enjoyed by coatings for cemented carbide tools. This is mainly because ceramic and cermet tools amount to less than 10% of the inserts employed in North America and Europe (although they account for about 35% of those used in Japan). Nevertheless, hard coatings for the ceramic and cermet tools can and do provide productivity benefits in certain applications (Table 5).

The chemical reactivity of silicon-nitride-based ceramics is relatively high and limits their usefulness in machining ferrous workpieces. However, application of an Al_2O_3 coating (which is chemically inert) enables users to exploit the high hot hardness of the silicon nitride substrate (Ref 38).

Current developments in cermets emphasize raising toughness through increases in nickel and cobalt binder contents. These changes have the desired effect but also raise the tools' chemical reactivity, compromising their usefulness on ferrous workpieces. Coatings can provide a solution to the problem, but the high process temperatures of conventional CVD coatings tend to produce brittle intermetallic compounds involving nickel and titanium. Hence, coatings for cermet tools have focused on those applied by the PVD process.

Reference cited in this section

38. V.K. Sarin and S.T. Buljan, Alumina Coated Silicon Nitride Cutting Tools, U.S. Patent 4,440,547, 1984

Future Potential

After two decades of material and process innovations, CVD hard coating technology is now mature. The multilayer approach has been very successful in expanding the functionality of the hard coating, and it is anticipated that this design will be duplicated with the newer PVD technology. The property enhancements obtainable in PVD, such as controlled residual compressive stress and fine grain morphology, are expected to be exploited further; indeed, the PVD counterparts may challenge similar CVD coatings as the process economics of the two methods begin to converge. PVD processes are also environmentally cleaner because they do not produce the gaseous effluents characteristic of CVD.

How will the newer coating technologies compare against conventional CVD? To truly compete with all present CVD coatings, an adherent PVD Al_2O_3 coating with crystalline microstructure must be developed. Beyond the conventional hard coating compounds, however, PVD techniques offer a larger range of possible compositions, including metastable compounds, that can perhaps be exploited in particular applications (Ref 39). Polycrystalline superlattice coatings such as TiN/NbN, TiN/Ni, and TiN/Ni-Cr are reported to have significantly higher microhardnesses than those of homogeneous nitrides and are promising for metalcutting applications (Ref 40).

The lower-temperature processes, such as medium-temperature CVD TiCN and plasma-assisted CVD, will grow as alternative coating technologies if the ability to deposit a variety of compositions is demonstrated. Combinations of various coating technologies will make sense when material and process economics are justified.

Diamond coatings on metalcutting inserts are expected to be commercially available soon (Ref 28, 41) as upscaling of equipment and optimization of performance are achieved in industrial tests. The major challenge in the coming years will be the successful synthesis of CBN superhard coatings by low-pressure methods. CBN coatings have more industrial potential than diamond because they will be useful in high-volume ferrous cutting applications. Researchers are now taking technical approaches similar to those that led to the realization of diamond coatings (Ref 42, 43), but interrelated issues of film stability, residual stress, coating thickness, adhesion to the matched tool substrate, and upscaling to large-area deposition are still outstanding.

References cited in this section

28. A. Inspektor, C.E. Bauer, and E.J. Oles, paper presented at Internat. Conf. Met. Coatings and Thin Films '94 (San Diego, CA), 25-29 April 1994, to be published in *Surf. Coat. Technol.*
39. O. Knotek, F. Loffler, and G. Kramer, in *Surf. Coat. Technol.,* Vol 54/55, 1992, p 241-248
40. X. Chu, M.S. Wong, W.D. Sproul, and S.A. Barnett, in *Surf. Coat. Technol.,* Vol 61, 1993, p 251-256
41. F.M. Cerio, J.A. Herb, and R. Cummings, in *Surf. Coat. Technol.,* Vol 62, 1993, p 674-679
42. S. Watanabe, S. Miyake, and M. Murakawa, in *Surf. Coat. Technol.,* Vol 62, 1993, p 558-563
43. T. Ikeda, T. Satou, and H. Satoh, in *Surf. Coat. Technol.,* Vol 50, 1991, p 33-39

Environmental Regulation of Surface Engineering

David J. Smukowski, Boeing Commercial Airplane Group

Introduction

ENVIRONMENTAL PROTECTION REGULATIONS are often related directly or indirectly to surface engineering processes. This article describes selected U.S. environmental statutes and regulations as they are pertinent to material surface finishers. For information about specific regulatory requirements, permitting conditions, and enforcement issues, the reader is advised to seek assistance from federal, state, and local regulatory agencies, consulting engineering firms, and law offices.

Acknowledgements

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Environmental Protection System

U.S. environmental protection has become a complex system of statutes, regulations, guidance documents, executive directives, and standards that are intended to protect human health and the environment. A basic understanding of these requirements will assist those who need to reduce or eliminate the environmental impact of their operations in a cost-effective manner.

History of the Environmental Movement. Winston Churchill wrote that "The further back you look, the further forward you can see." The history of the environmental movement shows that environmental management is inextricably linked to population, resources, and technology.

In the 17th and 18th centuries, resources such as land, timber, fish, minerals, and water were considered inexhaustible and free for the taking. This way of thinking changed as the population grew. By the late 18th century, New York, Chicago, and Philadelphia alone contained over one million people. By 1910, 50% of the U.S. population lived in cities.

During the era of the Great Depression, the Tennessee Valley Authority, the Civilian Conservation Corps, the Soil Conservation Service, and the Wilderness Society were created to provide jobs to the unemployed and begin nursing the land. When World War II brought massive industrialization without regard for air or water quality, many states drafted legislation to curtail pollution.

The social revolution of the 1960s and 1970s brought the Clean Air Act and the Clean Water Act, but these did little but divert wastes to landfills. In 1980 the Resources Conservation and Recovery Act (RCRA) was passed for the purpose of tracking hazardous waste from "cradle to grave." The 1990s opened a new era in which we better understand past practices and look less often for end-of-pipe or end-of-stack treatments. We now look at design, materials, and processes to eliminate the root causes of waste production and pollution.

Environmental Law. The term *environmental law* does not fully convey its meaning. Once a law is developed, rules for compliance are promulgated, and recordkeeping systems, monitoring procedures, and inspection schedules are developed to enforce compliance. For example, for the eight federal statutes discussed in this article, which constitute some 1,200 pages of text, another 13,000 pages of federal regulations have been developed to carry out the laws (Fig. 1), along with countless more pages of state and local laws, regulations, and guidance documents. These pages have evolved into a web of requirements that constitutes a classic "command and control" system of enforcement.

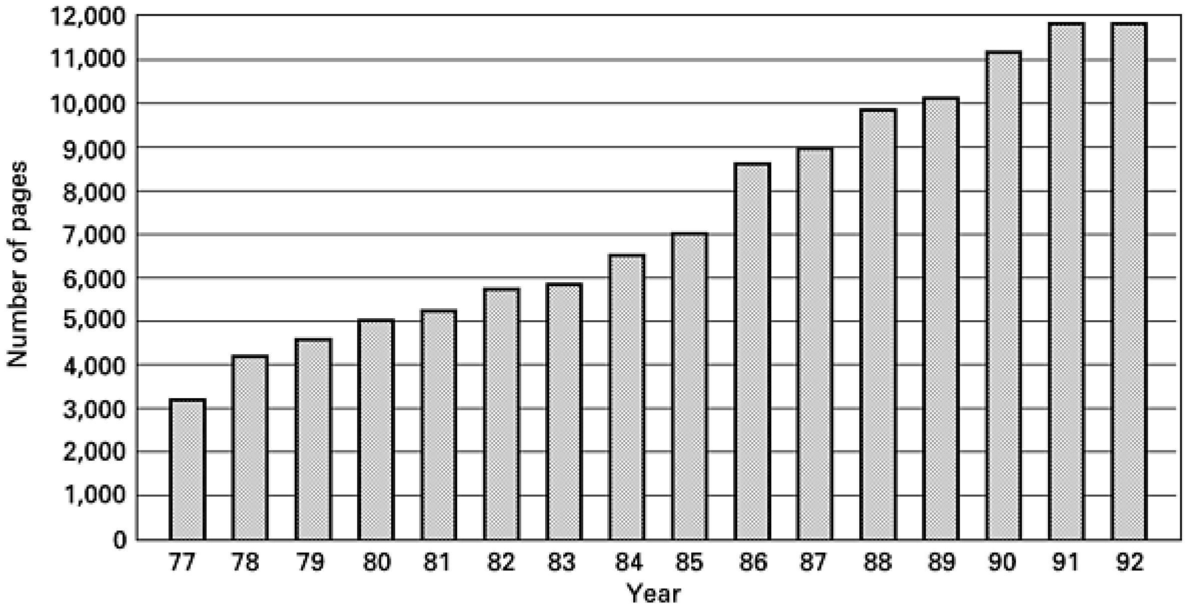

Fig. 1 Growth of federal regulation. The 1992 figure is given as of July 1. Source: 40 CFR

The Legislative Process. Federal and state procedures for making laws are similar. The first step in the federal procedure is that a bill is introduced in either the U.S. House of Representatives or the U.S. Senate. Each bill is assigned a number, preceded by an "S" (for a Senate bill) or "H.R." (for a House bill). Bills are then referred to committees of focused expertise for consideration. These committees hold hearings, study, investigate, and issue a report on the bill. When a bill is "reported out" of a committee, it is debated by the House and/or Senate. The House and Senate typically pass different versions of bills, which are then sent to a joint conference committee. When that committee comes to agreement, a bill is sent to the President for signature or veto within ten days. Once signed, a bill is public law.

State and Local Laws. Federal law generally sets only the minimum requirements of environmental law. States and local jurisdictions have the right to exceed federal standards to meet regional needs. In most large metropolitan areas, local rules will be considerably more stringent than the federal requirements in this article.

The Regulatory Process. Environmental laws empower administrative agencies, such as the Environmental Protection Agency (EPA) and the Occupational Safety and Health Administration (OSHA), to promulgate detailed regulations on how to meet the law. Alternatively, the President can write an Executive Order and direct an agency such as the Department of Defense to promulgate regulations.

Rulemaking includes collecting data from industry. The EPA often uses a mandatory questionnaire called a Section 114 request to collect data. The EPA then interprets the data and proposes regulations in the *Federal Register.* After a comment period, final regulations are published in the *Federal Register,* along with preamble discussion of the comments received and their interpretation by the agency. These regulations have the same effect as law and are incorporated into the *Code of Federal Regulations* (CFR).

Figure 2 shows the typical relationships between the legislative and regulatory processes.

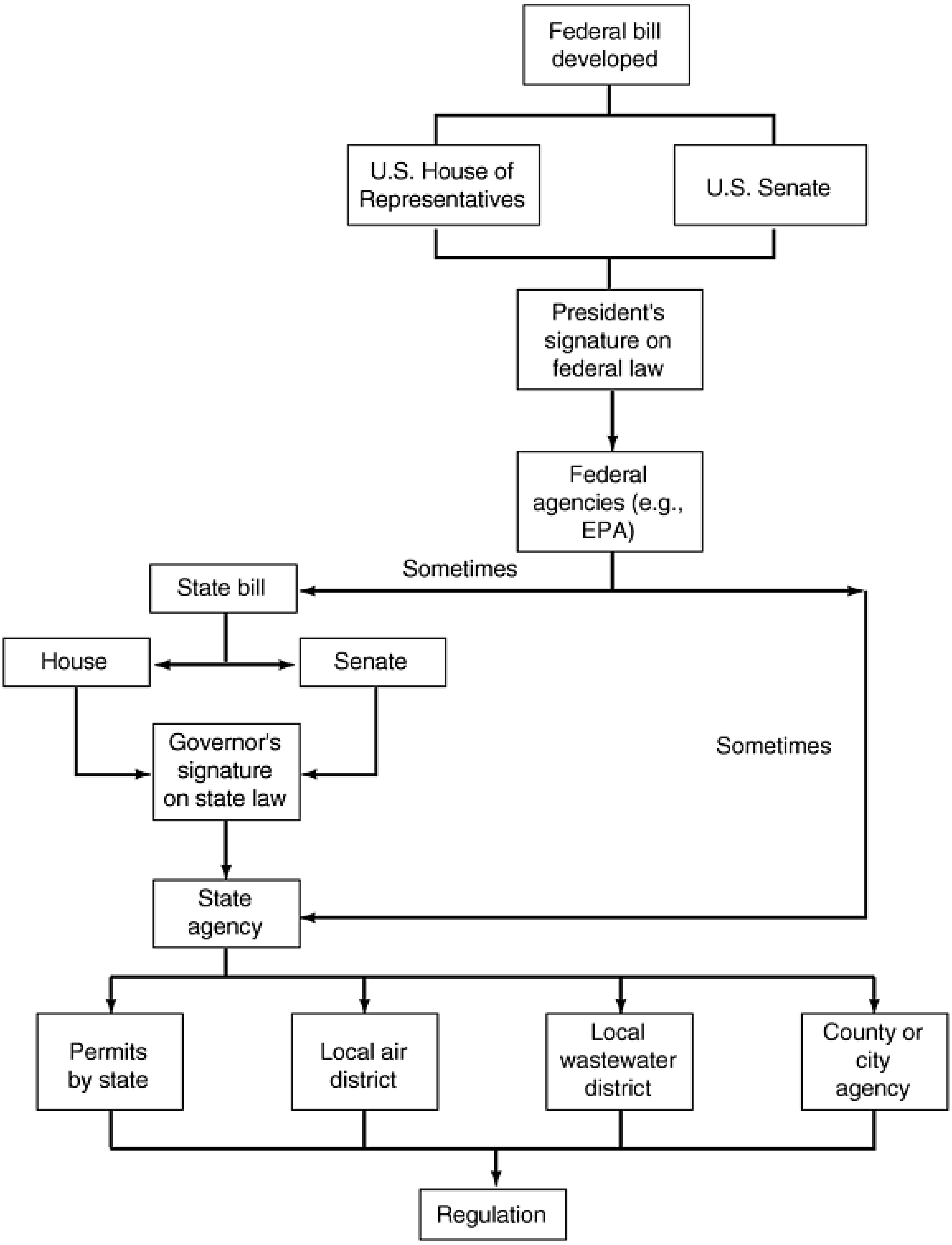

Fig. 2 Typical relationships between the legislative and regulatory processes

Content of Environmental Laws and Regulations. Most environmental laws and ensuing regulations contain the same elements:

- Broad statement of purpose
- Inventory of the problem
- Standards of compliance with emissions, discharges, or disposal
- Notification of the public

- Monitoring and records
- Government fee or funding mechanism
- Prohibitions and/or bans
- Technical control equipment and material standards
- Inspection and assistance
- Reports and/or plans
- Enforcement penalty requirements
- Permits
- Detailed compliance requirements, such as labeling and signs

These elements place the burden on the regulated community to provide information to the government that establishes compliance with the law. A facility must inform the government if it plans to engage in any activity that may result in storing, using, or releasing a regulated material. This begins a complex chain of planning, permit seeking, training, self-monitoring, and reporting. Noncompliance typically results in both civil and criminal penalties. Therefore, it is imperative that all surface preparation processes be understood in the context of environmental law.

The Clean Air Act

The federal Clean Air Act (CAA), written in 1965 and amended in 1970, 1977, and 1990, is the most controversial and industry-intrusive environmental law ever developed. Initially it researched air quality, federalized air pollution control, provided for health protection, and controlled mobile and stationary sources of pollutants (e.g., automobiles and factories).

The 1977 amendments added National Ambient Air Quality Standards (NAAQS), which set criteria for designating regions of the country that do not meet standards for particulates, nitrous oxide (NOX), sulfur oxide (SOX), lead, carbon monoxide, and ozone-depleting substances. These areas of "nonattainment" can then be targeted for stricter requirements.

The 1990 amendments are the most onerous to industry in that they ban, restrict, and/or rigidly control most chemical emissions from industry. Most of the requirements will be effective between 1995 and 2000, posing both drastic changes and opportunities for surface engineering. The basic requirements for surface engineering are scheduled to expand considerably through the year 2000, so the reader should review the most up-to-date literature available.

Overview. The CAA requires that material surface finishers:

- Reduce or eliminate the use of volatile organic compounds (VOCs), which create smog through photochemical reactions. Most VOCs will be reduced, categorically, by industry group.
- Control, reduce, or eliminate 189 chemicals determined to be hazardous air pollutants (HAPs). Under the National Emission Standard for Hazardous Air Pollutants (NESHAP), hundreds of regulations are being written for emitting industries.
- Phase out ozone-depleting substances
- Obtain an operating permit for sources of VOCs and HAPs that trigger threshold amounts
- Reduce emissions from power plants, to reduce the generation of "acid rain" from NOX and SOX

Applicability. Following are the broad thresholds for determining whether a surface finishing process requires an operating permit and may be subject to additional regulations. These thresholds are presented for general information only; the reader is advised to consult local authorities.

- *Source of VOCs:* Has the potential to emit more than 10, 25, 40, or 100 tons/year of VOCs, depending on the region. VOC emissions are the cumulative weight of chemicals emitted from cleaning, degreasing, painting, wiping, and similar processes, assuming operation for 24 hours/day, 365 days/year.
- *Source of HAPs:* Has the potential to emit more than 10 tons/year of any listed HAP (Table 1) or more than 25 tons/year of a combination of HAPs

- *Source of Ozone-Depleting Substances:* Emits any volume of chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), halons, or methyl chloroform (1,1,1-trichloroethane)
- *Source of NOX or SOX:* Has the potential to emit more than 25 tons/year

Table 1 List of hazardous air pollutants regulated by the Clean Air Amendments of 1990

CAS No.	**Chemical name**
75070	Acetaldehyde
60355	Acetamide
75058	Acetonitrile
98862	Acetophenone
53963	2-Acetylaminofluorene
107028	Acrolein
79061	Acrylamide
79107	Acrylic acid
107131	Acrylonitrile
107051	Allyl chloride
92671	4-Aminobiphenyl
62533	Aniline
90040	o-Anisidine
1332214	Asbestos
71432	Benzene (including benzene from gasoline)
92875	Benzidine
98077	Benzotrichloride

100447	Benzyl chloride
92524	Biphenyl
117817	Bis(2-ethylhexyl)phthalate (DEHP)
542881	Bis(chloromethyl)ether
75252	Bromoform
106990	1,3-Butadiene
156627	Calcium cyanamide
105602	Caprolactam
133062	Captan
63252	Carbaryl
75150	Carbon disulfide
56235	Carbon tetrachloride
463581	Carbonyl sulfide
120809	Catechol
133904	Chloramben
57749	Chlordane
7782505	Chlorine
79118	Chloroacetic acid
532274	2-Chloroacetophenone
108907	Chlorobenzene
510156	Chlorobenzilate

67663	Chloroform
107302	Chloromethyl methyl ether
126998	Chloroprene
1319773	Cresols/Cresylic acid (isomers and mixture)
95487	o-Cresol
108394	m-Cresol
106445	p-Cresol
98828	Cumene
94757	2,4-D, salts and esters
3547044	DDE
334883	Diazomethane
132649	Dibenzofurans
96128	1,2-Dibromo-3-chloropropane
84742	Dibutylphthalate
106467	1,4-Dichlorobenzene(p)
91941	3,3-Dichlorobenzidene
111444	Dichloroethyl ether (Bis(2-chloroethyl)ether)
542756	1,3-Dichloropropene
62737	Dichlorvos
111422	Diethanolamine
121697	N,N-Diethylaniline (N,N-Dimethylaniline)

64675	Diethyl sulfate
119904	3,3-Dimethoxybenzidine
60117	Dimethyl aminoazobenzene
119937	3,3'-Dimethyl benzidine
79447	Dimethyl carbamoyl chloride
68122	Dimethyl formamide
57147	1,1-Dimethyl hydrazine
131113	Dimethyl phthalate
77781	Dimethyl sulfate
534521	4,6-Dinitro-o-cresol, and salts
51285	2,4-Dinitrolphenol
121142	2,4-Dinitrotoluene
123911	1,4-Dioxane (1,4-Diethyleneoxide)
122667	1,2-Diphenylhydrazine
106898	Epichlorohydrin (1-Chloro-2,3-epoxypropane)
106887	1,2-Epoxybutane
140885	Ethyl acrylate
100414	Ethyl benzene
51796	Ethyl carbamate (Urethane)
75003	Ethyl chloride (Chloroethane)
106934	Ethylene dibromide (Dibromoethane)

107062	Ethylene dichloride (1,2-Dichloroethane)
107211	Ethylene glycol
151564	Ethylene imine (Aziridine)
75218	Ethylene oxide
96457	Ethylene thiourea
75343	Ethylidene dichloride (1,1-Dichloroethane)
50000	Formaldehyde
76448	Heptachlor
118741	Hexachlorobenzene
87683	Hexachlorobutadiene
77474	Hexachlorocyclopentadiene
67721	Hexachloroethane
822060	Hexamethylene-1,6-diisocyanate
680319	Hexamethylphosphoramide
110543	Hexane
302012	Hydrazine
7647010	Hydrochloric acid
7664393	Hydrogen fluoride (Hydrofluoric acid)
123319	Hydroquinone
78591	Isophorone
58899	Lindane (all isomers)

108316	Maleic anhydride
67561	Methanol
72435	Methoxychlor
74839	Methyl bromide (Bromomethane)
74873	Methyl chloride (Chloromethane)
71556	Methyl chloroform (1,1,1-Trichloroethane)
78933	Methyl ethyl ketone (2-Butanone)
60344	Methyl hydrazine
74884	Methyl iodide (Iodomethane)
108101	Methyl isobutyl ketone (Hexone)
624839	Methyl isocyanate
80626	Methyl methacrylate
1634044	Methyl tert butyl ether
101144	4,4-Methylene bis(2-chloroaniline)
75092	Methylene chloride (Dichloromethane)
101688	Methylene diphenyl diisocyanate (MDI)
101779	4,4'-Methylenedianiline
91203	Naphthalene
98953	Nitrobenzene
92933	4-Nitrobiphenyl
100027	4-Nitrophenol

79469	2-Nitropropane
684935	N-Nitroso-N-methylurea
62759	N-Nitrosodimethylamine
59892	N-Nitrosomorpholine
56382	Parathion
82688	Pentachloronitrobenzene (Quintobenzene)
87865	Pentachlorophenol
108952	Phenol
106503	p-Phenylenediamine
75445	Phosgene
7803512	Phosphine
7723140	Phosphorus
85449	Phthalic anhydride
1336363	Polychlorinated biphenyls (Aroclors)
1120714	1,3-Propane sultone
57578	beta-Propiolactone
123386	Propionaldehyde
114261	Propoxur (Baygon)
78875	Propylene dichloride (1,2-Dichloropropane)
75569	Propylene oxide
75558	1,2-Propylenimine (2-Methyl aziridine)

91225	Quinoline
106514	Quinone
100425	Styrene
96093	Styrene oxide
1746016	2,3,7,8-Tetrachlorodibenzo-p-dioxin
79345	1,1,2,2-Tetrachloroethane
127184	Tetrachloroethylene (Perchloroethylene)
7550450	Titanium tetrachloride
108883	Toluene
95807	2,4-Toluene diamine
584849	2,4-Toluene diisocyanate
95534	o-Toluidine
8001352	Toxaphene (chlorinated camphene)
120821	1,2,4-Trichlorobenzene
79005	1,1,2-Trichloroethane
79016	Trichloroethylene
95954	2,4,5-Trichlorophenol
88062	2,4,6-Trichlorophenol
121448	Triethylamine
1582098	Trifluralin
540841	2,2,4-Trimethylpentane

108054	Vinyl acetate
593602	Vinyl bromide
75014	Vinyl chloride
75354	Vinylidene chloride (1,1-Dichloroethylene)
1330207	Xylenes (isomers and mixture)
95476	o-Xylenes
108383	m-Xylenes
106423	p-Xylenes
0	Antimony compounds
0	Arsenic compounds (inorganic including arsine)
0	Beryllium compounds
0	Cadmium compounds
0	Chromium compounds
0	Cobalt compounds
0	Coke oven emissions
0	Cyanide compounds[a]
0	Glycol ethers[b]
0	Lead compounds
0	Manganese compounds
0	Mercury compounds
0	Fine mineral fibers[c]

0	Nickel compounds
0	Polycylic organic matter[(d)]
0	Radionuclides (including radon)[(e)]
0	Selenium compounds

CAS, Chemical Abstract Service. Note: For all listings that contain the word *compounds* and for glycol ethers, the following applies: Unless otherwise specified, these listings are defined as including any unique chemical substance that contains the named chemical (that is, antimony, arsenic, and so forth) as part of that chemical's infrastructure.

Source: Public Law 101-549, Title II

(a) X'CN where X = H' or any other group where a formal dissociation may occur [e.g., KCN or $Ca(CN)_2$].

(b) Includes monoethers and diethers of ethylene glycol, diethylene glycol, and triethylene glycol $R\text{-}(OCH2CH2)_n\text{-}OR'$ where n = 1, 2, or 3; R = alkyl or aryl groups; and R' = R, H, or groups which, when removed, yield glycol ethers with the structure $R\text{-}(OCH2CH)_n\text{-}OH$. Polymers are excluded from the glycol category.

(c) Includes mineral fiber emissions from facilities manufacturing or processing glass, rock, or slag fibers (or other mineral-derived fibers) of an average diameter of 1 µm or less.

(d) Includes organic compounds with more than one benzene ring and which have a boiling point greater than or equal to 100 °C (212 °F).

(e) A type of atom that spontaneously undergoes radioactive decay.

Requirements for VOCs under NAAQS. In general, under NAAQS an operation that releases VOCs is required to:

- Install and maintain emissions control and monitoring equipment
- Adhere to the regulations for emission limits and control
- Undergo inspections
- Pay emission fees to fund governmental programs
- Before increasing VOC emissions, offset new emissions at a ratio of 1.1 to 1, 1.15 to 1, 1.2 to 1, 1.3 to 1, or 1.5 to 1, depending on local air quality

In addition, existing sources must meet reasonably available control technology (RACT) standards defined by the control techniques guidelines (CTGs) of the EPA. New or modified sources must meet the lowest achievable emission rates (LAERs), typically identified as best available control technology (BACT). For example, control requirements include:

- Limiting the VOC solvent content of paint
- Limiting the vapor pressure of solvents
- Using a hood to capture emissions, which in turn are forced through carbon absorbers or ultraviolet oxidation systems
- Using high-transfer-efficiency application equipment
- Maintaining spent wipe solvent rags in closed containers

- Limiting plantwide emissions

Imposition of a permit incorporates all requirements such as offset limits, BACT and/or RACT, recordkeeping, and fees. These requirements are predicated on local air quality according to the NAAQS. Sections 181 to 185 of subtitle D of the CAA discuss these standards and their applicability.

Requirements for HAPs under NESHAP. Table 1 lists 189 chemicals determined to be HAPs. The EPA has published a list of sources that are to be covered under industry-specific regulations:

- Halogenated solvent cleaning (vapor degreasing)
- Aerospace components and assembly
- Chromic acid anodizing
- Hard chrome plating
- Reinforced plastic parts

By way of example, the following table lists many of the chemicals used in aerospace production:

Process	**Chemicals**
Raw materials	. . .
Machining/etching	Chlorofluorocarbons, volatile organic compounds, acids, oils
Cleaning	Volatile organic compounds, chlorinated solvents, chlorofluorocarbons, alcohol
Plating/anodizing	Heavy metals, acids
Coating/painting	Heavy metals, volatile organic compounds, chlorinated solvents
Stripping	Chlorinated solvents
Assembly	Glues, sealants, lubricants
Painting	Heavy metals, volatile solvents, chlorinated solvents
Maintenance	Halons, freons, oils, solvents

Regulations are required on a statutory timeline that began on November 15, 1992 and is scheduled to end on November 15, 2000. To determine whether a particular industry is covered by all or some of these regulations, the reader should consult local air authorities.

Maximum Available Control Technology. The sources listed above are required to use an emission standard known as maximum available control technology (MACT). For new facilities, MACT is the best demonstrated control technology and practices in a category or subcategory of emission sources. For existing facilities, MACT is defined, in theory, as the average emission limitation of the best controlled 12% of existing sources in the category or subcategory. In developing MACT standards, the EPA can consider:

- Process changes
- Materials substitution
- Enclosed systems and processes
- Collection, capture, or treatment of pollutants
- Design, equipment, work practice, or operational standard
- A combination of the above

Area Source Program. If a particular process does not fall into an identified category or subcategory, but a HAP from Table 1 is in use, it will probably be regulated by 1995 by an area source program. Such programs identify the emission of HAPs from sources that are believed to pose significant health risks even though they are not major sources. A rule of thumb is that if a HAP cannot be eliminated or replaced with a non-HAP, it will eventually be regulated by one or more regulations under NESHAP.

Accidental Releases. A forthcoming EPA regulation, which was due in November 1993, will address the prevention of accidental releases of any of 160 hazardous chemicals. As of this writing, the proposed regulation covers risk management, hazard assessment, training and procedures, emergency response, and the use, operation, replacement, and maintenance of equipment to monitor or prevent releases.

Requirements for Ozone-depleting Substances. Ozone-depleting substances are halogenated compounds that are stable in the lower atmosphere where we live (the troposphere) but are highly unstable at higher levels (the stratosphere). There they react with ozone and form new compounds that deplete the ozone layer, which screens much ultraviolet radiation from reaching the earth. Ozone-depleting substances include CFCs, HCFCs, halons, carbon tetrachloride, and methyl chloroform (1,1,1-trichloroethane).

To prevent further damage to stratospheric ozone, the United States has joined with most other industrialized countries to phase out ozone-depleting substances through production bans. This agreement, which was accomplished at a United Nations meeting, is known as the Montreal Protocol. The U.S. Congress accelerated the production ban schedule to January 1, 2000, and former President Bush, through executive order, further shortened the schedule to December 31, 1995. The phaseout of HCFCs is not scheduled to occur until the year 2015, but in all likelihood it will be rolled back.

Operating Permits. Operating permits are, or will be, required for any source that is subject to NAAQS or NESHAP. Permit programs fund state and local air quality authorities and give them enforcement tools.

Permits were required as early as November 15, 1993, depending on the status of EPA, state, and local rule development. If a source is identified as requiring a permit, it has 12 months to submit an application. The minimum requirements are that:

- A permit application and compliance plan must be prepared and submitted.
- Monitoring and reporting requirements are established and submitted at least every six months.
- Permit holders must certify annually that the facility is in compliance with permit requirements.
- A fee of at least $25/ton of pollutant must be paid annually.
- Permits are valid for no more than five years.
- Public comment periods and hearings are required.

Other Requirements. Regional offices of the EPA can provide detailed information about the subjects discussed in this section, as well as information about acid rain, mobile sources of pollutants, enforcement, and miscellaneous regulations.

The Resources Conservation and Recovery Act

The Resources Conservation and Recovery Act (RCRA, pronounced "rick-rah") is the primary law that governs the management of waste, both hazardous and solid. It provides for technical and financial assistance to resource programs, minimization of waste, safe disposal of waste, and regulation of hazardous waste. RCRA is known as the "cradle to grave" law in that as soon as a waste is conceived (a material is no longer useful) it must be documented and tracked through its storage, transport, treatment, and final disposition (normally by landfill, incineration, or deep-well injection).

Although signed into law in 1976, RCRA regulations were first published in 1980, when day-to-day waste management concerns for industry began. RCRA was amended in 1984 with the Hazardous and Solid Waste Amendments (HSWA), and it now controls the generation, treatment, storage, transportation, disposal, training, and labeling of waste. It also controls underground storage tanks, sumps, pollution prevention, recyclers, and transporters of waste.

The discussion of RCRA in this section is limited to very simple concepts, and the reader should consult a regional EPA office or equivalent state agency for detailed information.

Definition of Hazardous Waste. Fundamentally, once a material is discarded, it is a waste. RCRA regulates solid waste, which includes hazardous waste (such as sludges and spent acids) and nonhazardous waste (such as household garbage). The determination of whether a waste is hazardous (and therefore whether the facility will be subject to the requirements of RCRA) depends on whether the waste is a threat to human health and the environment. A hazardous waste is one that meets any of the following criteria:

- Appears on an EPA list ("F," "K," "P," and "U" lists are found in 40 CFR 261.3)
- Exhibits a hazardous characteristic (flammability, corrosivity, reactivity, or toxicity)
- Is a mixture of solid waste with hazardous waste. The resultant mixture is hazardous with some exceptions.

These criteria are summarized in Fig. 3. As with all environmental regulations, a variety of exclusions apply. If a waste is not hazardous, it generally can be discarded as municipal waste. If it is hazardous, the facility is regulated.

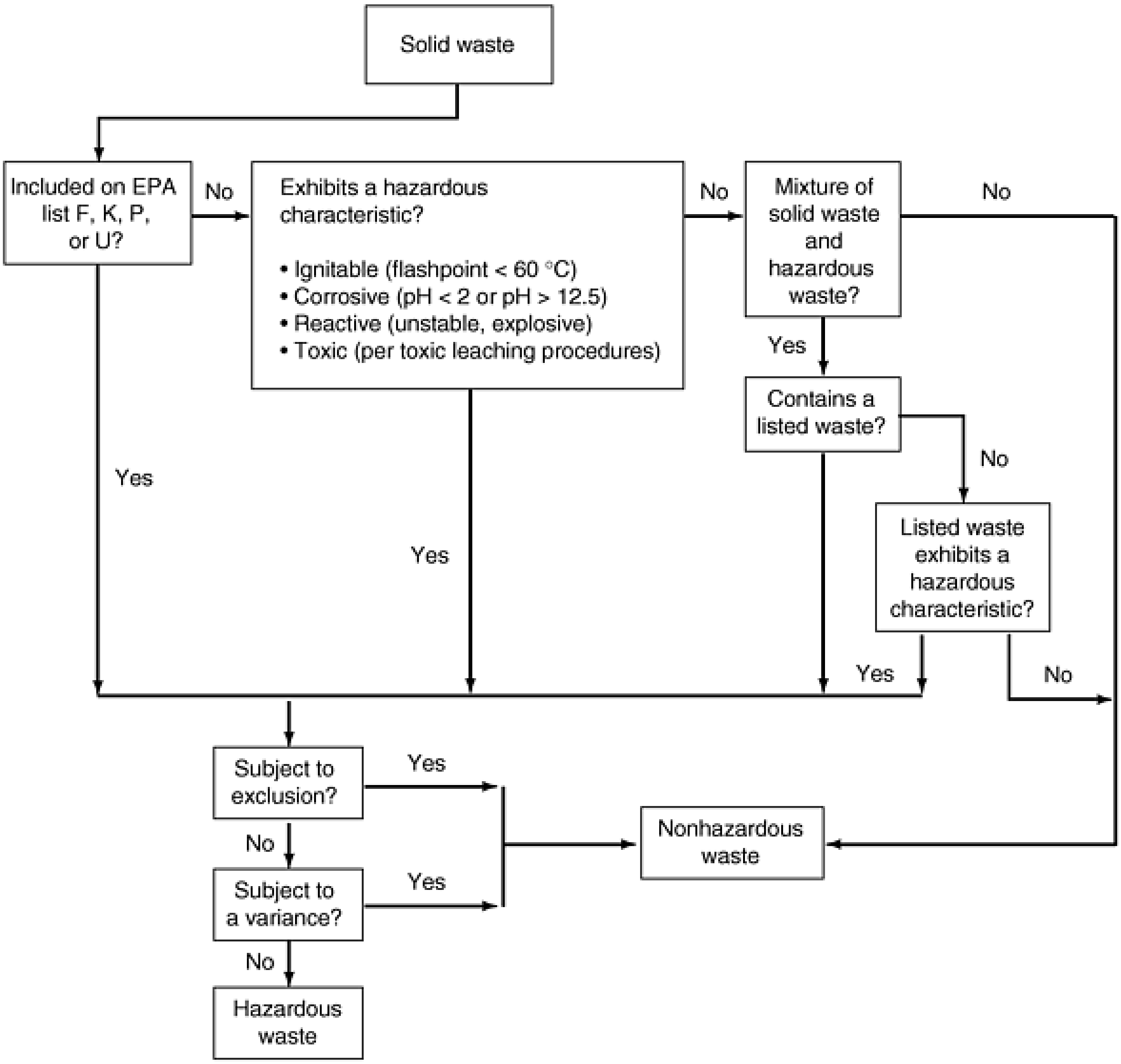

Fig. 3 Criteria for determining whether a solid waste is hazardous

Requirements for Hazardous Waste Generators. If a facility creates a hazardous waste, it must obtain an EPA identification number and follow regulations about such matters as containers and storage tanks, inspections, employee training, waste minimization, transportation, recordkeeping and recording, and selection of treatment, storage, and disposal (TSD) sites. How a facility is regulated depends on the amount of waste generated.

Large-quantity generators produce more than 1000 kg/month of hazardous waste or more than 1 kg/month of acutely hazardous waste. They may store wastes for only 90 days. In addition, they must:

- Use approved containers that are compatible with the waste and are marked with specific information. Storage procedures must meet fire code satellite requirements.
- Comply with sump and tank requirements. Hazardous waste tanks must meet requirements for secondary containment, leak detection, cathodic protection, overfill alarms, spill prevention, labels, integrity, and so on.
- Conduct a daily inspection of hazardous waste storage areas, transfer areas, and tanks.
- Create an emergency response program that includes a preparedness program, a prevention program, and a contingency plan that is carried out whenever there is a release of hazardous waste.
- Develop, and repeat annually, employee training programs for identifying, packaging, labeling, and transporting hazardous waste, as well as training programs about waste handling, identifying the

properties of waste on-site, and the use of safety equipment.
- Employ programs to minimize waste, including an annual report.
- Comply with transportation and packaging requirements.
- Comply with prohibitions on the disposal of certain wastes in landfills.
- Send wastes to a TSD facility that is approved to handle the types of wastes generated.
- Comply with a host of recordkeeping and reporting requirements.

Small-quantity generators produce between 100 and 1000 kg/month of hazardous waste. They may store up to 6000 kg of waste for up to 180 days (270 days if it is to be shipped more than 200 miles to a TSD). Small-quantity generators are subject to most of the same requirements as large-quantity generators, with some exceptions.

Conditionally exempt small-quantity generators produce no more than 100 kg/month of hazardous waste, no more than 1 kg/month of acutely hazardous waste, and no more than 100 kg/month of waste debris such as contaminated soil. They may store 1000 kg of hazardous waste for any period. While exempt from most requirements, they must determine which wastes are hazardous, keep records, store wastes legally, and transport wastes to an approved TSD facility.

Requirements for TSD Facilities. RCRA defines treatment, storage, and disposal as follows:

- *Treatment:* "Any method, technique, or process including neutralization, designed to change the physical, chemical, or biological character or composition of any hazardous waste so as to recover energy or material resources from the waste, or so as to reduce such waste to non-hazardous or less hazardous; safer to transport, store, or dispose of; amendable for recovery or storage; or reduced in volume."
- *Storage:* "The holding of hazardous waste for a temporary period, at the end of which, the hazardous waste is treated, disposed of, or stored elsewhere."
- *Disposal:* "The discharge, deposit, injection, dumping, spilling, leaking, or placing of any solid waste or hazardous waste into or on any land or water so that such solid waste or hazardous waste or any constituent thereof, may enter the environment or be emitted into the air or discharged into any waters, including ground waters."

A TSD facility uses surface impoundments (such as sludge ponds), waste piles, landfills, chemical/physical/biological treatment, and/or incineration to treat, store, or dispose of waste on-site. It is subject to extensive permit application requirements and conditions if it:

- Stores waste longer than 90 days
- Uses surface impoundments or waste piles
- Stores recyclable materials longer than 90 days
- Treats or disposes of hazardous waste

Such facilities typically specialize in waste management, due to the high cost of maintaining permit conditions. However, a manufacturing site can also use one or more of these TSD methods, and if so it is subject to the same rigorous requirements. All TSD facilities must have permits, which regulate such matters as waste analysis, inspections, security, training, waste management, facility maps, emergency response, air emission control, recordkeeping systems, groundwater monitors, infrastructure, containment, financial assurances, and closure. Unless TSD operations are primary to the business, it is unlikely that a surface treatment facility would want or need to maintain a TSD permit.

Superfund Amendments and Reauthorization Act

In December 1980, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), commonly known as "Superfund," was passed into law. It established a program to identify sites where hazardous materials are released into the environment and ensure that they are cleaned up by responsible parties.

What has more bearing on surface engineering processes is the 1986 reauthorization of CERCLA, known as the Superfund Amendments and Reauthorization Act (SARA). In addition to extending CERCLA, SARA Title III created the Emergency Planning and Community Right to Know Act (EPCRA), a sweeping system for informing. community emergency planners and the public about what chemicals are being used, where they are being used, and how much are being released into the air, water, or land as pollution.

Publicity of "SARA 313 releases" has done more to motivate research into alternative surface finishing processes than any other mechanism.

Overview. The EPCRA section of SARA includes two sets of significant requirements:

- *Requirements about release notification and emergency response planning:* Facilities must inform government agencies of hazardous material releases and have the appropriate equipment, personnel, and training to respond to a cleanup.
- *Requirements about reporting,* which are divided into three sections: 311, 312, and 313. Section 311 requires that material safety data sheets for chemicals used at a facility be given to the local fire department or an emergency planning committee. Section 312 requires a facility-wide inventory of what chemicals are where within the facility. Section 313 requires that an annual report about toxic releases be submitted each July 1 to the federal government.

Section 313. A U.S. facility is required to submit the annual toxic chemical release report if it has more than 10 employees, falls into certain industry categories (Standard Industrial Codes 20 to 39), uses a toxic chemical in excess of 10,000 lb/year, or manufactures a toxic chemical in excess of 25,000 lb/year. For each chemical used at the facility, an EPA form R must be submitted that shows:

- EPA permit numbers
- Storage and treatment data
- A pollution prevention report for the chemical
- The quantity of chemical released to air, water, or offsite transfer
- Business information
- Executive certification of the report's accuracy

Clean Water Act

Protection of water resources is a critical issue in the design and operation of a manufacturing facility that uses surface engineering processes. Nearly every facility of this type uses water in a variety of ways: for cooling, cleaning and rinsing, anodizing, and plating baths. Even facilities that do not use water directly in manufacturing processes should be aware of water issues because of concerns about stormwater and groundwater quality.

Wastewater Discharge. The primary water-related concerns about surface engineering processes are the quality and quantity of wastewater discharges and the design and operation of the facility to protect stormwater and groundwater. The procedure that is most heavily regulated by the Clean Water Act, and probably most costly to deal with, is the discharge of wastewaters to either surface waters or to publicly owned treatment works (POTWs).

NPDES Permits. Federal regulations (40 CFR 122) prohibit the discharge of wastewater to any surface water body without a National Pollutant Discharge Elimination System (NPDES) permit. The permit is administered by either the EPA or a designated state agency, depending on the location of the facility. It requires the discharger to characterize the volume and composition of the discharge, sets maximum discharge temperatures and flow rates, outlines how the discharger must monitor the discharge, and specifies maximum pollutant compositions based on either technology or water quality. (Technology-based limits are established by determining the level of treatment that is both technically and economically feasible for a particular industry. Water-quality-based limits are based on minimizing the potential effects of the discharge on the receiving water body.) NPDES permits remain in effect for five years, and the requirements of subsequent permits are typically stricter, as more aggressive technology-based or water-quality-based standards are developed.

Requirements of Dischargers. Wastewater discharges to POTWs do not require an NPDES permit but are regulated by comparable pretreatment standards imposed on specific industry categories (40 CFR 403). Many states or municipalities have permit programs to regulate these discharges. Pretreatment standards are technology-based and are calculated by determining the level of treatment that is both technically and economically feasible for a particular industry. They are set in a manner that prevents the discharge of materials that would adversely impact the operation of the POTW or that would pass through the POTW without receiving adequate treatment.

Facilities often have the option of discharging treated wastewater either directly to surface waters or to a POTW for further treatment prior to discharge. NPDES-permitted discharges to surface waters usually require more extensive treatment and monitoring than discharges to POTWs. On the other hand, indirect dischargers must pay a fee to the POTW to help cover the costs of its operations. The preferred choice is the option that allows all regulatory requirements to be met at a lower cost.

Requirements of Technology. The pollutants of most concern to operations using surface engineering processes are metals and toxic organics. Treatment technologies are available to remove these materials from wastewater streams.

The traditional method of removing metals is to modify the pH of the wastewater stream to precipitate insoluble metal hydroxides. The principal drawback is that significant quantities of hazardous sludges are formed that are costly to dispose of. These disposal costs can be reduced by using filter presses or dryers to reduce sludge volumes. Other treatment techniques have been developed to more cost-effectively remove, and even recycle, these pollutants.

A variety of techniques are available to remove or destroy toxic organics in wastewater: chemical oxidation, ozonation, and biological treatment. Each treatment process has different capabilities, and the preferred process will be a function of the characteristics of the wastewater stream and discharge requirements.

The costs of complying with increasingly complex safety, health, and environmental regulations are powerful incentives for implementing pollution prevention programs. Many products can be either redesigned or modified to allow the use of more environmentally acceptable materials and processes in manufacturing operations. The use of these materials and processes can help the manufacturer reduce or eliminate the need for additional wastewater treatment equipment. Many of these efforts are win-win situations, where implementing the new material or process results in both reduced emissions to the environment and lower costs to the manufacturer. Examples of successful pollution-prevention efforts are the use of boric-sulfuric acid anodizing to replace chromic acid anodizing operations and the use of zinc-nickel plating to replace cadmium plating.

Stormwater Discharge. Wastewater discharges are not the only area in which facilities are affected by water-related environmental concerns. Most facilities containing typical surface engineering processes need an NPDES permit for stormwater discharges. Facilities are required to obtain NPDES stormwater discharge permits if three conditions are met:

- The Standard Industrial Code of the facility is on the list of regulated operations, as given in 40 CFR 122.
- Stormwater from the facility is discharged to surface waters.
- Operations have the potential to cause stormwater contamination by allowing stormwater to contact hazardous materials at the facility. Examples of this include storing drums of hazardous materials in covered outdoor areas or having uncovered loading docks where hazardous raw materials or finished products are transported.

The NPDES stormwater discharge permit program requires dischargers to develop and implement stormwater pollution prevention plans to identify and correct problem areas.

Water Supply Issues. In addition to the water quality issues described above, water quantity issues are becoming increasingly important. In many areas of the country, water supply costs are rising dramatically, and in some areas increased supplies of water are simply unavailable. While reducing the water usage of a facility is typically not a regulatory concern, strong economic drivers exist for implementing water conservation programs. Many opportunities to cost-effectively reduce water consumption are available, including the use of double (and even triple) countercurrent rinsing, the replacement of once-through cooling systems with closed-loop systems, and the use of wastewater treatment techniques that recycle the treated effluent for use elsewhere in the facility.

Other water-related concerns at a typical facility include the potential impact of leaking sumps and underground storage tanks on groundwater. Requirements for the design, construction, operation, maintenance, and removal of underground storage tanks and sumps are outlined in 40 CFR 280. Recordkeeping and release reporting are also required.

Other Environmental Statutes

Several other federal statutes are germane to this article:

- The Safe Drinking Water Act (SDWA) provides substantial requirements for public water supply systems.
- The Toxic Substances Control Act (TSCA) regulates the invention, use, marketing, and importation of chemicals and evaluates health and environmental effects of chemicals. It requires a chemical manufacturer or importer to provide health and environmental data, limit how much chemical is used, have approval for distribution, provide warnings, and maintain test results. Engineers who reformulate materials are advised to understand TSCA.
- The Federal Insecticide, Fungicide, and Rodentacide Act (FIFRA) regulates the manufacture and use of pesticides.
- The National Environmental Policy Act (NEPA) declares national environmental policy and requires federal agencies to consider environmental concerns when taking actions such as issuing permits.

Local officials and environmental consulting firms can provide information about whether these statutes apply to a particular operation.

Cadmium Elimination in Surface Engineering

Mark W. Ingle, Corrpro Companies, Ocean City Research Corporation

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Introduction

CADMIUM is a soft, blue-white metal widely used as a corrosion control coating on ferrous (e.g., mild and high-strength steel) substrates. Electroplated cadmium coatings are typically applied at thicknesses of between 5.1 and 12.7 μm (0.2 and 0.5 mil) (Ref 1). Chromate treatments (based on hazardous chromic acid) are frequently applied to cadmium coatings as a final passivation process. Cadmium coatings have historically provided effective substrate corrosion control performance when applied to threaded fasteners, connectors, and general hardware (Ref 2, 3). The technical performance benefits and limitations associated with cadmium coatings are well established.

However, over the past decade, environmental and worker health regulations affecting cadmium use have been promulgated in the United States and in Western Europe. These regulations have increased the costs associated with cadmium coating application and cadmium-bearing waste disposal, creating economic incentives for industrial users to seek cadmium plating replacements. Unfortunately, no universal cadmium replacement has yet been identified. Thus, viable cadmium replacements must be identified on a case-by-case basis in which technical performance requirements, environmental issues, and costs are considered. Identification of effective cadmium replacements can reduce product costs and minimize regulatory compliance problems. Ineffective cadmium replacements can lead to degraded component-corrosion control performance and, in extreme cases, catastrophic component failures.

Acknowledgements

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References

1. J.P. McAdams, E.T. Clegg, F. Lafferman, and C. Levy, Government Specifications for Metal Finishing, *Metal Finishing Guidebook and Directory,* Vol 92 (No. 1A), Jan 1994, p 725-735
2. R.K. Smith, "Interim Report--Cadmium Plating Source Substitution," Contract DLA900-83-C-1744, Battelle Memorial Institute, May 1989
3. M. Ingle and T. Marchesani, Evaluation of Environmentally Acceptable Alternatives for Cadmium Plating, *Proceedings of the 5th Automotive Corrosion and Prevention Conference,* P-250, Society of Automotive Engineers, Oct 1991, p 25-41

Rationale for Replacing Cadmium Coatings

Historically, cadmium coatings have been applied to mild and high-strength steel components as an economical and effective means of controlling in-service substrate corrosion (see the article "Cadmium Plating" in this Volume). Although cadmium coating performance has not changed over the years, recent revisions to environmental and worker health laws in the United States and other countries have created a regulatory climate in which continued cadmium use is becoming cost-prohibitive:

- The U.S. Occupational Safety and Health Administration (OSHA) released the "Occupational Exposure to Cadmium; Final Rules" in 1992. OSHA estimates that compliance with these rules will cost domestic industry $159,616,000/year (Ref 4).
- Environmental laws in the United States make cadmium-bearing waste disposal or emissions expensive. In addition, 29 states have passed pollution prevention acts that mandate reductions in hazardous waste (such as waste that contains cadmium) (Ref 5, 6).
- The Swedish Ban on Cadmium was enacted in 1985. Based on this ban, Sweden can forbid the import of certain products containing cadmium (Ref 7).

These laws may increase operating costs, create liability risks, and restrict markets for certain cadmium-coated products. The following sections of this article provide additional details about regulations in the United States and Europe.

Cadmium Worker Health Effects and Laws. OSHA has evaluated the health effects of cadmium on workers and has determined that exposure to respirable particles/fumes represents the most significant risk factor. Cadmium and its compounds are not readily absorbed through the skin, but they can be ingested. Inhaling cadmium or its compounds can directly cause lung cancer, and it also allows the toxic metal to enter the bloodstream. Once in the blood, cadmium readily accumulates in the kidneys, degrading their function. Table 1 shows the estimated levels of lung cancer and kidney dysfunction resulting from varying levels of cadmium exposure.

Table 1 Impact of cadmium exposure levels on worker health

Cadmium TWA PEL[(a)]	Effective dates	Excess lung cancer rate per 1000 workers[(b)]	Excess kidney dysfunction rate per 1000 workers[(b)]
100 μg/m^3	1971-1992	58-157	900
5 μg/m^3	1993-present	3-15	14-23

Source: Ref 4

(a) TWA PEL, time-weighted average permissible exposure limit.

(b) Based on 45-year workplace exposure history.

From 1971 to 1992, OSHA defined the permissible exposure limit (PEL), over an 8-h time-weighted-average day, as 100 μg of cadmium fumes per cubic meter of workplace breathing air (Ref 4, 8). OSHA redefined the acceptable workplace cadmium exposure limits in 1992 by reducing the allowable airborne concentrations of cadmium in the workplace by 95%, from 100 to 5 $\mu g/m^3$ (Ref 8). In addition to redefining the PEL, the document "Occupational Exposure to Cadmium; Final Rules" includes extensive provisions for engineering controls on workplace breathing-air cadmium levels, worker safety training, medical monitoring requirements, and, as a worst case, employee respirator use. The current OSHA PEL of 5 $\mu g/m^3$ is one of the lowest for common industrial metals. OSHA estimates that compliance with the revised worker safety requirements will cost industries that produce, use, and dispose of cadmium approximately $159,616,000/year (Ref 4).

OSHA data show that the implementation of the 5 $\mu g/m^3$ PEL will reduce workplace health risks. Table 1 summarizes the OSHA health impact data and shows that by reducing cadmium exposure from the earlier 100 $\mu g/m^3$ to 5 $\mu g/m^3$, worker kidney dysfunction and lung cancer rates will decrease appreciably (Ref 4).

Environmental Regulations Related to Cadmium--United States. Table 2summarizes the impact of selected federal laws on cadmium production, application, and waste disposal. As shown, cadmium is considered a hazardous material and is regulated as a "hazardous chemical" or "toxic substance" (Ref 9). The federal laws shown in the table are typically administered on a state or local level through facility permits. Depending on specific permit requirements, the economic impact on facilities can be significant. Compliance costs for permits vary from state to state and are difficult to assess. However, the general consensus in the metal coating industry is that costs for hazardous materials handling and waste disposal are increasing.

Table 2 Federal environmental laws that affect cadmium use, emission, and waste disposal

Federal law	Acronym	Potential impact
Resource Conservation and Recovery Act	RCRA	Hazardous waste disposal regulations create overhead costs and compliance risks.
Comprehensive Environmental Response, Compensation, and Liability Act (Superfund)	CERCLA	Cadmium is a Section 304 hazardous substance. Applicable only to certain releases of cadmium compounds.
Superfund Amendments and Reauthorization Act (Title III)	SARA	Cadmium is a Section 313 toxic chemical. Emissions must be reported.
Clean Water Act and Amendments	CWA	States are reducing allowable cadmium concentrations in facility effluent. Compliance with the new limits may require additional cadmium recovery equipment.
Clean Air Act and Amendments	CAA	Recent amendments define cadmium as a hazardous air pollutant. Cadmium emissions may be taxed.

Source: Ref 9

In addition to the federal regulations, 29 states have enacted pollution prevention laws (Fig. 1). These laws affect cadmium-bearing hazardous wastes specified by the Resource Conservation and Recovery Act and toxic materials specified by the Superfund Amendments and Reauthorization Act, Title III, including cadmium particulates or solutions (Ref 6). State pollution prevention laws generally require industrial facilities to achieve percentage reductions in hazardous material consumption and hazardous waste generation via "source reduction," but the degree to which these laws encourage source reduction varies. Some states offer incentives and funding grants to eliminate hazardous materials, others employ user fees, and some mandate civil fines (e.g., a $15,000 fine for "blatant violators" of the New Jersey Pollution Prevention Act) (Ref 6, 10). These federal and state laws create a significant incentive for industrial users to replace cadmium coatings.

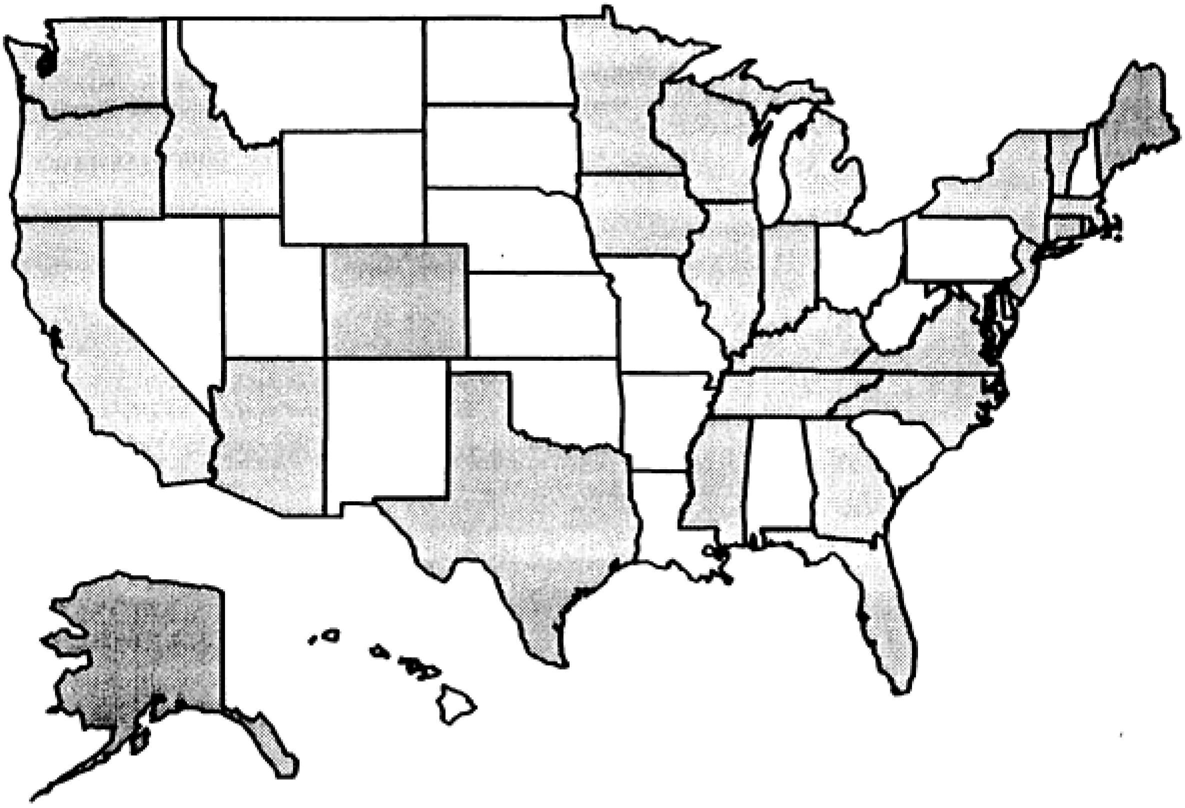

Fig. 1 States that have pollution prevention or hazardous waste minimization laws as of 1994 (shown in gray). Source: Ref 5,

Environmental Regulations Related to Cadmium Use--Europe. Certain European countries have taken more direct steps than the United States to control cadmium use and resulting environmental impacts, including a ban on cadmium use in Sweden, restrictions on cadmium use in Finland, and a virtual ban on cadmium chloride in Germany (Ref 5, 7, 11).

The Swedish Ban on Cadmium summarizes the environmental and worker health risks posed by the metal and then selectively forbids the production or importation of specific items containing cadmium (Ref 7). The following are some specific provisions of the ban:

- Section 45(j)--"The substance cadmium [defined as cadmium plating in Appendix 2 of the Swedish Ban] may not be used for surface treatment, as a stabilize, or as a pigment" (Ref 7).
- Section 45(j)--"Products whose surface has been treated with a cadmium substance or which contain such a substance as a stabilizer or pigment may not be imported commercially" (Ref 7).

The Swedish statute does not ban nickel-cadmium storage batteries and includes exemptions for certain safety products, but its effect on markets for cadmium-plated parts in Sweden is clear.

The trend toward restricting cadmium use is currently spreading throughout Europe. The German government has virtually banned the use of cadmium chloride and is reducing acceptable workplace exposure levels for other cadmium compounds (Ref 4). Finland has announced "prohibitions and restrictions" on products containing cadmium (Ref 11). These actions reflect a trend in the European Economic Community (EEC) that is effectively summarized in the following conclusion from a 1991 EEC report (Ref 12): "There is a significant threat of long term damage to man and the environment by cadmium if appropriate steps are not taken to reduce environmental contamination by this metal."

References cited in this section

4. "Occupational Exposure to Cadmium; Final Rules," U.S. Department of Labor, Occupational Safety and Health Administration, Title 29 *Code of Federal Regulations*, Part 1910.1027, 14 Sept 1992
5. W. Ryan and R. Schrader, *An Ounce of Toxic Pollution Prevention*, National Environmental Law Center, Jan 1993
6. R. Style, Are State Laws Motivating Business to Pursue Pollution Prevention?, *Pollution Prevention Review*, Vol 4 (No. 1), Winter 1993-94, p 61-70
7. "The Swedish Ban on Cadmium, Ordinance on Cadmium, Product Control Report, and Ordinance Relating to Deviations from the Ban on the Use of Cadmium for Surface Treatment or as a Stabilizer or as a Coloring Agent," Swedish Code of Statutes, SFS 1985:839, 21 Nov 1985
8. *Occupational Exposure to Cadmium*, U.S. Department of Labor, Occupational Safety and Health Administration, Publication 3136, 1992
9. Consolidated List of Chemicals Subject to Reporting under the Emergency Planning and Community Right-to-Know Act, *EPA Title III: List of Lists*, Jan 1992
10. "Pollution Prevention Program Rules," Office of Pollution Prevention, Environmental Protection and Energy, New Jersey Administrative Code 7:1K, 23 Dec 1993, as described in *New Jersey Register*, 7 Feb 1994
11. Finland: Products Containing Cadmium and Its Compounds, PSA 0729, *Commerce Business Daily*, 25 Nov 1992
12. Chemicals Group and Management Committee, "Co-operation on Existing Chemicals: Risk Reduction Lead Country Report on Cadmium," Report to the 16th Joint Meeting, Organization for Economic Co-operation and Development, 28-30 May 1991

Cadmium Coating Specifications

Cadmium coatings are applied in accordance with both consensus specifications (e.g., Society of Automotive Engineers) and federal and military specifications. Table 3 lists representative cadmium and cadmium alloy coating specifications. Unless directly specified, cadmium coatings are unlikely to be applied to a component, because cadmium electroplating costs are generally one to two times higher than those for conventional zinc electroplating (Ref 7, 13).

Table 3 Cadmium coating specifications

Specification	Title
General plating	
SAE AMS 2416	Plating, Nickel-Cadmium, Diffused
QQ-P-416E	Plating, Cadmium (Electrodeposited)
MIL-P-23408B	Plating, Tin-Cadmium (Electrodeposited)
SAE AMS 2400S	Cadmium Plating
Plating to minimize potential substrate embrittlement	
AIA NAS 672	Plating, High-Strength Steels, Cadmium

ASTM B 696	Standard Specification for Coatings of Cadmium, Mechanically Deposited
MIL-C-8837B	Coating, Cadmium (Vacuum Deposited)
MIL-C-81562B	Coatings, Cadmium, Tin-Cadmium, and Zinc (Mechanically Deposited)
MIL-STD-870	Cadmium Plating, Low Embrittlement, Electrodeposition
MIL-STD-1500	Cadmium-Titanium Plating, Low Embrittlement
SAE AMS 2401D	Cadmium Plating, Low Hydrogen Content

References cited in this section

7. "The Swedish Ban on Cadmium, Ordinance on Cadmium, Product Control Report, and Ordinance Relating to Deviations from the Ban on the Use of Cadmium for Surface Treatment or as a Stabilizer or as a Coloring Agent," Swedish Code of Statutes, SFS 1985:839, 21 Nov 1985

13. J. McKewan, `The Effects of Plating on Torque/Tension Relationship and Vibration Resistance," paper presented at the 1980 Automotive Engineering Congress and Exposition (Detroit, MI), Society of Automotive Engineers, 25-29 Feb 1980

Cadmium Replacement Identification

Identification of viable cadmium replacements requires engineering analysis of technical performance issues, environmental considerations, and economic factors. As such, a significant portion of the process of identifying cadmium replacements is based on qualitative data and engineering judgment. There is no direct or "one for one" cadmium replacement, so multiple replacements, or no viable replacements, may be identified for specific cadmium applications. This section provides general, qualitative guidance regarding potential cadmium replacements in terms of general performance, environmental, and economic factors. *Caution: Replacing coatings inherently creates performance risks that must be evaluated and accepted by qualified engineers before any coating or material change is implemented*.

To assist with the identification of cadmium replacements, key technical performance, environmental, and economic data have been collected and summarized in Table 4. These data are presented in a qualitative matrix in which the performance of replacements is rated relative to that of cadmium coatings. Because so many of the factors affecting the selection of cadmium replacements are based on case-specific issues, such as substrate material/heat treatment, component configuration, and production volume, specific references are provided to allow engineers to collect additional information. To improve clarity and provide information on how the qualitative ratings were generated, the following paragraphs discuss each column of the table, along with important issues that could affect cadmium replacement decisions.

Table 4 Cadmium replacement identification matrix

Cadmium replacement	**Specifications**	**Corrosion control performance**	**Environment-assisted cracking**	**Coating lubricity**	**Environmental/ worker health regulations**	**Cost/ performance factors**
Zn, Zn-Ni, Zn-Co, or ion vapor deposited	Commercial; MIL-C-83488 with MIL-C-81751 (Ref 3,	Better/comparable (Ref 3, 24)	Worse/comparable (Ref 3)	Comparable or more lubricious (Ref 12, 24)	Better, although some lubricious topcoats may be subject to volatile	Significantly higher costs (Ref 3, 23)

aluminum coating with lubricious topcoat (Ref 3, 24)	24)				organic compound regulations (Ref 24)	
Solid alloy without coating (e.g., nickel alloy, stainless steel) (Ref 17, 18)	QQ-N-281, QQ-N-286 (nickel alloy); AISI 304, AISI 316 (stainless steel)	Better (stainless steel may pit) (Ref 17, 18)	Better (Ref 17, 18, 28)	Not applicable; stainless steel and nickel alloys have been used as fasteners (Ref 17, 18)	Better, no coating process	Initial cost significantly higher; life cycle cost may be comparable
Zinc plating (Ref 7, 11, 21)	ASTM B 633[(a)]	Comparable/worse (Ref 3, 16)	Worse (Ref 7, 21)	Less/comparable (Ref 3, 24)	Better, although the type II or III chromate post-treatment is hazardous (Ref 9, 29, 30)	Initial costs lower; zinc coatings generate voluminous, white corrosion products (Ref 16)
Zinc-nickel plating (Ref 3, 25)	ASTM B 841; commercial (Ref 27)	Comparable (Ref 3, 25)	Worse/comparable (Ref 3, 25)	Less/comparable (Ref 3, 24)	Better, although nickel is included in EPA "Toxic 17" list; chromate post-treatment hazardous (Ref 9, 29, 30)	Initial costs may be higher; life cycle costs comparable (Ref 16)
Tin-zinc plating (Ref 3, 26)	Commercial (Ref 26)	Comparable/worse (Ref 3)	Worse/comparable (Ref 3)	Less/comparable (Ref 3, 24)	Better, chromate post-treatment hazardous (Ref 9, 29, 30)	Initial costs may be higher; life cycle costs comparable (Ref 3)
Ion vapor deposited aluminum (Ref 3, 23)	Commercial; MIL-C-83488 (Ref 23)	Comparable (Ref 3, 23)	Worse/comparable (Ref 3, 23)	Less; ion vapor deposited aluminum coatings on threaded fasteners can gall (Ref 3, 23)	Better, chromate post-treatment hazardous (Ref 9, 29, 30)	Significantly higher costs (Ref 23)

Note: See text for extensive detail.

(a) Specific bath chemistry is not specified and would have to be agreed on with vendors.

Cadmium Replacement. This column in Table 4 briefly describes materials or processes that have proven to be viable replacements for cadmium coatings on steel substrate components. The options presented range from simply substituting common zinc plating to employing solid, inherently corrosion-resistant materials (e.g., nickel alloys or stainless steel) to replace plated components.

Implementing a major design change (e.g., replacing a cadmium-coated fastener with a solid nickel alloy fastener) is sufficiently complex to require component-specific engineering review. To assist with this process, Table 4 lists references for commercial and federal agencies that are using cadmium replacements in specific applications. Generic

terms are used to describe replacements; if required, the listed reference may be consulted to identify specific products or processes.

The only cadmium replacements included in Table 4 are those specifically applicable to steel substrates. Cadmium applications to nonferrous parts are typically intended to address complex performance parameters that are beyond the scope of this article.

Specifications. This column in Table 4 provides a brief list of consensus or military specifications for the cadmium replacements. The term *commercial* denotes specifications developed by individual corporations, which are generally available from the referenced sources.

Corrosion Control Performance. This column in Table 4 summarizes the results of corrosion control tests conducted in realistic or natural marine and/or industrial atmospheres. These atmospheres are widely regarded as the most aggressive natural environments used to test coatings. Cadmium replacements that provide effective substrate corrosion control in these atmospheres will perform even more effectively in less harsh environments, such as those that might be encountered inside a climate-controlled building or sheltered compartment.

Corrosion control data generated using artificially accelerated or salt fog tests (e.g., ASTM B 117) are not included because such data have no demonstrable correlation with actual field performance. Figure 2 shows that salt fog and natural marine atmosphere data for an 18-day exposure period are inconsistent and contradictory (Ref 14). Similar data generated by an SAE-AISI task force on corrosion testing led to the following conclusion (Ref 15): "The ASTM B 117 salt spray (fog) gives a very poor simulation of on-vehicle behavior and thus should not be used for ranking the cosmetic corrosion resistance of automotive sheet steel products."

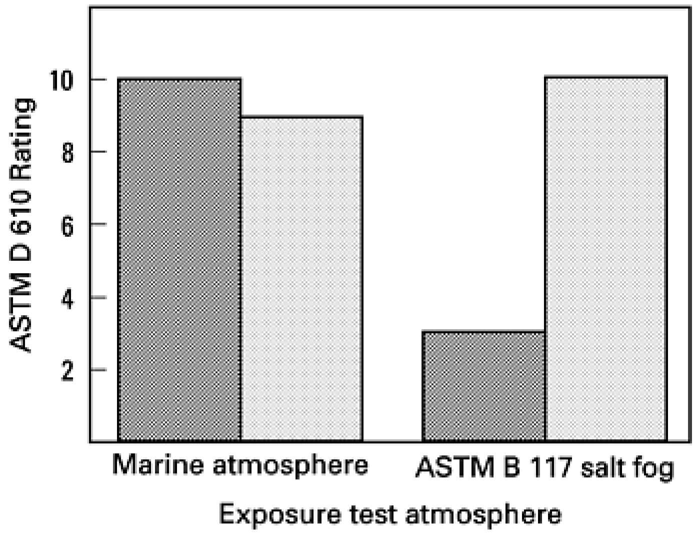

Fig. 2 Lack of correlation between ASTM B 117 salt fog test results and natural marine-atmosphere exposure test data for cadmium-plated (light-shaded bars) and zinc-plated (dark-shaded bars) mild steel. The ASTM D 610 rating scale extends from severe substrate corrosion (rating 1) to no substrate corrosion (rating 10). Source: Ref 14

As such, Table 4 summarizes only data generated by comparing the natural-atmosphere corrosion control performance of the listed replacements with that of the cadmium-coated experimental controls (e.g., AISI 1010 steel specimens coated with QQ-P-416, type I cadmium plating at thicknesses of 5.1, 12.7, and 25.4 μm, or 0.2, 0.5, and 1.0 mil). Only cadmium replacements that could be applied at thicknesses of 12.7 μm (0.5 mil) or less were included in the analysis. Following are the terms used to describe the qualitative ratings:

- *Better:* The replacement (applied at thicknesses similar to those of cadmium) controls steel substrate corrosion for a longer period of time than cadmium.
- *Comparable:* The replacement (applied at thicknesses similar to those of cadmium) controls steel

substrate corrosion as effectively as cadmium for a similar period of time. Coating self-corrosion or cosmetic appearance data did not influence this rating. For example, a zinc-base coating was considered comparable to a cadmium coating if it provided the same degree of protection to the substrate, even if it produced greater amounts of white corrosion product than a cadmium coating.

- *Worse:* The replacement (applied at thicknesses similar to those of cadmium) did not control steel substrate corrosion as effectively as cadmium. Because all of the systems included in Table 4 have already been used to replace cadmium in some applications, a rating of *Worse* typically signifies that thin layers of the replacement did not perform as effectively as thin layers of cadmium, even though thicker layers of the replacement may have been equivalent (Ref 3). Even if a system is rated *Worse* in this table, it still could be considered a viable cadmium replacement in applications that could accept thicker coatings, or applications in less corrosive environments.

As these ratings suggest, the coating thickness of cadmium replacements exerts a significant influence on corrosion control performance. Cadmium and virtually all of the replacement coatings sacrificially corrode to protect the substrate, so coating thickness exerts a significant influence on coating service life. In general, thicker sacrificial coatings contain more metal (i.e., greater coating weight) and will sacrificially corrode to protect the substrate steel for a longer period of time.

Figure 3 shows the relationship of zinc coating weight to service life (Ref 16). Although cadmium is a sacrificial coating, data from natural atmosphere exposure tests do show that cadmium coatings tend to provide effective corrosion control when applied in thin layers, whereas many of the cadmium replacements did not perform as effectively at comparable thicknesses. To maximize the service life of components coated with cadmium replacements, specifications should require the thickest layer possible that does not adversely affect fit or function.

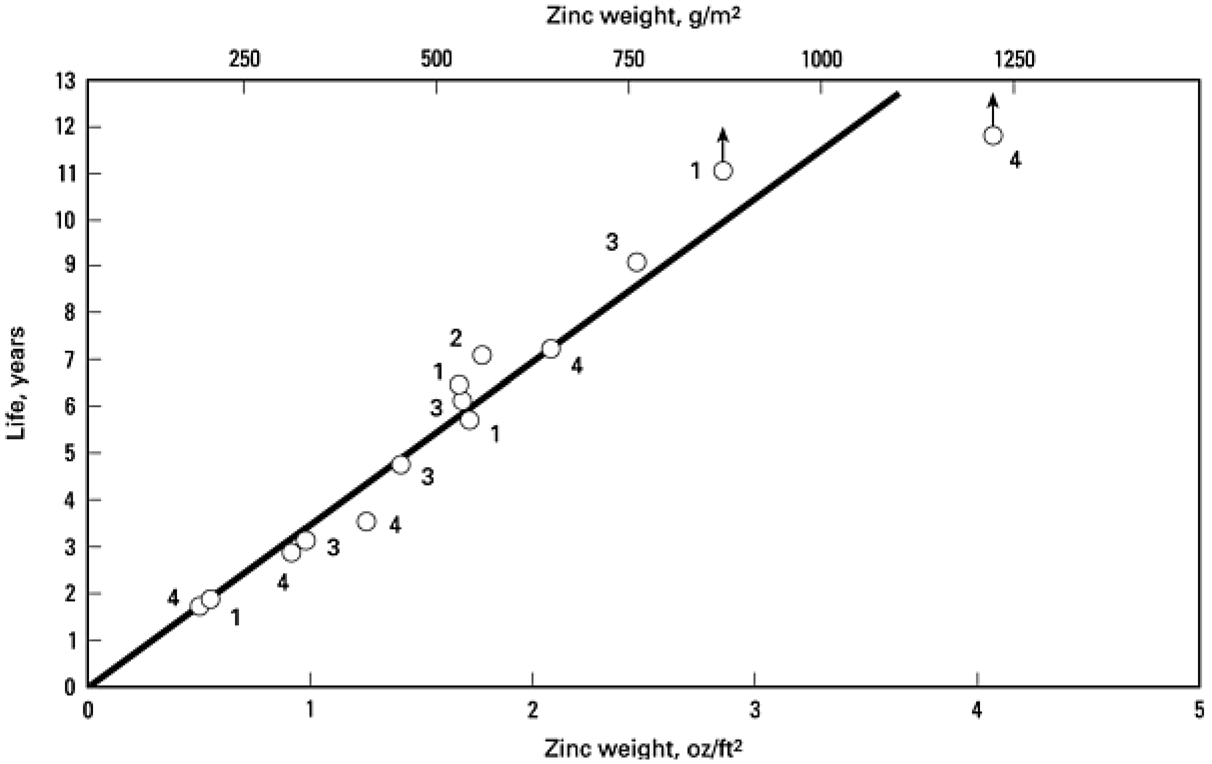

Fig. 3 Service lives of various zinc coatings according to the weight of the zinc present. Results are for exposure in a very aggressive industrial atmosphere. 1, electrodeposited; 2, electrodeposited (passivated with chromate solution); 3, hot-dip galvanized; 4, sprayed. Source: Ref 16

Environment-Assisted Cracking (EAC). This column in Table 4 compares the influence of cadmium replacement coatings on hydrogen embrittlement or overall EAC of a substrate steel. Again, Table 4 compares the performance of

replacement coatings to that of cadmium coatings under similar test conditions. A comprehensive analysis of hydrogen embrittlement and EAC is presented in Volume 13 of the *ASM Handbook* (Ref 17, 18), so a similar discussion is not presented here. However, for steels, susceptibility to hydrogen embrittlement or EAC generally correlates with increasing yield strength and hardness. Thus, any analysis of cadmium replacements intended for use on high-strength steels must consider the issues presented in this table.

In general, the Table 4 data were developed by evaluating AISI 4340 steels, heat treated to between 1241 and 1379 MPa (180 and 200 ksi), using constant extension rate tests (CERT) or other applicable EAC tests. Data regarding EAC of the solid nickel and stainless steels are not presented in Table 4 but are available in Ref 17 and 18.

Figure 4 shows how test data were summarized to create the qualitative Table 4 ratings. It presents CERT results from coated, high-strength steel specimens immersed in an aqueous 3.5% NaCl solution and/or an inert medium (Ref 19). The test specimens were baked after plating to reduce hydrogen mobility and/or drive off process hydrogen (Ref 19, 20). Thus, the results show how sacrificial corrosion can embrittle high-strength steels. Reduced CERT times to failure for coated specimens, relative to those for uncoated experimental control specimens, are associated with embrittling effects. Figure 4 shows that cadmium plating (QQ-P-416, type I) caused the least substrate embrittlement.

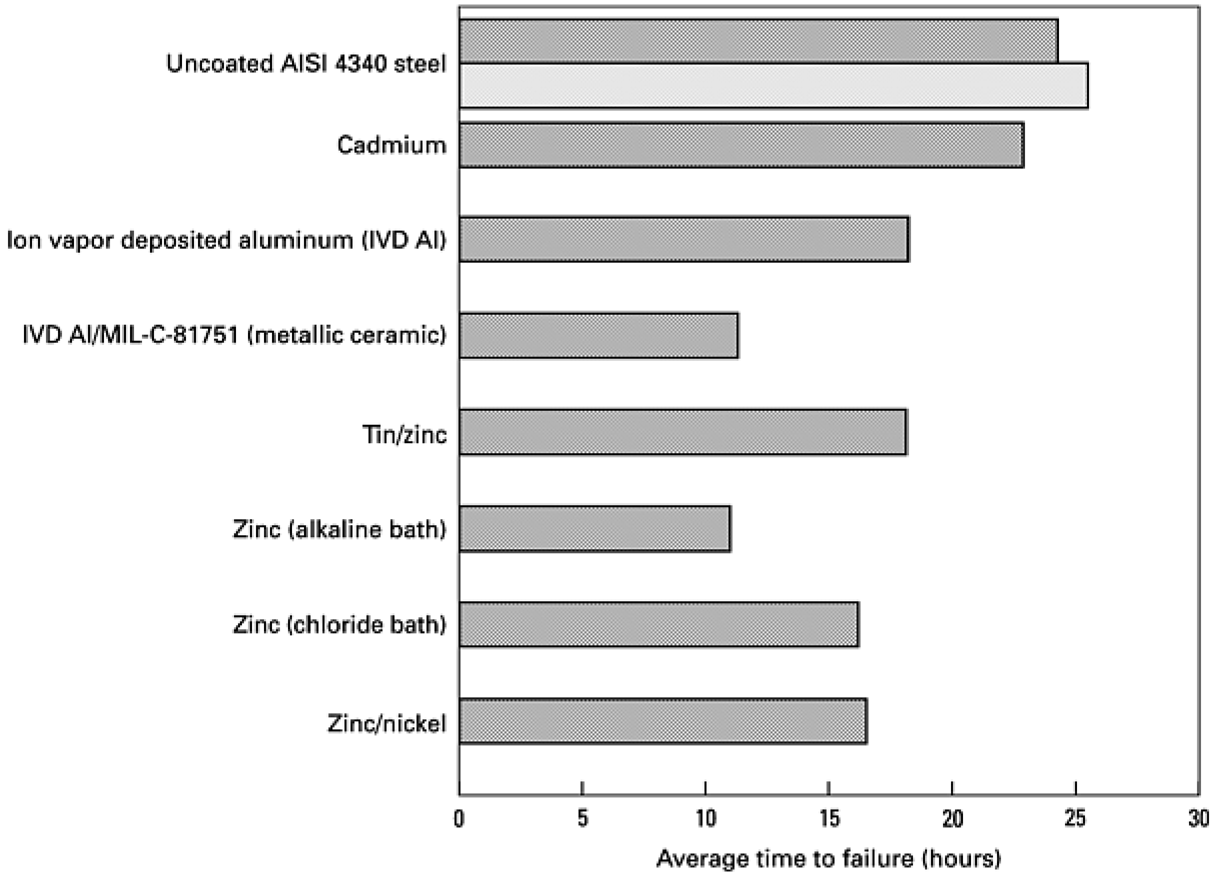

Fig. 4 Results of constant extension rate tests (2.5 × 10^{-2} μm/s, or 2.5 × 10^{-6} in./s) of AISI 4340 steel specimens (1241 MPa, or 180 ksi) with cadmium and replacement coatings evaluated in aqueous 3.5 NaCl (dark bars) and/or an inert medium (light bar). Source: Ref 19

These results are not surprising, given that cadmium has historically been used as a high-strength steel coating. The usefulness of cadmium as a coating for high-strength steels is reflected in the numerous low-embrittlement specifications listed in Table 3. Because cadmium coatings may be applied in accordance with specifications that minimize production-process-induced or corrosion-induced hydrogen charging, and because none of the alternative specifications minimizes embrittlement, any cadmium replacements intended for use on high-strength materials must be evaluated before coating changes are authorized. The evaluation process must consider component strength level, configuration, and intended service environments. *Caution: Failure to evaluate cadmium replacements applied to high-strength steels could result in*

catastrophic component failures. Analysis of Table 4 data suggests that on some high-strength, high-performance parts for which solid alloys are not acceptable, cadmium may be the only viable, currently available plating process.

Coating Lubricity. This column in Table 4 addresses the established usefulness of cadmium as a threaded fastener or connector coating (Ref 21). Because lubricity is such a complex and difficult-to-define performance parameter, the ratings specifically summarize threaded fastener performance, as measured by differences in curves showing the tensile load created in a threaded fastener as a function of applied torque. Replacement coatings are rated *less* lubricious if they exhibited lower fastener tensile loads for given torque levels than cadmium fasteners subject to the same test conditions. To ensure that the data reflect significant performance differences between coating systems, not simply an effect caused by the test conditions, only results from unlubricated tests (i.e., no added oil or grease) are summarized. Adding lubricants such as grease or oil to threaded fastener systems exerts a significant influence on torque-tension behavior and creates an added degree of complexity which is beyond the scope of this article (Ref 22).

Figure 5 shows the type of data summarized in Table 4 and shows how added lubricants influence threaded fastener lubricity. The average tensile load created in H-11, 22-4-22 threaded bolts is shown as a function of applied torque. The data show that the application of cetyl alcohol (a lubricant) had more impact on the torque-tension relationship for threaded fasteners than the metal coating type. The data also show that for a given torque level, the specimens coated with ion vapor deposited (IVD) aluminum exhibited far less tensile load than the cadmium-coated experimental controls. As a result, IVD aluminum was rated less lubricious than cadmium in Table 4. Any potential use of IVD aluminum as a cadmium replacement on threaded fasteners must account for the inherent limited lubricity of the aluminum coating (Ref 23).

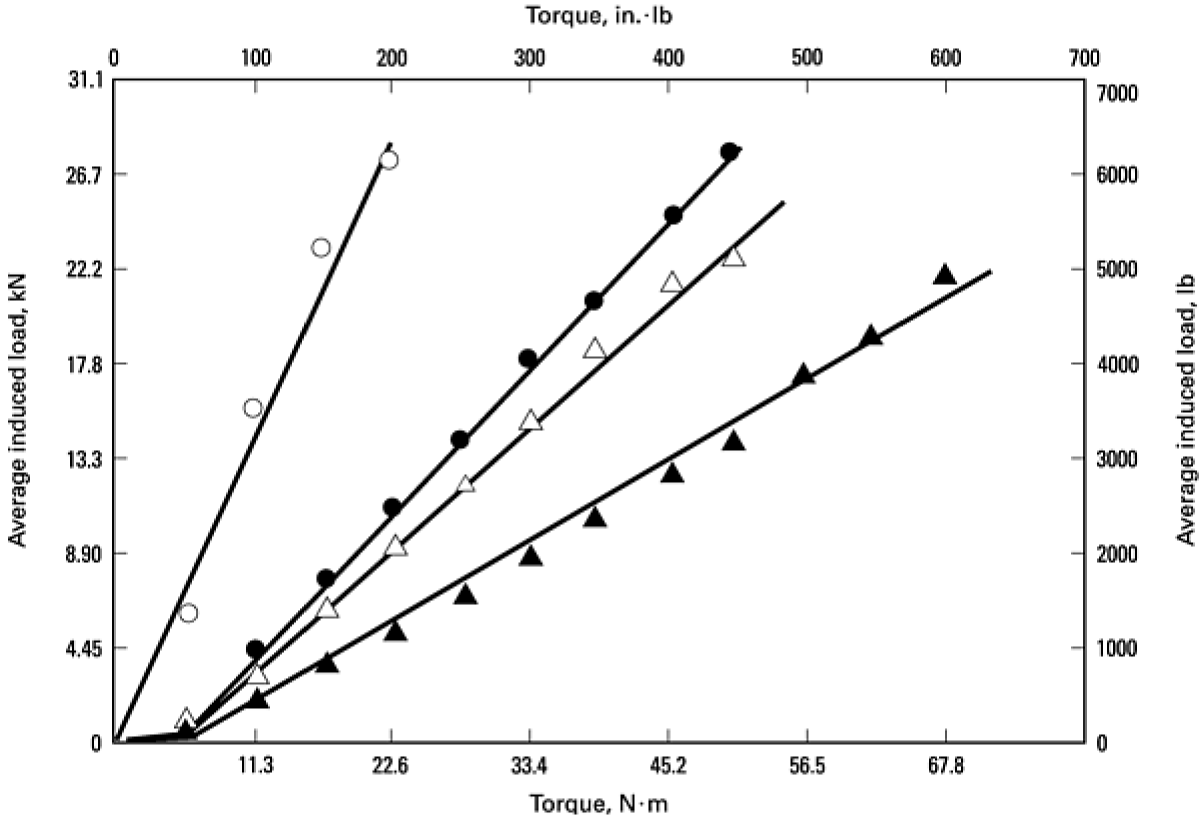

Fig. 5 Torque-tension test results for H-11, 22-4-22 threaded fasteners and alloy steel FN22 locknuts, coated with ion vapor deposited (IVD) aluminum or cadmium. ○, bolt and nut with IVD aluminum and cetyl alcohol; •, bolt with cadmium and nut with cadmium; △, bolt with IVD aluminum and nut with cadmium; ▲, bolt and nut with IVD aluminum. Source: Ref 23

Although results generated using added lubricants (e.g., grease or cetyl alcohol) are not summarized in Table 4, the application of a solid, dry film lubricant as part of the fastener production process was considered. Figure 6 shows

average torque-tension curves generated from testing replicate $\frac{1}{2}$-20-UNC, grade 5 fasteners plated with cadmium, zinc-nickel, and zinc-nickel with additional lubricious topcoats (i.e., dry film lubricants and polytetrafluoroethylene, or PTFE, systems) (Ref 24). Although only the averages are plotted in Fig. 6, standard deviation data show a considerable degree of variation around the mean. The standard deviation for the cadmium-plated fasteners (one of the most consistently lubricious or "well behaved" coating systems) was typically in excess of 15% of the average. The threaded fasteners coated with replacement systems demonstrated a similar, or even larger, range in tension for a given torque. Although the considerable data range is significant, the most important conclusion is that addition of a dry film lubricant or PTFE-type product over any sacrificial coating can create a system that is more lubricious than cadmium (Ref 24). The significant influence of dry film lubricants on overall system lubricity shows that cadmium should not be considered a unique or irreplaceable lubricious fastener coating.

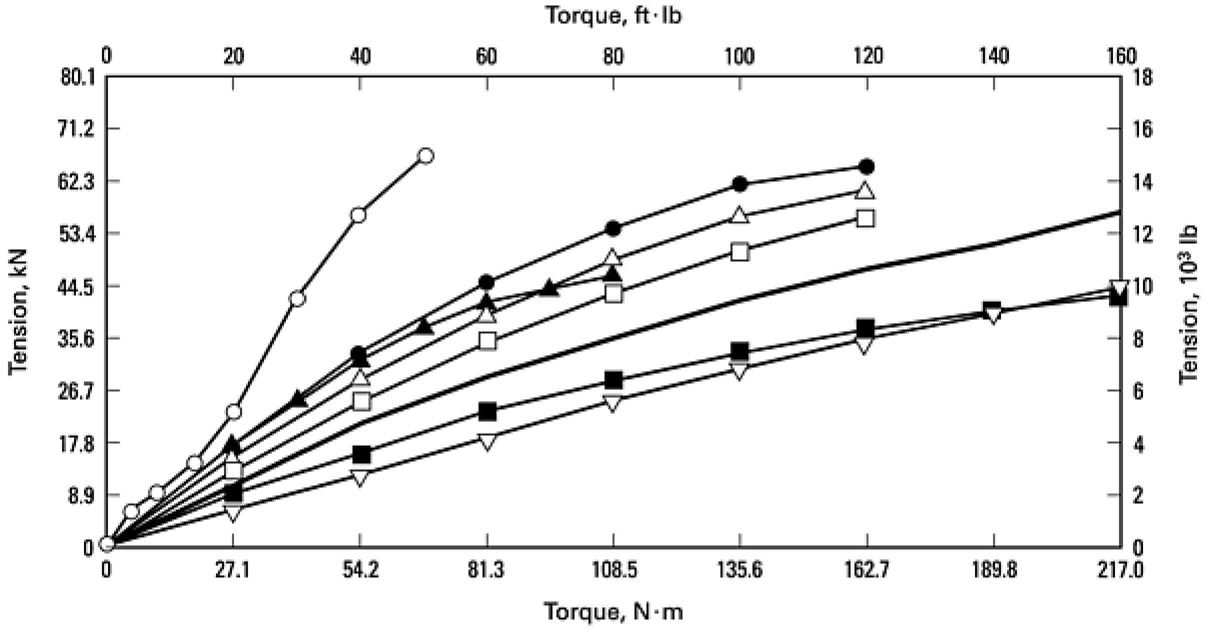

Fig. 6 Average torque-tension data from five replicate $\frac{1}{2}$-20-UNC grade 5 fasteners plated with cadmium, zinc-nickel, or zinc-nickel with lubricious topcoats. ○, dry film lubricant (MIL-L-56010); •, dry film lubricant (MIL-C-85614); △, organic sulfamate emulsion; ▲, aqueous polytetrafluoroethylene (PTFE)/phenolic; □, PTFE/phenolic A;■, PTFE/phenolic B; ▽, zinc-nickel; thick line, cadmium. Source: Ref 24

Environmental and Worker Health Regulations. This column in Table 4 compares the environmental compliance risks and potential worker health hazards created by the replacement coatings. Of course, all of the replacements shown in Table 4 create far fewer environmental and worker health risks than cadmium. However, when applicable, there are comments about potential environmental and worker health issues that could affect replacement coatings.

For all plating processes described in Table 4, a comment is provided regarding the hazards posed by the chromate passivation treatment. Chromate passivation treatments based on hexavalent chromium-ion solutions are frequently used as a final step in the plating process and are subject to many of the same environmental and worker health regulations as cadmium. Although chromate passivation treatments do improve the corrosion-control performance of plating systems, the Table 4 data were developed using both chromated and nonchromated plating layers (Ref 3). Replacing cadmium with one of the replacement plating processes shown in Table 4, along with eliminating the chromate passivation process, minimizes hazardous materials handling and disposal costs and simplifies regulatory compliance.

Cost and Performance Factors. This column in Table 4 compares the application costs for the replacement processes to those for cadmium. The summaries are based on numerous analyses. Some of the data were inconsistent or contradictory, and as such, specific cost estimates must be developed on a case-by-case basis before any cadmium replacements are used.

Table 4 shows that the costs of using solid alloy components are higher than those for cadmium-coated parts. Although the costs for solid stainless steel or nickel alloy components are typically higher than those for cadmium-plated items, the life cycle costs (i.e., the costs associated with recurring maintenance and repair) for these solid alloy parts may be lower than those for cadmium or other replacement plating processes. The costs for IVD aluminum coatings are also shown to be higher than those for cadmium plating, primarily because the IVD aluminum application process is conducted in a vacuum chamber under the influence of an electric field. The significant investment in sophisticated equipment makes the IVD aluminum coating process approximately 33% more costly than QQ-P-416 cadmium plating on a per-part basis (Ref 23).

Other comments in this column relate to issues that might affect the cadmium replacement selection process. A key noneconomic issue that could affect cadmium replacement selection is the in-service appearance of the sacrificial layer. Zinc coatings are known to develop voluminous white corrosion products while sacrificially corroding (Ref 16). These corrosion products may interfere with the function of precision components, or they may simply be cosmetically unappealing. Decisions about whether these products might affect the performance of individual components should be made by engineering staff.

References cited in this section

3. M. Ingle and T. Marchesani, Evaluation of Environmentally Acceptable Alternatives for Cadmium Plating, *Proceedings of the 5th Automotive Corrosion and Prevention Conference,* P-250, Society of Automotive Engineers, Oct 1991, p 25-41
7. "The Swedish Ban on Cadmium, Ordinance on Cadmium, Product Control Report, and Ordinance Relating to Deviations from the Ban on the Use of Cadmium for Surface Treatment or as a Stabilizer or as a Coloring Agent," Swedish Code of Statutes, SFS 1985:839, 21 Nov 1985
9. Consolidated List of Chemicals Subject to Reporting under the Emergency Planning and Community Right-to-Know Act, *EPA Title III: List of Lists,* Jan 1992
11. Finland: Products Containing Cadmium and Its Compounds, PSA 0729, *Commerce Business Daily,* 25 Nov 1992
12. Chemicals Group and Management Committee, "Co-operation on Existing Chemicals: Risk Reduction Lead Country Report on Cadmium," Report to the 16th Joint Meeting, Organization for Economic Co-operation and Development, 28-30 May 1991
14. J.P. Ault, Ocean City Research Corporation, personal communication, 1993
15. H.E. Townsend, R.D. Granata, D.C. McCure, W.A. Schumacher, and R.J. Neville, Progress by the Automotive and Steel Industries toward an Improved Laboratory Cosmetic Corrosion Test, *Proceedings of the 5th Automotive Corrosion and Prevention Conference,* P-250, Society of Automotive Engineers, Oct 1991, p 73-95
16. D.C.H. Nevison, Corrosion of Zinc, *Corrosion,* Vol 13, *ASM Handbook,* L.J. Korb and D.L. Olson, Ed., ASM International, 1987, p 759
17. A.I. Asphahani, Corrosion of Nickel-Base Alloys, *Corrosion,* Vol 13, *ASM Handbook,* L.J. Korb and D.L. Olson, Ed., ASM International, 1987, p 641-657
18. R.M. Davison, T. DeBold, and M.J. Johnson, Corrosion of Stainless Steels, *Corrosion,* Vol 13, *ASM Handbook,* L.J. Korb and D.L. Olson, Ed., ASM International, 1987, p 547-565
19. M. Ingle and J. Ault, Corrosion Control Performance Evaluation of Environmentally Acceptable Alternatives for Cadmium Plating, *Seventh Annual Aerospace Hazardous Materials Management Conference,* McDonnell Douglas Co., 27-29 Oct 1992
20. A.W. Grobin, Jr., Hydrogen Embrittlement Problems, *ASTM Standardization News,* March 1990, p 30-34
21. "Preliminary Use and Substitutes Analysis of Lead and Cadmium in Products in Municipal Solid Waste," U.S. Environmental Protection Agency, PB92-162551, April 1992
22. R.O. Parmley, *Standard Handbook of Fastening and Joining,* McGraw-Hill, 1989
23. V.L. Holmes, D.E. Muehlberger, and J.J. Reily, "The Substitution of Ion Vapor Deposited Aluminum for Cadmium," Report C87-101501, McDonnell Douglas Co., 31 Jan 1989

24. M.W. Ingle, I.C. Handsy, and B.S. Schorr, Evaluation of Environmentally Acceptable Multi-layer Coating Systems as Direct Substitutes for Cadmium Plating on Threaded Fasteners, *Proceedings of the 6th Automotive Corrosion and Prevention Conference,* P-268, Society of Automotive Engineers, Oct 1993, p 223-246
25. N. Zaki and E. Budman, Zinc-Nickel Alloy Plating Has Hit the U.S. Scene: Who Is Doing What and Why? *Products Finishing,* Vol 56 (No. 1), 1991
26. O.V. Schiffelgein, "Alloy Replacement of Cadmium Plating," Comprehensive Chemical Reduction Program Final Report, Boeing Document D180-30690-6, 6 Jan 1992
27. "Draft Electrodeposited Zinc-Nickel Alloy Plating, Process Specification for," Ground Systems Division, 49207-1236857, FMC Corp., 11 June 1990
28. "Standard Corrosion Control Manual," Commander, Naval Sea Systems Command, NAVSEA S9630-AE-MAN-010, updated Sept 1982, p 4-61
29. A.C. Zacaroli, Public Citizen-OCAW Petition for Emergency Rule on Hexavalent Chromium Denied by OSHA, *Occupational Health and Safety News, 1 April 1994*
30. C. Freeman, Occupational Safety and Health Administration, personal communication, 22 March 1994

Chromium Elimination in Surface Engineering

Barry Meyers and Stephen Lynn, The MITRE Corporation; Elwin Jang, United States Air Force, Sacramento Air Logistics Center

Introduction

CHROMIUM has been widely used in surface finishing of metals because of the favorable properties it imparts to substrates and because the processes used are relatively mature, well understood, widely specified, and cost-effective. In recent years, however, the use and emission of hexavalent chromium has come under increased scrutiny by various regulatory bodies due to its adverse health and environmental effects. Indications are that regulatory agencies will continue to require significant reductions in the emissions of chromium in the future. Typical solutions to this problem range from the addition of emissions control devices, to a change in the method of application of a material, to the complete re-engineering of the surface finishing process through process and material substitution.

Major uses of hexavalent chromium in surface finishing are in chromium plating and chromate conversion coating. Chromium plating is electrolytically applied to steel parts and can be either hard (engineering) plating, which is applied relatively thickly to impart desirable wear and abrasion resistance, or decorative plating, which, as the name implies, is for aesthetic purposes. (See the articles "Industrial (Hard) Chromium Plating" and "Decorative Chromium Plating" in this Volume.) Chromate conversion coating is a nonelectrolytic process in which the conversion coating is applied to light metals (aluminum, magnesium, cadmium plate) and alloys for corrosion resistance and/or as a paint base. (See the article "Chromate Conversion Coatings" in this Volume.) To a lesser extent, chromium is used in chromic acid anodizing, which also imparts corrosion resistance and paint adhesion properties to aluminum but, unlike conversion coating, is an electrolytic process.

This article focuses on alternatives to chromium in both hard chromium plating and chromate conversion coating. It addresses material and process substitutions that can be used to eliminate the use or emissions of chromium in the industrial processes described above. Other uses of chromium, such as in paints, are not covered. The focus of the article is on comparing the physical characteristics of each coating and the economics, environmental impact, advantages, and disadvantages of alternative processes.

Alternatives to Hard Chromium Plating

Hard chromium plating is the most widely used application of chromium in surface finishing. It is routinely used for applications that require hard, wear-resistant coatings on either new or refurbished parts. The coating applied is relatively thick (as opposed to decorative chrome), generally between 0.25 and 0.76 mm (10 and 30 mils), which makes it good for dimensional restoration. In aerospace applications, chromium plating is the preferred wear-resistant coating for hydraulics, landing gear, rotating shafts, gears, and surfaces subjected to sliding or rolling wear. The plating

characteristics of chromium plating are shown in Table 1. The thickness buildup, coating adhesion, hardness, and abrasion resistance properties are especially favorable.

Table 1 Plate characteristics of hard chromium plating and prospective alternative processes

Characteristic	**Chromium electrodeposition**	**Low-phosphorus electroless nickel (generic)**	**Ni-W-B electrodeposition (Amplate)**	**Ni-W-SiC electrodeposition (Takada)**	**Plasma spray (general)**	**High-velocity oxyfuel (general)**
Thickness buildup, mm (mils)	Up to 0.8 (up to 30)	Up to 0.5 (up to 15) (more uniform than chrome)	Up to 0.25 (up to 10) (more uniform than chrome)	Up to 0.4 (up to 15) (more uniform than chrome)	Up to 1.3 (up to 50) (rougher than chrome)	Up to 1.3 (up to 50) (rougher than chrome)
Coating adhesion, MPa (psi) (ASTM C 633)	>70 (>10,000)	>70 (>10,000)	>70 (>10,000)	>70 (>10,000)	>55 (>8000) (coating-dependent)	>70 (>10,000) (coating-dependent)
Hardness	800-1000 HV	670-750 DPH_{300}; with heat treatment, 980-1050 DPH_{300}	600-950 DPH_{300}(with heat treatment)	800 to >1000 DPH_{300}	800-1200 DPH_{300} (coating-dependent)	800-1450 DPH_{300} (coating-dependent)
Machine finish, μm (μin.) (RHR rms)	<0.2 (<8)	<0.2 (<8)	<0.2 (<8)	<0.2 (<8)	<0.2 (<8)	<0.2 (<8)
Corrosion resistance, h (ASTM B 117)	>24	>96	>400	>24	>24	>48
Porosity, %	<2	<1	<1	<1	5-13	<2
Abrasion resistance, mg (Taber CS-10, 1 kg, avg per 1000 to 10,000 cycles)	<25	<35 (dependent on heat treatment and composite additives)	<25	<20	<20 (coating-dependent)	<20 (coating-dependent)
Coefficient of friction	0.16	<0.20[a]	0.13	0.13	0.25[a]	<0.20[a]
Falex wear rate	Good	Moderate/poor	Excellent	Excellent	Moderate/poor	Good[a]
Threshold galling wear	Good	Moderate/poor	Excellent[a]	Excellent[a]	Good[a]	Good[a]
Chemical	Fair	Good	Excellent	Excellent	Good	Excellent

resistance						
Coating stripping ability	Good	More difficult	More difficult	More difficult	Difficult	More difficult
Fatigue loss, %	As high as 60	Less than for chromium[(a)]	Less than for chromium[(a)]	Less than for chromium[(a)]	Less than for chromium[(a)]	Less than for chromium[(a)]

RHR, roughness height rating.

(a) Needs additional testing

The chromium plating process is inexpensive, well understood (it has been widely used for many years), and easy to perform. The process involves degreasing, masking, and cleaning prior to plating. The parts are then racked and immersed in the plating bath for up to 24 h, depending on the desired thickness. Following the plating step, the parts are removed from the bath, masking is removed from the part, the part is baked for embrittlement relief, and finishing (such as grinding, lapping, polishing) is completed.

Several disadvantages of chromium plating are its high fatigue life debit, marginal corrosion resistance due to microcracking, high power consumption, nonuniform coverage, poor penetration into holes and tube bores, and the evolution of hydrogen in the process. As a result of the hydrogen evolution, misting occurs, which leads to high air emission rates and associated adverse health, safety, and environmental risks.

Potential process substitutions for hard chromium plating are discussed below. These include electroless nickel in certain applications, several nickel-tungsten composite plating options, and spray applications such as plasma spray coatings. (There are other possible substitutions, such as vacuum deposition processes and cobalt alloys, that are not discussed.) None of these has exhibited all of the desirable qualities of chromium plating. Certain tradeoffs, such as somewhat poorer physical properties, increased process time, and increased costs, are to be expected. Clearly, no one alternative should be viewed as a "drop-in" replacement for the elimination of all chromium in hard chromium plating.

Electroless nickel (EN) plating has been in existence for several decades. In this autocatalytic process, nickel ions are reduced to metal by the action of chemical reducing agents, without the need for an electric current. A commonly used reducing agent is sodium hypochlorite, which donates electrons to the metal ions with the substrate acting as a catalyst for the reaction.

The use of EN as an alternative to chromium plating is severely limited by its somewhat poorer physical properties. As is evident from Table 1, the hardness and abrasion resistance of low-phosphorus EN are good but lower than those of chromium plating. In addition, the wear rate and galling resistance are poorer than those of chromium plating (Ref 1).

One advantage of EN is that the deposit follows all of the contours of the substrate without the excessive buildup at the edges and corners that is common with chromium plating. Sharp edges and blind holes receive the same plating thickness. The process bath, however, is more sensitive to impurities than the chromium plating bath, and it must be closely monitored to maintain the proper concentrations and balance of the metal ions and reducing agents. In addition, the bath life is finite and less than that of chromium plating, which means that periodically it must be "dumped" and a fresh bath prepared. Deposition rate and coating properties are affected by temperature, pH, and metal ion/reducing agent concentration.

Electroless nickel plating can be used as a chromium plating alternative in limited applications, such as for very well lubricated conditions. It cannot be cost-effectively plated as thick as chromium, but because it plates more evenly, the need for substantial overplating can often be eliminated. The main drawback with EN is that the coating is not as hard as chromium plate. However, a postplating heat-treatment step can improve its hardness significantly. Although EN does not wear as well as chromium plating and is more susceptible to galling wear, on a positive note, it imparts greater corrosion protection than chromium plate and should not result in significant fatigue life debit.

Nickel-Tungsten Composite Electroplating. Two separate nickel-tungsten composite electroplating processes are available as potential alternatives to chromium plating: nickel-tungsten-boron (Ni-W-B) composite electroplate (Ref 2) and nickel-tungsten-silicon carbide (Ni-W-SiC) composite electroplate (Ref 3, 4). The two processes are similar in that they are both electrolytic and deposit a composite of nickel and tungsten onto the substrate. Both have been developed relatively recently and are not yet widely used. Each coating exhibits many of the desirable properties of chromium plating, but additional testing is required before the processes can be widely used in critical applications. The processes use less energy than chromium plating, so the platings are more uniform than chromium and can result in cost savings by allowing greater throughput and a minimal amount of overplating. In addition, the applications are tank-based, which makes a transition from chromium plating relatively straightforward.

Ni-W-B composite electroplating deposits a coating that is approximately 59.5% Ni, 39.5% W, and 1% B (Ref 2). The coating has a bright silver-white, highly lustrous appearance at thicknesses of up to 0.25 mm (10 mils), above which it becomes matte in appearance. The physical properties of the coating are listed in Table 1. The coating has favorable chemical and abrasion resistance, high ductility, a low coefficient of friction, and plates very uniformly and smoothly. However, as compared with chromium, Ni-W-B is less hard; postplating heat treatment raises the hardness significantly to a level that is equal to or slightly greater than that of chromium plate.

Ni-W-SiC composite plating is similar to Ni-W-B except that it uses silicon carbide interspersed in the matrix to relieve internal stresses and improve the coating hardness. The resulting deposit is roughly 46.3% Ni, 46.1% W, 4.3% Si, and 3.2% C (Ref 4). The appearance of the coating is similar to that of Ni-W-B, with the silicon carbide causing a nearly indiscernible darkening. The coating properties, which are also listed in Table 1, indicate favorable chemical resistance, abrasion resistance, and coefficient of friction. The hardness of the coating is somewhat greater than that of Ni-W-B, and with heat treatment it can exceed that of chromium plating.

The major disadvantages associated with these two nickel-tungsten processes are their lack of maturity, their potential increased costs over chromium, and, to a lesser extent, their reliance on nickel. Besides not having been scaled up to production, additional testing, which is ongoing at various locations, will be required to qualify these coatings for particular applications. The qualification process is not easy; engineers rightly err on the conservative side in approving such sweeping changes in potentially critical situations. Also, while no hard numbers exist, it has been estimated that these processes will cost considerably more than for chromium plating (Ref 5). However, these estimates do not consider the potential liability costs associated with the continued use of chromium. It is true that the use of nickel, and to a lesser extent the use of tungsten, may become more tightly regulated, but even so, there is much less nickel in these plating baths than there is chromium in a chromium bath, resulting in lower risk.

Spray Coating Applications. Several spray coating applications have shown promise as potential alternatives to chromium plating. Variations on this application include arc spray, flame spray, plasma spray, and high-velocity oxygen fuel (HVOF) spray. From a materials standpoint, the one having the best coating properties is HVOF spray, which is the type addressed in this section.

HVOF coatings are presently used in many industrial applications because they develop very hard, wear-resistant surfaces that have comparable performance requirements to those of chromium plating. HVOF spray is based on the detonation gun (D-gun) process developed by Union Carbide (Praxair). In HVOF coating application, an explosive gas mixture ignites in the barrel of the spray gun, which melts a powdered coating material and propels it (with a carrier gas) at supersonic speeds toward the substrate. The superior coating properties are a result of the high velocities that are reached in the process--the higher the velocity, the greater the force of impact at the substrate, resulting in fewer voids in the coating and more desirable properties.

There are presently numerous manufacturers of HVOF equipment and coating materials, each having a somewhat different design; the system and coating material selected contributes to the resulting coating properties. Table 2 lists the coating properties of some typical HVOF coatings that may be applicable to chromium plating elimination. Note that many HVOF coatings are chromium-base, so the use of the HVOF system would not necessarily result in chromium *elimination.* However, the HVOF process emits significantly less chromium than chromium plating, and recovered metal powders can be recycled.

Table 2 Physical characteristics of high-velocity oxyfuel spray deposited coatings

Characteristic	Tungsten carbide-	Cobalt-chromium-	Nickel-chromium-	Chromium carbide-	Iron-nickel-

	cobalt	**nickel-tungsten**	**molybdenum**	**Nichrome**	**chromium**
Thickness buildup, mm (mils)	>1.3 (>50)	>1.3 (>50)	>2.5 (>100)	>0.6 mm (>25)	>1.5 (>60) max
Coating adhesion, MPa (psi) (ASTM C 633)	>90 (>13,000)	>70 (>10,000)	>70 (>10,000)	>88 (>12,000)	>75 (>11,000)
Hardness	64-69 HRC	53 HRC	30-34 HRC	65 HRC	45 HRC
	800-1650 DPH_{300}	550-700 DPH_{300}	350-450 DPH_{300}	800-850 DPH_{300}	550-650 DPH_{300}
Machine finish, μm (μin.) (RHR rms as-sprayed)[(a)]	4-6 (150-250)	4-7.5 (200-300)	4.3-6 (170-250)	2.5-4.3 (100-170)	6-9 (250-350)
Corrosion resistance, h (ASTM B 117)	>48[(b)]	>48[(b)]	>48[(b)]	>48[(b)]	>48[(b)]
Porosity, %	<1	<1	<1	<1	<1
Abrasion resistance, mg (Taber CS-10, 1 kg, avg per 1000 to 6000 cycles)	<20	<20	<20	<20	<20
Coefficient of friction	0.18	<0.20[(b)]	<0.20[(b)]	<0.20[(b)]	<0.20[(b)]
Falex wear rate	Excellent	Excellent[(b)]	Excellent[(b)]	Excellent[(b)]	Excellent[(b)]
Threshold galling wear	Excellent[(b)]	Excellent[(b)]	Excellent[(b)]	Excellent[(b)]	Excellent[(b)]
Chemical resistance	Excellent	Excellent	Excellent	Excellent	Excellent
Coating stripping ability	More difficult	More difficult	More difficult	More difficult	Difficult
Fatigue loss	Less than for chromium[(b)]	Less than for chromium[(b)]	Less than for chromium[(b)]	Less than for chromium[(b)]	Less than for chromium[(b)]

(a) Ground machined finish is <0.2 μm (<8 μin.) for all coatings. RHR, roughness height rating.

(b) Significant uncertainty due to testing method or speculated effects based on metallurgical properties

References cited in this section

1. L. Weisenberger, "Hardness and Wear Resistance of Electroless Nickel Alloys," internal report, Allied Kelite

Witco Co.

2. Amorphous Technologies Inc., vendor literature
3. K. Takada, "An Alternative to Hard Chromium Plating," paper presented at the 27th Annual Aerospace/Airline Plating and Metals Forum (San Antonio, TX), 26-28 March, 1991
4. K. Takada, Method of Nickel-Tungsten-Silicon Carbide Composite Plating, U.S. Patent 4,892,627, 9 Jan 1990
5. "Alternatives to Hard Chromium Plating at McClellan Air Force Base," internal report, MITRE Corp., Nov 1993

Alternatives to Chromate Conversion Coating

Chromate conversion coating is a nonelectrolytic application to light metals, generally aluminum and its alloys, for the purpose of imparting corrosion protection and paint adhesion properties. The process is widely used in the aerospace industry and can be applied by brush, spray, wipe, or immersion. Chromate conversion coating offers numerous advantages over the potential alternatives:

- Greatly improved wet and dry paint adhesion
- Self-healing corrosion protection in case of scratched parts
- Simple application process and easy-to-maintain bath chemistry
- Mature process; in many applications has been the preferred coating for years

Presently, there are no drop-in substitutes to chromate conversion coating that adequately address each of its advantages.

The major disadvantage of chromate conversion coating is simply its use of hexavalent chromium. The tank-based process does not have the misting emission problem typical of chromium plating, but in applying the coating to entire aircraft, the subsequent rinse process can generate large quantities of chromium-containing wastes.

Several tests are routinely used to quantify the characteristics of conversion coatings. Paint adhesion can be measured using the wet tape adhesion method, scrape adhesion method, knife scribe test, crosshatch adhesion test, and others. Corrosion resistance is typically measured using the salt spray corrosion resistance test, ASTM B117, which is conducted on either unpainted or painted specimens. Examples of the performance of chromate conversion coatings in these tests are included in Table 3, which also shows the performance of alternatives.

Table 3 Coating characteristics of chromate conversion coating and prospective alternative processes

Characteristic	**Chromate conversion coating**	**Cobalt/ molybdenum-base coating**	**Oxide layer growth coating**	**Sulfuric acid boric acid anodizing**
Salt spray testing, unpainted, h	>336	>336	>168	>336
SO_2/salt spray testing, unpainted, h	<168	. . .	>168	>168
Salt spray testing, painted, h	>2,000	>1,500	>2,000	>2,000
	Pass	Pass	Pass	Pass
Paint adhesion, crosshatch test	Pass	Pass	Pass	Pass

Paint adhesion, wet tape	Pass	Pass	Pass	Pass
Electrical resistance, MΩ	<5,000	<5,000	>5,000	>5,000
	<10,000 after salt spray	<10,000 after salt spray	>10,000 after salt spray	>10,000 after salt spray

Potential alternatives to chromate conversion coating are discussed below. These include a proprietary cobalt and molybdenum-based process, a multistep process that grows a corrosion-resistant oxide layer, and various others.

Cobalt/molybdenum-base conversion coating is a project of a major aerospace company and a supplier of conversion coatings, Parker-Amchem. It is a developmental process that uses cobalt and molybdates rather than chromates. Laboratory tests have shown that the coating is capable of meeting the important corrosion resistance and paint adhesion characteristics (Table 3), but the process has not been scaled up to production levels.

The cobalt/molybdenum process requires one additional process tank and rinse step for sealing, which could have considerable cost impact. In addition, it requires heated baths, resulting in increased energy usage. This makes the estimated cost associated with the process about twice as much as that of chromate conversion coating (Ref 6), keeping in mind that liability costs, which could be significant, are not factored into the costs of chromate conversion coating. Although this is a significant increase, the cost is not as much as for the oxide layer growth process described below. Probably the greatest disadvantage of the cobalt/molybdenum-base process is that it is still developmental and has not been scaled up to production levels.

Advantages of this coating process are that it would be universally applicable to parts that are presently chromate conversion coated. It is still a tank-based process for immersion application (it is also being developed for spray, brush, and wipe applications), and it requires only slightly more time than the present coating process.

Oxide layer growth in high-temperature deionized water was developed and refined within the past decade (Ref 7, 8, 9), and this process is somewhat more mature than the cobalt/molybdenum process. Several variations are in different stages of development. This process uses a series of steps, including immersion in boiling distilled water, to build a corrosion-resistant paint base on aluminum. Following the growth of the corrosion-resistant oxide layer, several proprietary baths are used to seal and enhance the properties of the coating. The coating meets the corrosion protection and paint adhesion requirements of a conversion coating (see Table 2) and has been tested extensively by the Navy (Ref 10).

The major drawback of the oxide layer growth process is its cost. It requires many additional steps, involving numerous tanks of chemicals at various elevated temperatures. Consequently, the energy costs and processing times, as well as capital costs, increase substantially. In fact, it is estimated that the tank-based process may cost up to ten times as much as the present chromate conversion coating process (Ref 6).

A variation on the process involves spray application within a cabinet coater, a chamber large enough to handle the applicable parts. The various solutions are then applied sequentially using a steam generator. The concept is a joint venture of the developer of the process and another company, Electrosteam Generator Corporation. It saves on heating costs and reduces the volume of chemical required, but it is still in the developmental stage.

Other chromate conversion coating alternatives may prove to be of use in eliminating chromium from conversion coatings. These include sulfuric acid/boric acid anodizing (SBAA), various phosphate treatments, and other emergent technologies.

SBAA was developed by a major aerospace company to replace chromic acid anodizing (Ref 11). The process imparts exceptional paint adhesion and corrosion protection at a cost comparable to that of chromate conversion coating, and it may prove valuable as a replacement for chromate conversion coatings on some parts. However, SBAA is an anodic process, so it is not universally appropriate to all parts, especially parts with steel inserts or those having sharp edges, welds, crevices, and other areas that entrap fluids. This problem severely limits the applicability of SBAA as a chromate conversion coating alternative.

Phosphate coatings do not provide as high a quality of coating as the present process. However, in applications where the conversion coating/primer/topcoat is treated as a "system" for testing purposes (i.e., the *bare* salt spray corrosion resistance is not considered important), this type of coating could be an appropriate substitute. It is in use within the automotive industry, but it has the disadvantages of additional process steps, long process cycle time, and increased energy consumption.

Table 4 lists several experimental and developmental technologies that may lead to breakthroughs with respect to replacement of chromium in conversion coatings in some applications. Another developmental technology is the "no-rinse" conversion coating, which, although not a chromium-eliminating technology, has the capability to reduce the amount of chromium discharged. The Navy and Air Force have worked to develop a conversion coating that can be applied to an entire aircraft with no rinse step, which is where the majority of the chromium emissions occur during brush or wipe applications of the conversion coating.

Table 4 Emergent alternative conversion coat technologies

Process description	Status
Trivalent chromium conversion coatings	Meets no corrosion in 500 h requirement (ASTM B 117 salt spray test)
	Still contains chromium
	Electrolytic process
Hydrated alumina coating	Poor paint adhesion
	Meets no corrosion in 500 h requirement (ASTM B 117 salt spray test)
Hydrated metal salt coating (Mg, Ni, Mn, Sn, Ti, Fe, Ba, Cu, Co, Ca)	Does not meet salt spray requirement
	Poor adhesion
Peroxide oxidant coating	Does not meet salt spray requirement
	Poor adhesion
	Unstable chemical baths
Oxyanion analogs (molybdates, tungstates, vanadates, and permanganates)	Moderate corrosion resistance
	Poor paint adhesion
	Molybdates with borate seem best
	Expensive

Potassium permanganate coating	Moderate corrosion protection (168 h)
	Poor wet tape adhesion
	Does not work well on 2024 or 7075
	Requires boiling deionized water
	Multistep process, expensive
Rare earth metal salts (cerium)	Corrosion protection close to that of chromium
	Good paint adhesion
	Unstable chemical bath
	Expensive
	Has good future potential
Zirconium oxide/yttrium oxide in aqueous polymeric solution	Good paint adhesion
	Moderate salt spray protection (100 h)
	Commercially used for >10 years
	One step
	Expensive
Silanes or titanates	Good adhesion
	Moderate corrosion resistance
	Contain flammable solvents
	Thickness dependent, must be cured
	Difficult to dispose of
	Good corrosion protection on 1000-, 3000-, and 6000-series

	alloys
	Poor wet paint adhesion
	Single process bath
	Environmentally benign
	Very promising

References cited in this section

6. "Alternatives to Chromate Conversion Coating at McClellan Air Force Base," internal report, MITRE Corp., Dec 1993
7. J. Bibber, Corrosion Resistant Aluminum Coating Composition, U.S. Patent 4,711,667, 8 Dec 1987
8. J. Bibber, Corrosion Resistant Aluminum Coating Composition, U.S. Patent 4,755,224, 5 July 1988
9. J. Bibber, Corrosion Resistant Aluminum Coating Composition, U.S. Patent 4,898,963, 7 Nov 1989
10. S. Spadafora et al., "Non-Chromated Surface Pretreatment for Aluminum," Report NAWCADWAR-92077-60, Defense Printing Service, 18 Aug 1992
11. Boeing Aircraft Co., vendor literature

Vapor Degreasing Alternatives

Dennis Zupan, Brulin Corporation; Tony L. Green, Lockheed Aeronautical Systems Company; Donald W. Benjamin, AlliedSignal Aerospace; Bruce Hooke, Boeing Commercial Airplane Group; Calvin Fong, Northrop Corporation

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Introduction

VAPOR DEGREASING has been widely used for many years in the automotive, aerospace, and other manufacturing and processing industries to degrease and clean parts prior to chemical processing, bonding, painting, and other treatments. The chemicals traditionally used for this process are trichloroethylene (TCE) and perchloroethylene (PCE); however, these compounds have proven to be serious health and environmental hazards. Concern about these hazards led to the use of alternate chemicals: chlorofluorocarbons (CFC) and 1,1,1-trichloroethane (TCA). These compounds are less toxic and appeared, at least initially, to have no adverse effects on the environment.

Since the early 1980s, however, there has been mounting evidence that the ozone layer is being depleted, and the release into the atmosphere of CFC and TCA from their use in various industrial operations and consumer products has been identified as a contributor to this problem. CFC and TCA are classified by federal law as class 1 ozone depleting chemicals (ODC).

The traditional vapor degreasing process is described in the article "Solvent Cold Cleaning and Vapor Degreasing" in this Volume. This present article discusses the regulatory mandates that affect the use of industrial degreasing methods and describes several of the modified and alternative processes that are being used in place of traditional vapor degreasing.

Regulatory Constraints

Industry has used vapor degreasing with either a volatile organic compound (VOC) or an ODC as the solvent for many years, and the process has gained widespread acceptance. However, many laws have been put into place to regulate or restrict the use of traditional vapor degreasing, and many new regulations are pending. As these laws come into effect, it

becomes increasingly more expensive to operate and maintain these systems and to dispose of the waste they generate. Aqueous degreasing techniques (see the section "Aqueous Systems" in this article) have been developed that offer industry an attractive alternative because they are less expensive to operate and maintain, they allow for easier disposal of waste, and they are also subject to fewer regulations. This section addresses many of the regulations in the United States that affect traditional and alternative degreasing systems. Additional information is available in the article "Environmental Regulation of Surface Engineering" in this Volume.

Environmental Protection Agency (EPA) Regulations. In 1967, the U.S. Congress enacted the Clean Air Act, which made provisions for the attainment and maintenance of ambient air quality. The passage of the Clean Air Act, which is administered by the EPA, marked the start of major regulatory initiatives to control the emissions of VOC from industrial processes. In 1977, Congress passed the Clean Water Act to maintain and ensure the quality of water that is used for recreation and consumption. Both of these acts contain language that requires monitoring and control of emissions to the air and water. The Clean Air Act also requires the EPA to promulgate a National Emission Standard for Hazardous Air Pollutants (NESHAP). The NESHAP standard limits the amount of hazardous air pollutants that can be released to the environment and requires the use of the maximum achievable control technology (MACT) to control the emissions. Both TCE and TCA are included as pollutants on the NESHAP list.

Because of these regulations, TCE and PCE have become costly to use for vapor degreasing applications. The higher costs are due to the limits on emissions and the controls required to capture these emissions, plus the restrictions on the disposal of waste materials. In the face of these rising costs, many industries switched to using CFC and TCA as vapor degreasing solvents. However, in 1990 the EPA amended the Clean Air Act to adopt the Montreal Protocol, which calls for worldwide cessation of the production of ozone-depleting chemicals. This step had the effect of making CFC and TCA as costly to use as TCE and PCE, and eventually they will be unavailable for use.

The primary alternatives to ODC and VOC materials are aqueous degreasing systems. Because the components are solids and soluble in water, compliance with the Clean Air Act can be easily achieved. It is compliance with the Clean Water Act that is the key regulatory issue with aqueous degreasers. Users of these systems should select component materials with great care. Some materials that are currently considered to be essentially nonhazardous (such as phosphates and glycol ethers) could be restricted in the future.

The Occupational Health and Safety Administration (OSHA) is a U.S. government agency that provides guidelines to employers to ensure the workplace safety of their employees. Through a variety of tests by OSHA and other organizations, OSHA has established safe 8-h exposure levels of 50 ppm for TCE and 25 ppm for PCE. When CFC and TCA replaced TCE and PCE as vapor degreasing solvents, the permissible exposure limits for CFC and TCA were set at 350 ppm. In other words, the ODC are seen as being less toxic to workers than either TCE and PCE.

The new aqueous degreasing materials have exposure limits that are, for the most part, higher than those for the ODC or VOC materials. The routes of exposure for ODC and VOC materials are inhalation, ingestion, and adsorption. For aqueous materials, inhalation is generally not an issue, and thus the primary routes of entry are limited to ingestion and adsorption. For these reasons, the aqueous degreasers are generally considered to be safer to work with than the ODC and VOC materials.

The Superfund Amendments and Reauthorization Act (SARA), enacted in 1986, deals with communities' "right-to-know." The right-to-know encompasses everything from where a toxic waste site may be located to what type and how much of certain chemicals are being used and/or stored at manufacturing facilities in the area that could cause problems should they be released into the environment.

The ODC and VOC materials used for vapor degreasing are on the list of chemicals that must be reported to the state in order to comply with the right-to-know law. Most materials used for aqueous degreasing do not appear on this list and have no reporting requirements.

The Resource Conservation and Recovery Act (RCRA) of 1976 requires that hazardous waste be disposed of in a manner that will not cause any adverse environmental or health effects. The RCRA also established that industrial manufacturers and processors must have plans for hazardous waste and solid waste management. Recycling of materials plays an important part in these plans.

Aqueous degreasing techniques offer the potential for easier and less expensive recycling as compared to vapor degreasing. In addition, the waste generated by aqueous degreasing does not cause the adverse environmental and health effects associated with VOC and ODC waste.

Aqueous Systems

Aqueous degreasing can be accomplished by hot tank or dip tank systems. Ultrasonic cleaning and spray cleaning are system options.

Hot Tank Systems

Heated, aqueous degreasing systems have been designed to replace vapor degreasers of various capacities. The equipment and processes described in this section have successfully replaced vapor degreasers in many applications within the aerospace industry, primarily to remove forming lubricants from detail parts prior to heat treatment, inspection, or finishing operations.

Advantages. The main advantage to these aqueous systems is that they are in regulatory compliance for air emissions. These systems are generally safer to operate and maintain than those using vaporized chlorinated solvents. They can remove many hydrocarbon-based oils, salts, and water-based materials. Treatment of spent aqueous solutions and rinse water can also often be accomplished on site.

Disadvantages. These systems generally require wash, rinse, and dry stages as a minimum. This often means that additional floor space is required as a vapor degreaser provides a clean, dry part using a single tank. Some utilities costs may be higher because heat must be provided to at least two liquid tanks and sometimes to a forced-air drier. More attention must be paid to racking considerations in an aqueous process because more space for solution flow is needed around the part surface. Process cycle times for aqueous degreasing are several times longer than for vapor degreasing due to the multiple steps required.

Equipment/Materials. In general, at least two tanks will be required: one to contain the wash solution and at least one to contain the rinse water. Additional rinse stages will significantly reduce water usage, but this advantage must be weighed against the additional capital cost and floor space required. The preferred material of construction for these tanks is stainless steel. Cost, compatibility with the cleaning solution, and life expectancy of the tanks are considerations when specifying tank material. When retrofitting a vapor degreaser tank with sufficient freeboard, a fresh water spray rinse or mist above the immersion wash or rinse tanks can improve rinsing, reduce overall water usage, and compensate for evaporative losses from the immersion tank(s).

Agitation of the fresh and rinse solutions is required. The flow of fresh solution past the part surface aids in cleaning and rinsing. A solution-recirculation system powered by centrifugal pumps is commonly used. The pumps are protected by a strainer and followed by cartridge or bag filters. These pumps deliver solution to a manifold that feeds an array of nozzles located near the tank walls. These nozzles should be oriented to maximize solution flow past the parts. Air sparging is not acceptable with many aqueous solutions due to the potential for foaming. When air sparging is used on the first (dirty) rinse stage, unacceptable levels of foaming may also be observed. This is due to carryover of soap solution. If agitation is vigorous, cleaning can also be enhanced by the mechanical scrubbing effect of the impinging fluid. This is often difficult to achieve in large tanks. Ultrasonic agitation also may be impractical on these larger systems, although the feasibility of using ultrasonic equipment ultimately depends on part geometry, economic factors, and other application requirements. Controllers should be used to maintain a constant temperature within the tank to ensure uniform cleaning.

Level controllers can be used in both the wash and rinse stages to add fresh water automatically to make up for evaporative losses. A conductivity meter can also be used to determine when the rinse needs to be freshened due to soap carryover. If the cleaning solution will foam, the pipe providing this make-up water should feed into the tank at a point below the surface to prevent foaming due to air entrainment and splashing. This should also be considered in the plumbing layout of the wash tank drainage system. A free fall of degreasing solution into a waste holding tank can quickly fill the tank with foam and create a severe maintenance problem. Electrically isolating the parts or basket from the tank walls may be required to prevent galvanic corrosion resulting from the formation of an electrolytic cell within the wash tank.

If parts must be dry and ambient evaporation rates are unacceptable, a forced-air drier may be required. High volumes of heated air are used. Flow rates and temperatures can be as high as practical while preventing part damage. The material

handling system will probably have to disengage from the parts basket to allow for an airtight seal to improve drying and to minimize humidity in the shop area. High-pressure air (air knives) can be used to blow the water off the parts. These are most useful if the part and basket geometry allows the air knife apertures to get consistently within a few inches of the parts. The noise generated by these air knives should be considered if their use is intended.

Process Description. Parts are washed, rinsed, and dried conventionally. First, the parts must be placed in the basket or rack that supports and moves the work through the various processing stages. More spacing between parts is often required when racking for an aqueous process than with a vapor degreaser due to the greater reliance on liquid flow past the part surface. More consideration must also be given to part movement and/or part flotation when racking, due to the large increase in density of the cleaning medium. Special racking schemes or agitation systems may also be required for parts with hidden surfaces such as tubing. Tumblers or rotating baskets sometimes improve cleaning for small parts. When the load is racked for processing, the cleaning cycle is initiated. An automated material-handling system can be incorporated to move the basket through the wash, rinse, and dry stages, thus allowing the operator to perform other activities such as loading or unloading another basket.

The primary variables affecting cleaning performance in the wash stage are the solution temperature and concentration, the immersion time, the thickness and composition of the soil layer to be removed, and the level of agitation. Agitation is an especially important factor.

Higher temperatures generally result in better cleaning. Sometimes the bulk melting point of a paste or grease must be achieved for good cleaning. Temperatures above 65 to 70 °C (150 to 160 °F) can cause excessive wear of equipment, however, and increase the possibility of drying the soap solution onto the parts while transferring to the rinse stage(s).

The chemical supplier recommendations and engineering requirements developed through testing will help determine the concentration of soap required in the wash stage. This can vary between 3 and 20% by volume. Although higher concentration may improve cleaning, it will also result in more burden on the rinse stage and on waste treatment. Titration methods are often used to determine the soap concentration, and incremental additions of concentrated soap are often used to maintain the bath at its concentration set point. Eventually (after 3 to 12 mo), spent baths must be dumped and replaced with fresh solutions due to the buildup of emulsified oils and general degradation of the bath effectiveness. Cleaning performance of previous baths under similar conditions is often the best indicator for predicting bath life.

Immersion times of 15 to 30 min in the wash stage are standard. Increasing the wash stage time beyond this adds little in terms of cleaning benefits and often results in a cleaning cycle that is too long.

Agitation levels are usually fixed once the equipment is installed but should be designed to achieve solution flow rates as high as practical while considering issues such as equipment and utility costs, solution foaming, and part damage.

An often overlooked factor in improving cleaning performance is the soil that must be removed. Parts are sometimes grossly overcontaminated during prior operations and improved performance can often be achieved by reducing the amount of soil to be removed. In some cases, it is possible to eliminate a superfluous cleaning step entirely. Replacement of a hard-to-clean lubricant is another approach. The use of specific forming lubricants in many shops has evolved over the years in part because of the presence of the vapor degreaser. Lubricants that were compatible with the vapor degreaser solvents were preferred over water-based products that would not clean or that promoted acid formation within the solvent. For many applications, an aqueous cleanable lubricant can be just as successful in the upstream operation as the vapor degreasable one was.

After washing is complete, the basket is moved to the rinse stage(s). If soap drying onto the parts is a problem, a fine mist of warm fresh water or rinse water directed at the parts above the wash stage may be helpful. The parts are immersed in the rinse stage(s) for at least 5 min. Multiple rinse stages help conserve water but require more floor space and utilities. If a final spray rinse of fresh water is available above the immersion rinse stage, this should also be utilized. Temperatures above 65 °C (150 °F) can cause excessive wear on equipment and can produce mineral deposits on the tank walls.

After rinsing is complete, the basket is moved to the forced-air drier. Drying time will depend on the design of the system and the amount of parts and water going in. Parts with geometries that trap solution may need to be tilted or blown off with air knives to dry. Fifteen minutes is a reasonable length of time for a drying cycle.

Parts are generally unracked after the wash, rinse, and dry steps are complete. If parts are to be re-racked for the next operation (i.e., heat treatment), consideration may be given to a common rack that could be used by both operations. This could allow the elimination of a racking and unracking step.

Regeneration of aqueous cleaners is performed by removing the soils or contaminants (oils) from the cleaning solution. Oils that float to the surface of a wash tank can often be removed by manual or automatic skimming. Parts being pulled up through a floating oil or foam patch run the risk of having the soil redeposited. Agitation systems can be designed to create a surface flow that propels these floaters over a knife-edged weir. The weir can feed a more sophisticated device such as a coalescer, centrifuge, or ultrafilter to effect a more complete separation. The oil can be captured and the cleaner returned to the bath. Pumps used in conjunction with these systems should be of a low shear type design (i.e., diaphragm pumps) to minimize mixing of the oil and cleaner. Emulsifying-type cleaners are more difficult to regenerate using equipment than surfactant-type cleaners. Aqueous cleaners that strongly emulsify the soils often require nothing more elaborate than the cartridge filtration mentioned in the "Equipment/Materials" section above. When the bath becomes saturated with soils, cleaning performance will become unacceptable and dumping the spent bath and replacing it with fresh solution will be required.

Maintenance. Equipment should be designed with maintainability in mind. Pumps should be protected by strainers. They should have valves on either side for isolating. Pumps and motors should be easy to access and replace. Seals, pumps, piping, and other components should be compatible with the temperatures and chemistries of the solutions. Heat exchangers should also be accessible for replacement in the event of failure. Temperature, level, and conductivity sensors should be located in the body of the tank and should be easily accessible. Regeneration equipment should be easy to maintain, or it runs the risk of being turned off.

Example. A 1,1,1-trichloroethane vapor degreaser was being used to degrease detail aluminum aircraft parts prior to air furnace heat treatment. These parts are contaminated with forming lubricants from blanking and brake press operations. The original tank was 8 m (27 ft) long, 1.5 m (5 ft) wide, and 8 m (27 ft) deep. Very few of the parts going through this system were more than 3.5 m (12 ft) long, and other larger degreasing systems were available within the same building. To retrofit this vapor degreaser to an aqueous system, the tank was modified with the addition of a dividing wall down the center. This structural wall created two 4 m (13.5 ft) long, 1.5 m (5 ft) wide by 8 m (27 ft) deep tanks. Tanks were also modified by adding recirculating agitation systems as described above. Additional heating capacity was required, which was added via steam heat exchangers in the recirculation system. Heat transfer through the dividing wall was found to limit the maximum temperature difference achievable between these two tanks to about -12 °C (10 °F).

A steam-heated, forced-air drier was placed at the factory-floor level adjacent to the tanks and within reach of the overhead crane. A drying cart was used to allow the parts basket to be side loaded into the dryer after being disengaged from the crane. The parts basket and overhead crane system was modified for the smaller working envelope. Multiple-parts baskets and racks are available that are compatible with the adjacent heat-treat furnace material handling system. One load can be processed through the wash and rinse stages, while another is in the drier.

Dip Tank Systems

Dip tank cleaning systems are effective for many applications. Part configuration is a factor: the shape of the part must allow excess cleaning fluid and rinse water to drain away when the parts are removed from the tank. If these fluids do not drain away properly, it could lead to corrosion of ferrous metals and excessive depletion of the cleaning chemical from the wash tank. The proper racking of parts will help to eliminate this possibility.

Arrangement of parts in the dip basket is very important. The parts should not overlap and there should be space between each part to allow the cleaning solution to circulate. The most common reason for unsatisfactory results is failing to follow these requirements.

Ultrasonic dip tank methods are mostly used for small parts on a relatively small scale because the equipment is very expensive. This method is able to remove much heavier contamination than a simple dip tank can accomplish. Ultrasonic cleaning is also effective where partially hidden recesses (i.e., blind holes) are present in the part configuration.

It must be pointed out that an ultrasonic tank that has been configured for solvent cleaning is not suitable for aqueous cleaning. The sonic frequencies need to be changed from 25 to 40 kHz or higher for aqueous cleaning. Once the frequency (transducer) modification has been made, meaningful cleaning evaluations can proceed. Additional information on ultrasonic cleaning and equipment is available in the article "Ultrasonic Cleaning" in this Volume.

Spray washer methods are recommended when production requires very high throughput, or when parts have irregular surfaces. This method will remove very heavy oils and greases and other contaminants.

Contaminant Removal. After being removed from the parts, some oil and grease will end up floating (because they are lighter than water) in the wash tank. These contaminants must be removed from the wash tank so that they do not interfere with the efficiency of the cleaning solution.

Skimming is the most practical method for removing these contaminants. Devices for this purpose are readily available from industrial supply companies. They feature an oil attractive surface that rejects water; the oil is removed from the skimming surface by wiper blades and is collected for disposal.

Ultrafiltration may be a viable option for large tank systems. A great deal of experimentation has taken place involving ultrafiltration of aqueous cleaning chemicals. It has been found that with either polymeric or ceramic membranes, a filter pore size of 0.3 to 0.5 μm with a 500,000 molecular weight cutoff is the most efficient at removing oil, grease, and other contaminants while still allowing the cleaning chemical and the water to pass through. Ultrafiltration equipment is very expensive, but it can be cost effective in situations where waste disposal is severely restricted.

Cleaning tank maintenance is an important consideration. It must be remembered that the major losses from the cleaning tank will be water due to evaporation. Actual cleaning chemical losses will depend on part configurations and their effect on dragout (process chemical loss).

With all aqueous cleaning methods, maintenance of recommended solution concentrations is very important. The manufacturer of the process chemical is best able to provide the methods for maintaining process chemical concentrations.

Rinse Water Quality. The quality of the rinse water has a significant impact on the cleanliness of the part. Tap water will effectively rinse a surface but often will leave a residue that has nothing to do with the cleaner used. The type of rinse water that should be used depends on the cleanliness requirements of the part. Those with strict requirements should be rinsed with the highest quality water, namely distilled water. Next cleanest is deionized water, then soft water (water treated with Zeolite resin), and finally tap water.

Converting an Existing Vapor Degreaser

Converting an existing vapor degreaser to an aqueous cleaning system can enhance the cleaning process and costs less than purchasing entirely new equipment. Figure 1 is a schematic drawing of a vapor degreasing system converted for aqueous cleaning; see the article "Solvent Cold Cleaning and Vapor Degreasing" in this Volume for schematics of conventional vapor degreasers. In some cases, only minimal modifications are needed. Depending on thickness of tank walls, reinforcement may be required to accommodate the increased weight and volume of cleaner in the tank. The refrigerant freeboard coils can be disconnected because they will no longer be required.

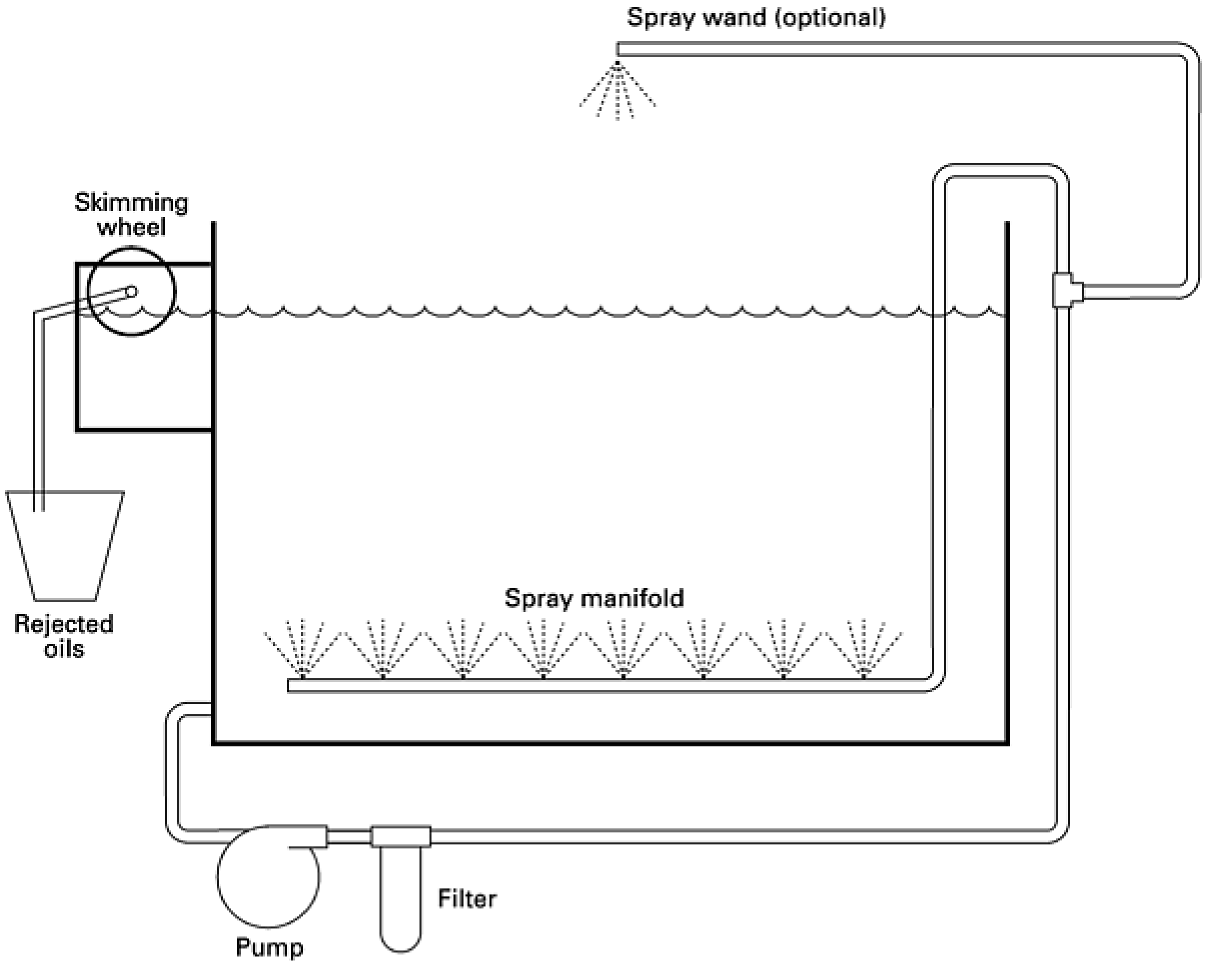

Fig. 1 Schematic of a vapor degreasing system converted for aqueous cleaning

A circulation system will be needed for effective aqueous cleaning. This can consist of a circulation pump and spray manifolds (under solution level), a "lightening" tank mixer, air sparging (not recommended for some alkaline cleaners, which can foam), and even ultrasonic agitation. If the degreaser has a hand spray wand, this can still be used for more aggressive cleaning (again, this would not be recommended for some alkaline cleaners, which can foam).

For alkaline cleaners that reject oils (as opposed to emulsification-type cleaners), some type of oil removal device will be necessary. There are several options available to accomplish this. Skimming devices such as belts or wheels work well. Coalescers, separation tanks, and microfiltration are also effective at removing oils.

Filtering is another option for prolonging the life of the cleaner. Filter media such as fabric and paper cartridges, bags, or ceramic can be used. Selection of proper filter size depends on the molecular size of the contaminants and the molecular size of the cleaning agent ingredients.

A series of rinse tanks to remove the cleaner will need to be added to the cleaning area as well as some type of drying device to remove the rinse water from the workpieces.

Advanced Vapor Degreasing Systems

Another option to traditional vapor degreasing is the so-called advanced vapor degreasing system (Fig. 2). This system is quite different from a conventional vapor degreaser. Instead of using a single vapor degreasing step, the advanced vapor degreaser is a three-stage system involving the use of a solvating chemical (aliphatic esters), a rinsing agent (perfluoro hexane), and a vapor rinse.

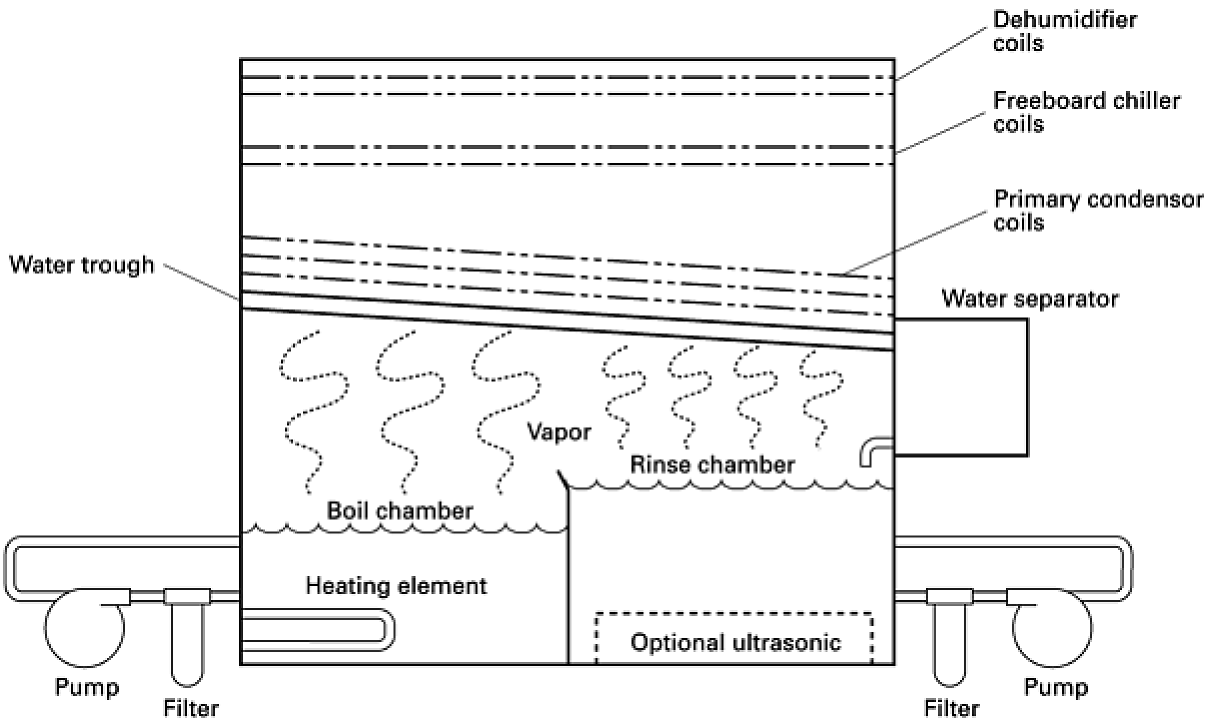

Fig. 2 Schematic of an advanced vapor degreasing system

Equipment for an advanced vapor degreasing system consists of a boil chamber containing a solvating chemical, a rinse chamber containing the rinsing agent, a pump and filter system for both chambers, primary condenser coils, freeboard chiller coils, dehumidifier coils, a water separator, and a freon compressor. Some systems include an optional ultrasonic unit.

The boil chamber generates vapors that rise to the point where the primary condenser coils suppress the vapor column. Distillate generated from this vapor rinse is collected through a trough system and then funneled into a water separator and finally into the rinse chamber. The added rinse solution from this process overflows into the boil chamber (which is already combined with the solvating agent), completing the process cycle.

Parts to be cleaned are first immersed into the boiling solvating chemical/rinse agent mixture. They are then immersed into the rinse agent, which displaces the remaining solvating chemical; the use of an ultrasonic unit at this stage enhances the removal of solvating chemical. Finally, the parts are raised into the vapor column where they are rinsed with condensate vapor and then dried.

Compliant Organic Coatings

Thomas E. Kearney, Courtaulds Aerospace

Introduction

THE FEDERAL CLEAN AIR ACT requires the Environmental Protection Agency (EPA) to establish a set of health-related standards for air pollutants. One of these pollutants is ozone, which is the primary component of the condition known as smog. Because smog is caused in part by the photochemical oxidation of solvent vapors from coating application sources, this regulation has had a profound impact on how coatings are formulated and applied. A whole new class of products has been developed, compliant coatings, that contain lower amounts of organic solvents. This article discusses the compliant coating products available for use in the aerospace industry, including their characteristics and their limitations compared to conventional noncompliant materials.

As of this writing, the use of compliant coatings is not universally required. The National Ambient Air Quality Standard defines the maximum amount of ozone that can be present in an area in order to maintain the air quality required. States with nonattainment regions (regions where the amount of ozone exceeds the maximum) are required to develop a state implementation plan (SIP) that demonstrates how the state will achieve the standard. A SIP usually requires the use of compliant coatings. In attainment areas (regions that meet the air quality standard), compliant coatings are not required. However, the EPA is currently developing control technique guidelines for the aerospace industry that will standardize these organic emission regulations across regions.

Rule 1124

The most stringent regulations within the United States have been implemented by California because of its severe air quality problems. The South Coast Air Quality Management District (SCAQMD) has issued a regulation, Rule 1124, that generally has been the bellwether document for the aerospace industry. As a result, coatings suppliers have concentrated on developing products to meet this rule. Its method of control is to designate the maximum allowable specific weight of volatile organic compounds (VOCs) per unit volume of material. In Rule 1124 the limits are expressed in grams per liter; other regulations may use pounds per gallon. Following are the definitions used in this rule:

- *Primer* is applied directly to an aerospace component for the purposes of corrosion prevention, protection from the environment, functional fluid resistance, and/or adhesion of subsequent coatings.
- *Topcoat* is applied over a primer for purposes such as improved appearance, identification, or maximum corrosion protection of exterior surfaces.
- *Flight test coating* is applied to an aircraft or missile prior to flight testing to protect the aircraft from corrosion and provide required marking during flight test evaluation.
- *Impact-resistant coating* protects aerospace components such as aircraft landing gear, landing gear components, and other surfaces subject to erosion, abrasion, or impact from runway debris.
- *Maskant for chemical milling* is applied directly to an aerospace component during chemical milling of that component.
- *Fuel tank coating* is applied to the interior of integral fuel cells of an aircraft to protect it from corrosion and/or bacterial growth.

Table 1 presents the Rule 1124 requirements in condensed form. It includes the products that require, or will require in the near future, substantially reduced VOC contents. The bulk of VOC emissions from the aerospace industry are from primers, topcoats, and chemical milling maskants. This paper addresses the methods most commonly used to bring these products into compliance: waterborne coatings, exempt-solvent-based coatings, high-solids coatings, powder coating, and electrodeposition, along with the application equipment used.

Table 1 Maximum allowable volatile organic compound contents

Coating	Pre-1985	Current	As of 1 Jan 1996
Primer	650	350	350
Topcoat	600	420	420
Flight test coating used on missiles or single-use aircraft	840	420	420
Impact-resistant coating	600	420	420
Maskant for chemical milling	1200	250	250

Fuel tank coating	720	720	420

Note: All values are given in grams per liter of coating.

Waterborne Coatings

Water can be used in organic coatings to form either emulsions or solutions. However, polymers that can be solubilized in water usually form films with poor moisture resistance, which makes them unsuitable for aerospace environments. The most successful approach has been to use emulsions in which water is the major carrier but is not a solvent for the resins in the coating. These materials are not free from VOC, however. Some organic solvents must be included to control evaporation and flow and to provide film coalescence.

The VOC content in waterborne coatings is determined on a basis that excludes water from the calculation:

$$g/L = \frac{W_s - W_w}{V_m - V_w}$$

where g/L is the grams of VOC per liter of coating, W_s is the weight of VOC in grams,W_w is the weight of water in grams,V_m is the volume of material in liters, andV_w is the volume of water in liters.

Waterborne Primers. The compliant waterborne primers used in the aerospace industry have been based on epoxy resins and polyamine or polyamide curing agents. There are two approaches to formulating these primers. One is to supply the product as an emulsion that can be mixed and applied in a manner similar to that used for solvent-based primers. The second method is to provide a very-high-solids material that can be dispersed in water to form an emulsion just prior to application. A pre-emulsified product is easier for the user to handle, but the water-reducible high-solids material may be preferred for its shipping and storage properties.

Following are some of the characteristics of waterborne primers:

- These products require a scrupulously clean substrate for proper adhesion. They are not forgiving of imperfect surface preparation.
- Drying time can be substantially slower when humidity is high. Drying can be assisted by increasing the air flow across the wet primer.
- Surfactants and water-miscible cosolvents may cause water sensitivity if the primer is exposed to harsh environments before it is completely cured.
- When a waterborne primer is supplied as an emulsion, viscosity may be substantially higher than with a solvent-based primer. However, this is a false body and the applied film will be smooth and uniform.
- The higher density of water, compared to that in most organic solvents, results in less overspray and improves transfer efficiency. (Transfer efficiency is discussed in the section "Application Equipment" in this article.)

Primers supplied for military and commercial applications differ in that the latter must be resistant to the phosphate ester hydraulic fluid used in these aircraft. The densely cross-linked surface that is usually required for resistance to phosphate esters is difficult to achieve with an emulsion, so these products have been primarily used for military aircraft. The specification for military aircraft primers is MIL-P-85582. However, products have recently been developed that will meet some commercial requirements for phosphate ester resistance. Boeing Aircraft Company has qualified a waterborne product to their specification BMS10-11 for commercial use, which requires phosphate ester resistance.

Implementation of waterborne epoxy primers has been successful. In general, their adhesion properties, corrosion protection, and service life have been comparable to those of conventional solvent-based materials.

Waterborne Topcoats. To date, waterborne topcoats have been limited to single-package emulsions, which are most often used as replacements for solvent-based lacquers. However, one manufacturer has developed a two-package aliphatic urethane resin system that shows promise. Coatings made with this material are now under evaluation.

Waterborne Chemical Milling Maskant. In chemical milling, metal is removed by chemical etching rather than by mechanical methods. The maskant is a coating of any kind that defines which areas on the part are to remain unetched (it protects those areas from the action of the etchant). Chemical mill masking has historically been the largest contributor of VOC emissions in the aerospace industry. The solvents used have been toluene, a combination of aromatic solvents, and more recently perchloroethylene. Perchloroethylene is attractive because it has been classified as an exempt solvent in many states. However, it is being considered for reclassification as an air toxin, which would restrict its use.

Prior to July 1993, the VOC emissions limit for chemical milling maskant in Rule 1124 was 1200 g/L (10 lb/gal). The current regulation is 250 g/L (2 lb/gal). This VOC reduction can be achieved by collecting solvent emissions with air pollution control equipment, such as carbon absorption beds, or by using water-based products.

Water-based chemical milling maskants have been available for several years. Two approaches have been used.

The anode dipping process takes its name from the fact that the emulsified particles are attracted to the part to be masked in much the same way that metallic ions are attracted to the anode in electroplating. It is similar to the method used to produce rubber latex gloves. The part to be masked is immersed in a solution of a multivalent salt. After flashoff, the part is dipped into a bath of a latex rubber. The salt on the surface causes the latex to coagulate on the part to an even film thickness of 200 to 250 μm (8 to 10 mils). This must be cured at a low bake (85 to 90 °C, or 190 to 200 °F) for about 1 h. As the water leaves the film, some porosity may remain, and usually a third dip in a seal coat is required. This process provides excellent edge protection and an even film over the part. It also lends itself very well to automation because all parts, regardless of size, can be handled in the same manner. The disadvantage is that it is a three-tank process that requires extra floor space and substantial expenditure on capital equipment.

The single tank method uses a chemically resistant emulsion polymer, formulated with fillers and additives to control the film thickness and adhesion properties. Multiple dips are usually required to achieve the necessary film thickness. The parts are rotated between dips to eliminate variation in film thickness from top to bottom ("wedging"). A bake between coats and after completion is required. The single-tank process can usually be installed in the existing facility, and shop personnel may adapt to it more easily because it more closely approximates the procedure for solvent-based material. The disadvantages are that it may be difficult to achieve coverage on edges and complex parts, and that a longer force-dry at lower temperatures is usually required to avoid entrapment of water.

In both processes, the emulsion bath should be closely monitored to control tank stability. The viscosity and pH should be checked at least weekly.

Exempt-Solvent-Based Coatings

Exempt solvents are a class of organic materials that are nonphotochemically reactive and therefore are not precursors to the formation of ozone. Chemically, these are chlorinated hydrocarbons and chlorofluorocarbons (CFCs). The exempt solvents that have been most commonly used in coating formulations are 1,1,1-trichloroethane (TCA, also known as methyl chloroform) and methylene chloride.

Although these compounds are not smog producers, they have been shown to deplete the ozone layer in the upper atmosphere. Therefore, their use will be restricted in the future. The SCAQMD has established a policy to phase out CFCs on or before December 31, 1995. The Montreal protocol, to which the United States is a signatory, is an international agreement that requires the use of ozone-depleting compounds to be discontinued by the year 2000. However, because these products are still widely used in compliant coating formulations, they may be used for a year or two more, and they are included in this discussion.

The calculation for determining the VOC content of exempt-solvent-based materials is similar to that used for waterborne coatings:

$$g/L(VOC \text{ less exempt}) = \frac{W_s - W_{es}}{V_m - V_{es}}$$

where g/L (VOC less exempt) is the grams of VOC per liter of coating, less exempt compounds, W_s is the weight of the nonexempt volatile compound in grams, W_{es} is the weight of the exempt compound in grams, V_m is the volume of material in liters, and V_{es} is the volume of the exempt compound in liters.

Exempt-Solvent-Based Primers. TCA is the exempt solvent that is most generally used in primers. It is compatible with most organic resins, but it has a lower solubility parameter and a faster evaporation rate than other solvents used in formulating aerospace materials. TCA has been successfully used to formulate epoxy primers for both the military and commercial markets. The military specification is MIL-P-23377F, Class 3. The commercial specifications include Boeing Aircraft BMS10-11; McDonnell Douglas DMS2104, Composition B; and Gulfstream GMS5004. TCA has been popular because it requires no modification of existing procedures or equipment.

Following are some characteristics of exempt-solvent-based primers:

- These products have a tendency to dry spray because of the fast evaporation rate. Additional TCA may be required to ensure a sufficiently wet film.
- The commercially available TCA usually contains 3 to 5% of a stabilizer to prevent the formation of corrosive chloride compounds. This stabilizer is classified as a VOC.
- Because of the high density of chlorinated solvents, there tends to be less overspray than with conventional primers.
- Care must be taken to avoid the use of aluminum pressure vessels with these primers. A violent reaction with aluminum can occur under some circumstances.

Exempt-Solvent-Based Topcoats. There are no exempt-solvent-based topcoats currently in use in the aerospace industry. Until recently, Grumman Aerospace had a specification in use (GM4209) that was based on this technology, but this material has been discontinued because of the restrictions on the use of chlorinated solvents.

High-Solids Coatings

Coatings may be made compliant simply by reducing the amount of organic solvent in the formula. However, to produce the high-performance epoxies and urethanes required for the aerospace industry at a sprayable viscosity, suppliers must use much lower-molecular-weight resins and curing agents than in the past. These are typically liquid resins, and the drying time is strongly dependent on the cross-linking rate and the buildup in molecular weight. The result is a much longer tack-free time than with conventional noncompliant materials. In addition, this reaction causes the molecular weight to increase, which increases the viscosity and shortens the usable work life. In spite of these difficulties, coating suppliers have been able to produce materials that meet the needs of the industry.

High-Solids Primers. High-solids primers have proven to be a viable alternative to waterborne primers and exempt-solvent-based primers for achieving VOC compliance. They are usually low-molecular-weight epoxies reacted with low-viscosity polyamides or polyamines. These primers have a VOC content of 340 g/L or less.

Following are some of the characteristics of high-solids primers:

- These products normally require up to 4 h of drying before topcoating and 12 h or more to dry hard.
- The usable pot life is 4 h or less because of the comparatively rapid buildup in viscosity.
- Care must be taken to avoid applying a wet film that is overly heavy. Higher solids cause the film thickness to increase very quickly.

Compared to waterborne primers, high-solids primers offer:

- Better chemical and fluid resistance
- Less sensitivity to surface contamination
- Better compatibility with high-solids topcoats

The military specification for high-solids aerospace primers is MIL-P-23377F, Class 2. Commercial high-solids primer candidates are now in the qualification phase.

High-Solids Urethane Topcoats. High-solids has been the method most often selected for meeting the VOC requirements for topcoats. Development in this area has been concentrated primarily on aliphatic urethanes. Coatings formulated with these materials have the desirable properties of weatherability, durability, and flexibility. Low-molecular-weight polyesters and acrylics have become generally available that can be cross-linked with aliphatic isocyanate prepolymers to form urethanes. For instances where the use of isocyanates is limited, or greater chemical or fluid resistance is required, topcoats have been formulated with an epoxy resin base.

The low-molecular-weight components necessary to achieve a sprayable viscosity present difficulties similar to those experienced with high-solids primers. The drying time is again related to the increase in molecular weight, and there is a tradeoff between drying time and usable work life. Formulators attempt to balance these properties by using catalysts for the isocyanate-hydroxyl reaction. Increasing the amount of catalyst shortens the tack-free time but also results in a more rapid increase in viscosity. Conversely, less catalyst means a longer drying time and a longer pot life. Depending on the needs of the user, a satisfactory compromise of properties usually can be achieved.

Following are some of the characteristics of high-solids urethanes:

- Complete drying may require 8 to 12 h or more. However, a second coat, if required, can be applied after the film takes on an initial set, and most of the solvent is released in about 2 h.
- The usable pot life is typically 4 h or less.
- Hot humid weather may result in blistering or "solvent pop" if the film thickness is not properly controlled. Under colder conditions there may be a greater tendency to sag or run.

The specification covering high-solids urethanes for military applications is MIL-C-85285. Type I is 420 g/L (3.5 lb/gal) for aircraft applications, and type II is 340 g/L (2.8 lb/gal) for ground support equipment. An example of a commercial high-solids specification is BMS10-60 TY II, Grade B, which has a maximum VOC content of 420 g/L (3.5 lb/gal).

High-Solids Self-Priming Urethane Topcoat. The self-priming topcoat was developed by the Naval Air Warfare Center. The specification is TT-P-2756. The self-priming topcoat combines the functions of a primer and those of a topcoat into a single product that is environmentally compliant. In addition, the corrosion inhibitors incorporated in the formula are chromate-free. This product, commonly known as Unicoat, has been in use for several years at Navy and Air Force depots. In general, its performance has been satisfactory; it works best when applied over a chromated conversion coating such as MIL-C-5541. The use of self-priming topcoats should be avoided if the aircraft will be exposed to harsh environmental conditions over a long period of time.

High-Solids Epoxy Topcoats. The use of epoxy topcoats is indicated when exposure to ultraviolet light is not a factor and good fluid resistance is required, as in the interior of commercial aircraft. Sample specifications are Boeing Aircraft BMS10-11, type II or McDonnell Douglas DPM110. These products have a VOC content of 420 g/L (3.5 lb/gal). The Navy has issued a specification MIL-C-22750E for a high-solids epoxy that can be used where the use of urethanes is restricted, as on shipboard. This specification requires a VOC content of 340 g/L (2.8 lb/gal). These epoxy topcoats have the short pot life and longer drying time of most high-solids materials.

Powder Coatings

Powder coatings are not yet in general use in the aerospace industry, but there is a great deal of interest because of the benefits they offer in terms of VOC content reduction and efficiency of application. Further development may overcome some of the limitations of these coatings. As the name implies, these coatings are applied as powder to a given surface. The solid ingredients, resin pigments, extenders, and so forth are melted together to produce a completely homogenous plastic mass. This is cooled to room temperature and ground to a powder.

The powders that have been considered for use in the aerospace industry are thermoset, meaning that the components react at elevated temperatures to form a cured film. The powder is applied electrostatically (i.e., the electrically charged particles are sprayed on the part to be coated, which is grounded) and is held in place by electrostatic attraction. The coating is then fused together and cured at temperatures from 135 to 200 °C (275 to 400 °F). The types of thermoset

powders available fall into the general categories of epoxies, polyesters, polyurethanes, and acrylics. Many of the aerospace applications are on aluminum or aluminum-alloy substrates, which are sensitive to changes in strength properties when exposed to high temperatures. For this reason the principal types used have been epoxy-resin-based materials that can be cured at temperatures as low as 120 °C (250 °F). Powders based on other polymers usually require temperatures of 175 to 200 °C (350 to 400 °F) to achieve optimum properties.

The advantages of powder coatings are that no VOCs are present, up to 98% of the powder can be deposited on the part, application is easy, and minimal rework is required. The disadvantages for aerospace applications are that powder coatings cannot be used on assemblies or aircraft exteriors that cannot be heated, and that epoxy-resin-based products have poor ultraviolet stability and so cannot be used on exterior surfaces.

Electrodeposition

Electrodeposition (electrocoating) is similar to electroplating but deposits organic materials rather than metal ions. It uses the principle of *electrophoresis*, the movement of charged suspended particles under the influence of an applied voltage. This process may be either *anodic*, in which the anode is the coated part, or *cathodic*, in which the organic coating is deposited on the cathode (Fig. 1). Because of problems associated with coating-substrate interaction in anodic systems, the cathodic process is chosen for aerospace applications. The types of materials deposited by electrocoating are epoxies, acrylics, or polyesters cross-linked with melamines or blocked isocyanates. A bake of 135 to 230 °C (275 to 450 °F) is required to cure the deposited film.

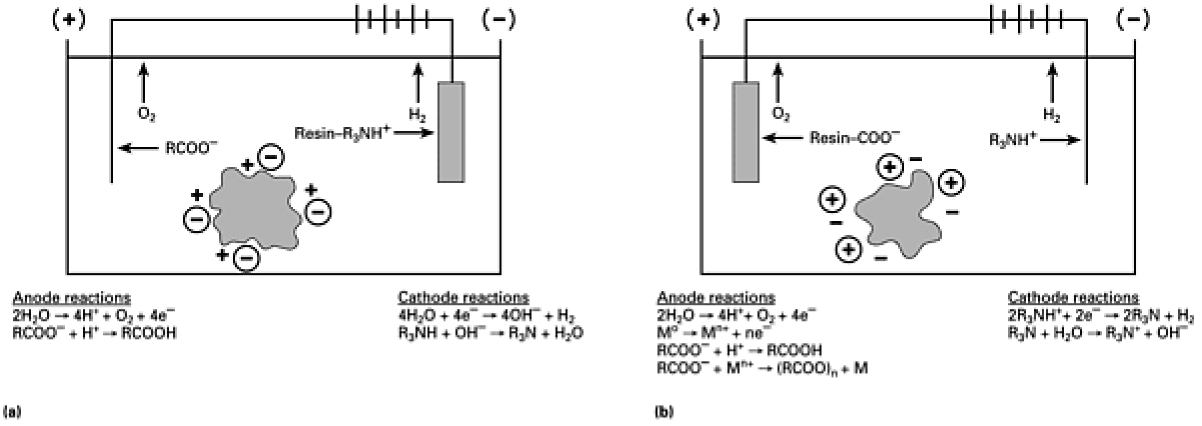

Fig. 1 Electrodeposition process. (a) Cathodic deposition (resin deposits on the negative electrode). (b) Anodic deposition

The advantages of electrodeposition are that:

- The process emits very low levels of VOC.
- The coating film is deposited at a uniform thickness so that the total film weight can be controlled.
- The deposited film has superior adhesion and film density.

The disadvantages of electrodeposition in the aerospace industry are that:

- The initial equipment cost is high.
- The large variation in the sizes of parts to be coated makes it difficult to determine an optimum bath size.
- Electrocoat baths are sensitive to degradation, so turnover at fairly frequent intervals is important. If the bath components are not depleted and replenished at a sufficient rate, it may be necessary to discard the aged product and recharge with fresh material.
- The heat required for curing can affect the temper of aluminum alloys. Careful monitoring of the time

and temperature of the bake is necessary.

Electrodeposition seems to have enough advantages to ensure that it will be used in many applications in the aerospace industry, such as the coating of small parts.

Application Equipment

The regulations for VOC compliance often dictate the transfer efficiency of the spray equipment used to apply the coatings. Transfer efficiency is defined as the percentage of material actually applied to the object out of the total nonvolatile material sprayed. Rule 1124 requires that the transfer efficiency be a minimum of 65% or that the excess overspray be collected by air pollution control equipment. The types of spray equipment commonly used are described below.

Air-atomized spray equipment is the conventional equipment that has been in use for many years. The coating is broken into very fine particles by an air flow at a pressure of 200 to 480 kPa (30 to 70 psi). This method usually results in the best appearance because of the excellent breakup. However, air-atomized spray equipment has a transfer efficiency of only 20 to 30%.

Airless spray equipment forces the coating through a small orifice (diameter of 0.22 to 0.53 mm, or 0.009 to 0.021 in.) under high pressure (6200 to 11,700 kPa, or 900 to 1700 psi). This atomizes the liquid paint into fine particles, but even so the particles are much larger than those produced by air atomization. The transfer efficiency is better than that of air atomization, about 45%, but because of the comparatively large particle size it is difficult to achieve a satisfactory film appearance.

Air-assisted airless spray equipment is similar to airless spray equipment, except that compressed air under low pressure is introduced at the top and the bottom of the fan pattern to break up the tails of the large particles. This produces a better appearance than airless spray. In addition, because lower hydraulic pressures are used (700 to 2750 kPa, or 100 to 400 psi), the transfer efficiency is somewhat better.

High-volume, low-pressure spray equipment is similar to that used for conventional air atomization. The difference is that the guns are constructed with special air and fluid nozzles that allow the coating to be atomized at low air pressures and velocities. This creates a soft spray effect that produces higher transfer efficiencies, usually 60 to 70%.

Electrostatic spray equipment charges the atomized particles so that they are electrically attracted to the grounded metallic part. The resulting "wrap effect" greatly reduces overspray and improves transfer efficiency to 60 to 90%. This technique is effective only if the resistivity of the liquid coating is at least 0.05 MΩ · m. The more highly polar solvents used in aerospace coatings, such as methyl ethyl ketone, are very conductive and result in low resistivities. Some solvents with high resistivity, such as aromatics or esters, must be included in the formula to achieve the desired transfer efficiency.

Compliant Wipe Solvent Cleaners

Mark T. Carroll, Lockheed Fort Worth Company

Introduction

WIPE SOLVENTS are used to remove contaminants from a workpiece before it undergoes manufacturing operations that require clean surfaces, such as bonding, sealing, painting, welding, plating, specialized surface treatment procedures, and others. Traditional wipe solvent cleaners include:

- Methyl ethyl ketone
- Methyl isobutyl ketone
- Trichloroethene (trichloroethylene)
- Tetrachloroethylene (perchloroethylene)

- 1,1,1-trichloroethane (methyl chloroform)
- Acetone
- Toluene
- Dichloromethane (methylene chloride)
- Tetrachloromethane (carbon tetrachloride)
- Benzene
- Xylene
- Ethylene glycol ethers
- Diethylene glycol ethers
- 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113)
- Combinations of these materials

The U.S. Environmental Protection Agency (EPA) has classified these materials as being either hazardous air pollutants or ozone layer depleting substances. Some relevant regulations are identified in Table 1, along with a curtailment schedule that will either limit or prohibit the use of certain materials in the future. The article "Solvent Cold Cleaning and Vapor Degreasing" in this Volume provides additional information about these cleaners.

Table 1 U.S. regulations related to curtailment in the use of solvent materials

U.S. Regulation	Material	Curtailment schedule
Clean Air Act Amendments of 1990, Hazardous Air Pollutants	190 chemicals, including benzene, chloroform, methyl ethyl ketone, methyl isobutyl ketone, toluene, xylene, trichloroethylene, ethylene glycol ethers, and diethylene glycol ethers	Discontinue use by late 1997
EPA Industrial Toxics (33/50) Program (voluntary)	17 toxic chemicals,including benzene,carbon tetrachloride, chloroform, methyl ethyl ketone, methyl isobutyl ketone, toluene, 1,1,1-trichloroethane, trichloroethylene, and xylene	33% reduction of use by end of 1992; 50% reduction by end of 1995 (from 1988 levels)
Presidential Directive to Accelerate Phase-Out of Ozone Layer Depleting Substances, Feb 1992	Chlorofluorocarbons, halons, 1,1,1-trichloroethane, and carbon tetrachloride	Production phase-out: 50% beginning Jan 1993, 100% by Jan 1996. (Air Force will ban purchases after April 1994)

Alternate Materials

Innovative methods will be required to develop wipe solvent materials that will meet EPA requirements for the emission of volatile organic compounds, the reduction or elimination of hazardous air pollutants, and the elimination of ozone layer depleting substances. Besides meeting EPA requirements, the alternate wipe solvents must be effective in their required applications.

Frequently, the contaminating materials that need to be removed from a surface are actually a combination of materials, and therefore the use of mixed solvents is required to remove them. For example, one of the most widely used wipe solvent cleaners is the MIL-C-38736 formulation (Ref 1), which contains solvents that remove oil-and water-soluble contaminants (Table 2). Particulate materials that are insoluble are removed by the wiping action during cleaning. Some of the solvents in this formulation are classified as hazardous air pollutants. This cleaner also has a very high vapor pressure, which contributes to volatile organic compound emissions, and a low flash point, which warrants it a classification as a flammable material.

Table 2 Compositions of MIL-C-38736 wipe solvent cleaners

Solvent	Concentration,%
Type I	
Aromatic naphtha	50
Ethyl acetate	20
Methyl ethyl ketone	20
Isopropyl alcohol	10
Type II (nonphotochemically reactive)[a]	
Toluene	18.5
Ethyl acetate	35.5
Methyl ethyl ketone	36
Isopropyl alcohol	10

(a) A nonphotochemically reactive solvent is any solvent or solvent combination with an aggregate of less than 20% of its total volume composed of the chemical compounds listed in (1),(2), or (3) below and which does not exceed the individual volume percentage composition limitations. (1) A combination of hydrocarbons, alcohols, aldehydes, esters, ethers, or ketones having an olefinic or cycloolefinic type unsaturation, not to exceed 5% of the total volume. (2) A combination of aromatic compounds with eight or more carbon atoms to the molecule, except ethylbenzene, not to exceed 8% of the total volume. (3) A combination of ethylbenzene, ketones having branched hydrocarbon structures, trichloroethylene, or toluene, not to exceed 20% of the total volume.

Alternate nonhazardous air pollutants and higher vapor pressure materials that can be used to formulate a cleaner that is as efficient as the MIL-C-38736 formulation are available. A series of naphtha-type hydrocarbon materials with a variety of flash points and vapor pressures is available from one manufacturer, whereas naphtha-type hydrocarbons and blends of them that contain dibasic esters are produced by another producer (Table 3). In many cases, glycol ethers (carbon chain >8) can be substituted for methyl ethyl ketone, because they are not classified as hazardous air pollutants and can be selected with low vapor pressures and high flash points.

Table 3 Characteristics of isoparaffins

Commercial name[a]	Flash point		Distillation range		Evaporation rate[b]	Vapor pressure[c]	
	°C	°F	°C	°F		kPa	mm Hg
Isopar C	-7.2	19	97-103	207-217	560	13.1	98

Isopar E	7.2	45	117-137	243-279	155	6.9	52
Isopar G	41.1	106	160-174	320-345	27	1.9	14
Isopar H	53.3	128	179-189	354-372	9	0.83	6.2
Isopar K	52.7	127	177-197	351-387	8	0.76	5.7
Isopar L	62.2	144	191-201	376-405	4	0.69	5.2
Isopar M	88.9	192	223-251	433-484	0.5	0.41	3.1
Isopar V	136.1	277	273-317	523-592	<0.1	0.03	0.26
Axarel 9100	93.3	200	. . .	. . .	<0.1	<0.01	<0.1

(a) Isopar is a registered tradename of Exxon Chemical Co.; Axarel is a registered tradename of DuPont Chemical Co.

(b) Based on butyl acetate = 1.

(c) Vapor pressure determined at 25 °C (77 °F).

Another solvent to consider is ethyl lactate, which is completely miscible with water and most organic solvents. This material, which has a flash point higher than 37.8 °C (100 °F), is reported to be an excellent wipe solvent cleaner for many applications. It is approved by the U.S. Federal Drug Administration for use as a food additive and, therefore, is considered relatively nontoxic.

The terpene hydrocarbon materials also can be used as alternate solvent materials. They include naturally occurring organic compounds, such as *d*-limonene, dipentene, α-terpinene, terpinolene, α-terpineol, and other proprietary terpene hydrocarbons. A major objection to these materials is their odor, which can become overwhelming with prolonged use. Other objections include their instability (auto-oxidation and decomposition), their reactivity with certain polymers and elastomers, and the presence of nonvolatile residue upon evaporation. However, a new class of these materials with low odor and flash points higher than 93.3 °C (200 °F) have been developed (Ref 2). These newer formulations also claim to be low in nonvolatile residue content.

A nonflammable, noncombustible material that is widely used as a wipe solvent cleaner is 1,1,1-trichloroethane (methyl chloroform). Because it is classified as a Class I ozone layer depleting substance, its manufacture will be discontinued in 1994. Reported substitutes listed in the EPA Significant New Alternatives Program (SNAP) are tetrachloroethylene (perchloroethylene), trichloroethene (trichloroethylene), and dichloromethane (methylene chloride), which are all highly toxic materials, and some of the fluorochlorohydrocarbons, which are classified as Class II ozone layer depleting substances. The use of the latter materials will be severely limited by the EPA after 1994. It should be noted, however, that the SNAP alternatives are for vapor degreasing and cold cleaning operations, rather than wipe solvent cleaning operations.

One company manufactures a series of perfluorocarbons that are nonflammable, noncombustible solvents (Table 4). However, the cleaning efficiency of these materials is very poor, and they are only being considered at this time as rinsing

and drying agents in new degreasing systems, in combination with either isopropyl alcohol or terpene hydrocarbons. It is also likely that the EPA will ban their use in the near future.

Table 4 Characteristics of perfluorocarbons

Commercial name[(a)]	Chemical name	Flash point	Boiling point		Vapor pressure[(b)]	
			°C	°F	kPa	mm Hg
PF-5050	Perfluoropentane	None	29	84	81.3	610
PF-5052	Perfluoro-*N*-methyl morpholine	None	50	122	36.5	274
PF-5060	Perfluorohexane	None	56	133	30.9	232
PF-5070	Perfluoroheptane	None	82	180	10.5	79
PF-5080	Perfluorooctane	None	101	214	3.9	29

(a) Products of 3M Co.

(b) Vapor pressure determined at 25 °C (77 °F).

Aqueous cleaners, including the newer enzyme cleaning materials, are another class of materials that should be considered as wipe solvent cleaner candidates. These materials have been used previously in wipe solvent cleaning operations and are currently replacing the use of vapor degreasing operations in many manufacturing facilities. Objections to using these materials in wipe solvent cleaning operations include a slow evaporation rate, an unacceptable amount of residue, an inability to remove uncured polymers, such as fuel tank sealant materials encountered in manufacturing operations and carbonaceous soils encountered in the exterior cleaning of aircraft and support equipment during operation and maintenance.

Water-soluble, oil-soluble, and insoluble materials are all encountered in production operations. Wipe solvent cleaners have been developed that combine several of the solvents already discussed (Table 5). These cleaners have low vapor pressures and flash points higher than 37.8 °C (100 °F), which means they are classified as nonflammable. Evaluation tests have shown that these wipe solvent cleaners are very efficient in general-purpose wipe solvent cleaning operations.

Table 5 Combination wipe solvent cleaners

Formulation[(a)]	Flash point		Evaporation rate[(b)]	Vapor pressure[(c)]	
	°C	°F		kPa	mm Hg

Propylene glycol propyl ether, isoparaffins, and ethyl lactate	46.1	115	20	0.23	1.7

(a) Developed by Lockhead Fort Worth Co.

(b) Based on butyl acetate = 1.

(c) Vapor pressure determined at 25 °C (77 °F).

References cited in this section

1. "Cleaning Compound, Solvent Mixtures," MIL-C-38736, U.S. Military Specification
2. A. Richard Koetzle, "High Temperature Flash Point, Stable Cleaning Composition," U.S. Patent 5,112,516, 12 May 1992

Evaluation of Wipe Solvent Cleaners

The specific procedure for using wipe solvent cleaners involves wetting a clean cloth with the solvent, wiping the surface to be cleaned, and removing the residual solvent from the surface with a clean, dry cloth. The wipe solvent must either dissolve the contaminants or keep them in suspension until they can be removed from the surface with the clean, dry cloth. If the solvent evaporates too quickly, then the contaminants are merely redeposited on the surface. Because a wipe solvent cleaner is likely to be used as a general-purpose cleaner in production operations, it would need to clean all types of surfaces, such as metals, including those that have been chemically treated, anodized, or plated; primers; paints; coatings; rubbers; plastics, and others. It is actually unlikely that a single wipe solvent cleaner would be suitable for all cleaning operations. It is also obvious that extensive evaluations would be required to ensure the applicability of the wipe solvent cleaner to the cleaning processes under consideration.

An initial evaluation should include a literature review to determine the properties of the selected wipe solvent cleaner materials, such as toxicity, flash point, vapor pressure, and corrosion potential. Consultation with an industrial hygienist and an environmental professional is also recommended to ensure the acceptability of the candidate material.

Laboratory screening tests can then be conducted to determine the general cleaning efficiency properties of the candidate material, as well as its compatibility with the surface materials to be cleaned. These tests can include a simple water-break test and adhesion tests using an adhesive material that is representative of those that will be applied in production operations. Compatibility tests can consist of exposing the materials to be cleaned to the wipe solvent cleaner and then observing deterioration and other deleterious effects that might occur.

Evaluation Parameters by Property. After selecting the potential candidates, based on screening test results, extensive evaluation tests must be conducted. For general-purpose wipe solvent cleaner operations, the properties summarized in Table 6 and described below should be determined.

Table 6 Tests for wipe solvent cleaners

Attribute	Test method
Cleaning efficiency	Contaminate substrate with standard contaminant. Expose to 48.9 °C (120 °F) for 24 h. Clean with candidate cleaner. Perform mechanical property test simulating subsequent operations.
Compatibility	Expose substrates to candidate cleaners. Observe for deterioration of substrates.

Corrosion potential	Immersion corrosion, ASTM F 483; sandwich corrosion, ASTM F 1110; hydrogen embrittlement, ASTM F 519; and stress cracking, ASTM G 38
Vapor pressure	Calculate using Eq 1 (described in text)
Volatile organic compounds	ASTM D 3960
Flash point	ASTM D 3278
Odor	ASTM D 1296 or subjective evaluation using operators performing cleaning operations in open and confined areas
Dry residue	Apply candidate cleaners to a cleaned reflective surface. Allow to evaporate. Observe for residue and/or streaking.
Composition	Chromatography, ASTM D 3545; infrared analysis, ASTM E 1252
Water content	ASTM D 1364
Acidity	ASTM D 1613
Refractive index	ASTM D 1218
Density	ASTM D 1475

The cleaning efficiency property of the wipe solvent cleaner will determine if subsequent operations can be satisfactorily performed. The surfaces to be cleaned should be contaminated with a solution such as that described in AMS 3166 (Ref 3) and shown in Table 7, followed by cleaning with the candidate wipe solvent cleaner. After the contaminating material is applied to the test substrate, it should be exposed to a temperature of 48.9 °C (120 °F) for 24 h, in order to ensure that crevices and imperfections in the substrate are sufficiently contaminated. Next, the test substrate should be cleaned with the proposed wipe solvent material. Because the laboratory tests listed in Table 6 do not guarantee that the wipe solvent will in fact be suitable for use in actual manufacturing operations, physical property tests, such as sealant adhesion, adhesive strength, paint and primer application and adhesion, and subsequent chemical surface treatments and processing should be conducted to determine if the wipe solvent is effective in removing the contaminant. It is also important to ensure that subsequent manufacturing operations will not be compromised.

Table 7 Standard contaminant for testing the cleaning efficiency of wipe solvent cleaners

Ingredient	Parts by weight
Glycerol monostearate	3.0
Glycerol trioleate	9.0

Caprylic acid	3.0
Lauryl alcohol	1.3
Cholesterol	1.2
Mineral oil	2.7
Petrolatum	3.0
Lecithin	0.3
Water	70.0

Heat and blend and add 0.5 wt% lamp black. Do not heat above 93.3 °C (200 °F).

It should be noted that new compliant wipe solvent cleaner formulations may not be as efficient in preparing some substrates as the wipe solvent cleaner formulations that are currently used. Therefore, it may be necessary to use additional techniques to obtain a satisfactory surface for the intended purpose. For example, evaluation tests have revealed that some substrates cleaned with the wipe solvent cleaners listed in Table 5 required the application of an adhesion promoter to ensure the adhesion of fuel tank sealants.

Compatibility tests will determine the effects of the wipe solvent cleaner on the substrates being cleaned and adjacent materials that the cleaner may contact. The materials should be exposed to the wipe solvent cleaner for a typical time period. After exposure, the materials should be observed for etching, staining, and oxidation in metals; deterioration, softening, and swelling in elastomers; cracking or crazing in plastics; and loss of adhesion for any coated surfaces. Whether these changes are permanent or transitory should also be determined. These test results should indicate which substrates will require different wipe solvent cleaners.

Compatibility tests that were conducted on the formulations given in Table 5 indicated that these cleaners were satisfactory for use on most of the substrates investigated. However, they could not be used in cleaning operations involving most elastomers (specifically, the silicone, natural, neoprene, butyl, and nitrile rubbers) and some plastic materials, such as acrylics, polycarbonates, polystyrene, and polyurethane. Alternate cleaners, such as diluted isopropyl alcohol and, in some cases, acetone, were required for the wipe solvent cleaning of these substrates.

The corrosion potential of the wipe solvent cleaner is an extremely important property that must be determined for metal-cleaning operations. In some cases, the wipe solvent cleaner contacts the metals for a short period of time, whereas in cases such as assembly cleaning, it can become trapped in the faying surfaces of joints, which would allow long-term contact with metal surfaces. Numerous corrosion tests are available to indicate potential problems in these applications.

The most simple test is the total immersion corrosion test, described in ASTM F 483. In applications where entrapment of the wipe solvent cleaner may occur, the sandwich corrosion test described in ASTM F 1110 is satisfactory. If the metals being cleaned are subject to hydrogen embrittlement or stress-corrosion cracking, then corrosion tests such as these described in ASTM F 519 and ASTM G 38 should be conducted. Other corrosion tests are available and should be selected if they better simulate the requirements of the wipe solvent cleaner operation in question.

Vapor pressure is directly related to evaporation rate for a given solvent type, such as alcohols or ketones. Generally, the lower the vapor pressure, the lower the evaporation rate. Because the EPA tends to require a maximum pressure of 6 kPa (45 mm Hg) for wipe solvent cleaners, it is obvious that the evaporation rate of new wipe solvent cleaners will be much slower than that experienced traditionally. This is beneficial in that less cleaner will be required for a given cleaning operation. A potential hazard, however, is that there is a greater chance of the wipe solvent cleaner being trapped in the

faying surfaces of manufactured assemblies. In addition, areas that are hard to reach will be more difficult to wipe dry during wipe cleaning operations. The vapor pressure of candidate wipe solvent cleaners can be calculated using Eq 1:

$$VP = \sum_{j}^{i} \frac{(VP)_i (W)_i /(MW)_i}{\sum_i \left[(W)_i /(MW)_i + \sum_j \left[(W)_j /(MW)_j \right] \right]} \qquad \textbf{(Eq 1)}$$

where *VP* is the composite vapor pressure of the volatile organic compound in the solvent cleaner, $(VP)_i$ is the vapor pressure at 20 °C (68 °F) of the "*i*"th component in the solvent cleaner, $(W)_{i \text{ or } j}$ is the weight in grams of the "*i*"th (or "*j*"th) component in the solvent cleaner, $(MW)_{i \text{ or } j}$ is the molecular weight of the "*i*"th (or "*j*"th) component in the solvent cleaner, *i* is the volatile organic compound component(s) in the solvent cleaner, and *j* is the exempt component(s) in the solvent cleaner, as defined by appropriate federal, state, and local regulations.

Volatile organic compounds are contained in many of the new wipe solvent cleaners. The emission of these compounds must be minimized to meet most established clean-air requirements. Because wipe solvent cleaners are normally used in all areas of production operations, unique methods must be developed to conform to these emission requirements.

To control the emissions from the solvents listed in Table 5, which have very low vapor pressures that result in reduced evaporation rates, one company immediately places the used wiping cloths that are wet with wipe solvent into an aluminum-coated plastic bag. The bags are then collected at the end of each shift and compacted into sealed drums for later disposal. This method reduces volatile organic compound emissions by approximately 75%. The drums of compacted cloths can be used as high-energy, supplemental fuel in cement manufacturing and incinerated in permitted hazardous waste incinerators. Volatile organic compound content is determined using the test method described in ASTM D 3960.

Flash Points. Wipe solvent cleaners with flash points higher than 37.8 °C (100 °F) are classified by the Occupational Safety and Health Administration (OSHA) as combustible materials, whereas those cleaners with flash points below that temperature are classified as flammable materials. The former type of cleaner is preferred because of safety concerns. In cases where nonflammable, noncombustible materials are required, only a limited number of compliant materials are available, and their cleaning efficiency may not suffice for the specific operation. If this is the case, alternate cleaning procedures, such as providing an inert atmosphere or establishing cleaning areas where ignition sources can be eliminated, should be investigated. Flash point is determined using the procedure described in ASTM D 3278.

Odor is a rather subjective property of wipe solvent cleaners. In addition to conducting a standard test, as defined in ASTM D 1295, other tests should be conducted under the conditions of actual production environments. These environments should include open-area cleaning, as well as confined-space cleaning. A number of different operators should be used to obtain a general consensus on the odor of the wipe solvent cleaner. This odor should be mild and not objectionable to personnel engaged in the cleaning operations. Methods of minimizing odor include an increase in ventilation and the use of respirators.

Dry Residue. The wipe solvent cleaner must evaporate without leaving residue on the surface that could interfere with subsequent manufacturing operations. This property can be determined by applying the candidate cleaner to a test substrate, allowing it to evaporate, and then observing the resulting surface for evidence of residue and streaking. Optimally, the test substrate should be a cleaned, reflective surface.

Other properties to evaluate include composition, water content, acidity, refractive index, and density. It is useful to determine these properties by conducting receiving inspection-type tests to ensure that the wipe solvent cleaner has the same composition as when evaluated. These tests will also indicate if accidental contamination of the cleaner has occurred. The relevant test methods are identified in Table 6.

Industrial hygiene and safety is another important aspect of the wipe solvent cleaner that must be evaluated. The cleaner should not contain components listed by OSHA as being hazardous materials, which are toxic under use conditions. It is also important to not exceed threshold limit value, which is typically a minimum of 150 parts per million for a wipe solvent cleaner, although lower values may be satisfactory if suitable protection techniques are incorporated. To determine the protection methods required to limit the exposure of cleaning personnel to the wipe solvent cleaners, monitoring tests should be conducted on the air near those personnel. Depending on the cleaning operation (open or

confined areas) and area ventilation, it may be necessary to use respirators while conducting cleaning activities. Eye and skin protection should also be investigated and the necessary devices made available to personnel.

Reference cited in this section

3. "Solvents, Cleaning, for Cleaning Prior to Application of Sealing Compounds," AMS 3166, Society of Automotive Engineers

- A
- **abrasion**
  - (1) A process in which hard particles or protuberances are forced against and moved along a solid surface. (2) A roughening or scratching of a surface due to abrasive wear . (3) The process of grinding or wearing away a surface through the use of abrasives.
- **abrasive**
  - (1) A hard substance used for grinding , honing , lapping , superfinishing , polishing, pressure blasting, or barrel finishing . Abrasives in common use are alumina, silicon carbide, boron carbide, diamond, cubic boron nitride, garnet, and quartz. (2) Hard particles, such as rocks, sand, or fragments of certain hard metals, that wear away a surface when they move across it under pressure. See also superabrasives .
- **abrasive blasting**
  - A process for cleaning or finishing by means of an abrasive directed at high velocity against the workpiece. Abrasive blasting methods include grit blasting , sandblasting , and shotblasting .
- **abrasive disk**
  - (1) A grinding wheel that is mounted on a steel plate, with the exposed flat side being used for grinding. (2) A disk-shaped, coated abrasive product.
- **abrasive flow machining**
  - Removal of material by a viscous abrasive media flowing under pressure through or across a workpiece.
- **abrasive jet machining**
  - Material removal from a workpiece by impingement of fine abrasive particles that are entrained in a focused, high-velocity gas stream.
- **abrasive machining**
  - A machining process in which the points of abrasive particles are used as machining tools. Grinding is a typical abrasive machining process.
- **abrasive wear**
  - The removal of material from a surface when hard particles slide or roll across the surface under pressure. The particles may be loose or may be part of another surface in contact with the surface being abraded. Compare with adhesive wear .
- **abrasive wheel**
  - A grinding wheel composed of an abrasive grit and a bonding agent.
- **abrasivity**
  - The extent to which a surface, particle, or collection of particles will tend to cause abrasive wear when forced against a solid surface under relative motion and under prescribed conditions.
- **accelerated aging**
  - A process by which the effects of aging are accelerated under extreme and/or cycling temperature and humidity conditions. The process is meant to duplicate long-time environmental conditions in a relatively short space of time.
- **acicular ferrite**
  - A highly substructured nonequiaxed ferrite formed upon continuous cooling by a mixed diffusion and shear mode of transformation that begins at a temperature slightly higher than the transformation temperature range for upper bainite. It is distinguished from bainite in that it has a limited amount of carbon available; thus, there is only a small amount of carbide present.
- **acicular ferrite steels**
  - Ultralow carbon (<0.08%) steels having a microstructure consisting of either acicular ferrite or a mixture of acicular and equiaxed ferrite .
- **acid cleaning**
  - Process in which a solution of mineral acid, organic acid, or acid salt, in combination with a wetting agent and detergent, is used to remove oxide, shop soil, oil, grease, and other contaminants from metal surfaces, with or without the use of heat.
- **acrylic**
  - A coating based on a polymer containing short-chain esters of acrylic and methacrylic acid. Their physical properties can be controlled in part by the choice of the alcohol used to make the ester.

- **activation**
    - (1) The changing of a passive surface of a metal to a chemically active state. Contrast with passivation . (2) The (usually) chemical process of making a surface more receptive to bonding with a coating or an encapsulating material.
- **active**
    - The negative direction of electrode potential . Also used to describe corrosion and its associated potential range when an electrode potential is more negative than an adjacent depressed corrosion rate (passive) range.
- **active metal**
    - A metal ready to corrode, or being corroded.
- **actual contact area**
    - In tribology, the total area of contact formed by summing the localized asperity contact areas within the apparent area of contact . Also known as real area of contact.
- **addition agent**
    - See additive .
- **additive**
    - (1) A material added in small quantities to a solution to modify its characteristics. For example, additives may be added to a plating solution to modify the character of the deposit. (2) In lubrication, a material added to a lubricant for the purpose of imparting new properties or of enhancing existing properties. Main classes of additives include anticorrosive, antifoam, antioxidant , antiwear, detergent , dispersant , extreme-pressure lubricant , and VI improver additives. (3) In polymer engineering, a substance added to another substance, usually to improve properties, such as plasticizers , initiators, light stabilizers, and flame retardants.
- **adherend**
    - A body held to another body by an adhesive. See also substrate .
- **adhesion**
    - The attractive force that exists between a deposit and its substrate that can be measured as the force required to separate a deposit and its substrate. Contrast with cohesion .
- **adhesion promoter**
    - A coating applied to a substrate , before it is coated with an adhesive, to improve the adhesion of the substrate. Also called primer .
- **adhesive**
    - A substance capable of holding materials together by surface attachment. Adhesive is a general term and includes, among others, cement, glue, mucilage, and paste. These terms are loosely used interchangeably. Various descriptive adjectives are applied to the term adhesive to indicate certain physical characteristics: hot-melt adhesives, pressure-sensitive adhesives, structural adhesives, ultraviolet/electron-beam cured adhesives, and water-based adhesives.
- **adhesive bond**
    - Attractive forces, generally physical in character, between an adhesive and the base materials. Two principal interactions that contribute to the adhesion are van der Waals bonds and dipole bonds.
- **adhesive film**
    - A synthetic resin adhesive, with or without a film carrier fabric, usually of the thermosetting type, in the form of a thin film of resin, used under heat and pressure as an interleaf in the production of bonded structures.
- **adhesive strength**
    - The strength of the bond between an adhesive and an adherend .
- **adhesive wear**
    - (1) Wear by transference of material from one surface to another during relative motion due to a process of solid-phase welding. Particles that are removed from one surface are either permanently or temporarily attached to the other surface. (2) Wear due to localized bonding between contacting solid surfaces leading to material transfer between the two surfaces or loss from either surface. Compare with abrasive wear .
- **adsorption**
    - The adhesion of the molecules of gases, dissolved substances, or liquids to the surfaces of solids or liquids with which they are in contact.
- **aerated bath nitriding**

- A type of liquid nitriding in which air is pumped through the molten bath creating agitation and increased chemical activity.

- **AFS 50-70 test sand**
  - A rounded quartz sand specified for use as an abrasive in the dry sand-rubber wheel test (ASTM G 65). Using the U.S. Sieve Series, none of this sand will be retained on Sieve No. 40, 5% maximum will be retained on Sieve No. 50, 95% minimum will be retained on Sieve No. 70, and none will pass Sieve No. 100. This places all the particle diameters between 425 and 150 μm. See also sieve analysis .
- **age hardening**
  - (1) Hardening by aging (heat treatment) usually after rapid cooling or cold working. (2) (of grease). The increasing consistency of a lubricating grease with time of storage.
- **age softening**
  - Spontaneous decrease of strength and hardness that takes place at room temperature in certain strain hardened alloys, especially those of aluminum.
- **agglomerate**
  - The clustering together of a few or many particles, whiskers, or fibers, or a combination thereof, into a larger solid mass.
- **aging**
  - (1) The storage of porcelain enamel slips or powders before use. (2) The change occurring in porcelain enamel slips or powders with the lapse of time. (3) In heat treatment, a change in the properties of certain metals and alloys that occurs at ambient or moderately elevated temperatures after hot working or a heat treatment (quench aging in ferrous alloys, natural or artificial aging in ferrous and nonferrous alloys) or after cold working (strain aging). The change in properties is often, but not always, due to a phase change (precipitation), but never involves a change in chemical composition of the metal or alloy.
- **air cap**
  - A device for forming, shaping, and directing an air pattern for the atomization of wire or ceramic rod.
- **air feed**
  - A thermal spraying process variation in which an air stream carries the powdered material to be sprayed through the gun and into the heat source.
- **air gap**
  - In extrusion coating, the distance from the die opening to the nip formed by the pressure roll and the chill roll.
- **air hole**
  - A hole in a casting caused by air or gas trapped in the metal during solidification.
- **air setting**
  - The characteristic of some materials, such as refractory cements, core pastes, binders , and plastics, to take permanent set at normal air temperatures.
- **alclad**
  - Composite wrought product comprised of an aluminum alloy core having one or both surfaces a metallurgically bonded aluminum or aluminum alloy coating that is anodic to the core and thus electrochemically protects the core against corrosion .
- **aliphatic solvent**
  - A type of solvent comprised mainly of straight-chain hydrocarbons. Examples are gasoline, kerosene, hexane, and naphtha.
- **alkaline cleaner**
  - A material blended from alkali hydroxides and such alkaline salts as borates, carbonates, phosphates, or silicates. The cleaning action may be enhanced by the addition of surface-active agents and special solvents.
- **alkyd**
  - A coating based on a polyester binder . The polyester binders are chemical combinations of molecules that contain more than one acid or alcohol group. Alkyds are widely used in water-based house paints and automotive primers.
- **alligatoring**
  - (1) Pronounced wide cracking over the entire surface of a coating having the appearance of alligator hide. (2) The longitudinal splitting of flat slabs in a plane parallel to the rolled surface. Also called fishmouthing.

- **allowance**
  - (1) The specified difference in limiting sizes (minimum clearance or maximum interference) between mating parts, as computed arithmetically from the specified dimensions and tolerances of each part. (2) In a foundry, the specified clearance. The difference in limiting sizes, such as minimum clearance or maximum interferences between mating parts, as computed arithmetically. See also tolerance .
- **aluminizing**
  - Forming of an aluminum or aluminum alloy coating on a metal by hot dipping, hot spraying, or diffusion .
- **amorphous**
  - Not having a crystal structure; noncrystalline.
- **Amsler wear machine**
  - A wear and traction-testing machine consisting of two disk-shaped specimens oriented such that their axes are parallel and whose circumferential, cylindrical surfaces are caused to roll or roll and slide against one another. The rotation rates of each disk may be varied so as to produce varying degrees of sliding and rolling motion.
- **anchorite**
  - A zinc-iron phosphate coating for iron and steel.
- **anchor pattern**
  - A pattern made by blast cleaning abrasives on an adherend surface in preparation for adhesive application prior to bonding. Pattern is examined in profile.
- **angle of attack**
  - In tribology, the angle between the direction of motion of an impinging liquid or solid particle and the tangent to the surface at the point of impact.
- **angle of incidence**
  - In tribology, the angle between the direction of motion of an impinging liquid or solid particle stream and the plane of the surface.
- **angle-ply laminate**
  - A laminate having fibers of adjacent plies, oriented at alternating angles.
- **anion**
  - A negatively charged ion.
- **anionic detergent**
  - A detergent that produces aggregates of negatively charged ions with colloidal properties.
- **anneal to temper**
  - A final partial anneal that softens a cold-worked nonferrous alloy to a specified level of hardness or tensile strength.
- **anode**
  - The electrode in electrolysis at which negative ions are discharged, positive ions are formed, or other oxidizing reactions occur. Contrast with cathode .
- **anode corrosion**
  - The dissolution of a metal acting as an anode .
- **anode film**
  - (1) The layer of solution in contact with the anode that differs in composition from that of the bulk of the solution. (2) The outer layer of the anode itself consisting of oxidation or reaction products of the anode metal.
- **anodic cleaning**
  - Electrolytic cleaning in which the work is the anode . Also called reverse-current cleaning.
- **anodic coating**
  - A protective, decorative, or functional coating, formed by conversion of the surface of a metal in an electrolytic oxidation process.
- **anodic etching**
  - Method of revealing microstructure by selective dissolution of the polished surface under application of a direct current. Variation with layer formation: anodizing.
- **anodic inhibitor**
  - A chemical substance or mixture that prevents or reduces the rate of the anodic or oxidation reaction. See also inhibitor .
- **anodic pickling**
  - Electrolytic pickling in which the work is the anode.

- **anodic protection**
  - (1) A technique to reduce the corrosion rate of a metal by polarizing it into its passive region, where dissolution rates are low. (2) Imposing an external electrical potential to protect a metal from corrosive attack. (Applicable only to metals that show active-passive behavior.) Contrast with cathodic protection .
- **anodic reaction**
  - Electrode reaction equivalent to a transfer of positive charge from the electronic to the ionic conductor. An anodic reaction is an oxidation process. An example common in corrosion is Me $Me^{n+} + ne^-$
- **anodizing**
  - An electrolytic oxidation process in which the surface of a metal, when anodic, is converted to a coating having desirable protective, decorative, or functional properties.
- **anolyte**
  - The portion of electrolyte in the vicinity of the anode; in a divided cell, the portion of electrolyte on the anode side of the diagram.
- **antioxidant**
  - Any additive for the purpose of reducing the rate of oxidation and subsequent deterioration of a material.
- **antipitting agent**
  - An additive for electroplating solutions to prevent the formation of pits or large pores in the electrodeposit.
- **antiskinning agents**
  - Chemicals added to a paint to help prevent the formation of a surface film on the paint.
- **apparent area of contact**
  - In tribology, the area of contact between two solid surfaces defined by the boundaries of their macroscopic interface.
- **arc of contact**
  - The portion of the circumference of a grinding wheel or cutter touching the work being processed.
- **aromatic**
  - A type of solvent based on benzene ring molecules. Aromatics are often used as diluents in acrylic lacquers. Typical examples are benzene, xylol, and toluol.
- **asperity**
  - In tribology, a protuberance in the small-scale topographical irregularities of a solid surface.
- **atmospheric corrosion**
  - The gradual degradation or alteration of a material by contact with substances present in the atmosphere, such as oxygen, carbon dioxide, water vapor, and sulfur and chlorine compounds.
- **atomic replica**
  - A thin replica devoid of structure on the molecular level. It is prepared by the vacuum or hydrolytic deposition of metals or simple compounds of low molecular weight. See also replica .
- **atomization**
  - In thermal spraying, the division of molten material at the end of the wire or rod into fine particles.
- **attack-polishing**
  - Simultaneous etching and mechanical polishing.
- **attrition**
  - Removal of small fragments of surface material during sliding contact.
- **attritor**
  - A high-intensity ball mill whose drum is stationary and whose balls are agitated by rotating baffles, paddles, or rods at right angle to the drum axis.
- **attritor grinding**
  - The intensive grinding or alloying in an attritor. Examples: milling of carbides and binder metal powders and mechanical alloying of hard dispersoid particles with softer metal or alloy powders.
- **austempering**
  - A heat treatment for ferrous alloys in which a part is quenched from the austenitizing temperature at a rate fast enough to avoid formation of ferrite or pearlite and then held at a temperature just above M_s, the martensite start temperature, until transformation to bainite is complete. Although designated as bainite in both austempered steel and austempered ductile iron (ADI), austempered

steel consists of two-phase mixtures containing ferrite and carbide, while austempered ductile iron consists of two-phase mixtures containing ferrite and austenite .

- **austenite**
  - A solid solution of one or more elements in face-centered cubic iron (gamma iron). Unless otherwise designated (such as nickel austenite), the solute is generally assumed to be carbon.
- **austenitizing**
  - Forming austenite by heating a ferrous alloy into the transformation range (partial austenitizing) or above the transformation range (complete austenitizing). When used without qualification, the term implies complete austenitizing.
- **autocatalytic plating**
  - Deposition of a metal coating by a controlled chemical reduction, catalyzed by the metal or alloy being deposited.
- **average grain diameter**
  - The mean diameter of an equiaxed grain section whose size represents all the grain sections in the aggregate being measured. See also grain size .
- **B**
- **babbitting**
  - The process by which a babbitt metal is mechanically or chemically bonded to a shell or stiffener, which supports the weight and torsion of a rotating, oscillating, or sliding shaft. The babbitt metal, being softer than the support and having excellent antifrictional properties, prevents galling and/or scoring of the shaft over long periods of use.
- **babbitt metal**
  - A nonferrous bearing alloy originated by Isaac Babbitt in 1839. Currently, the term includes several tin-base alloys consisting mainly of various amounts of copper, antimony, tin, and lead. Lead-base babbitt metals are also used.
- **back emission**
  - The electrical breakdown of air resulting from an excessive charge buildup in porcelain enamel powder film during powder application. This reaction is due to the self-limiting characteristic of electrostatic powders. Also known as back ionization.
- **backing**
  - (1) In grinding, the material (paper, cloth, or fiber) that serves as the base for coated abrasives . (2) In welding, a material placed under or behind a joint to enhance the quality of the weld at the root. It may be a metal backing ring or strip; a pass of weld metal; or a nonmetal such as carbon, granular flux or a protective gas atmosphere . (3) In plain bearings, that part of the bearing to which the bearing alloy is attached, normally by a metallurgical bond .
- **backing film**
  - A film used as auxiliary support for the thin replica or specimen-supporting film.
- **back ionization**
  - See back emission .
- **bainite**
  - A metastable aggregate of ferrite and cementite resulting from the transformation of austenite at temperatures below the pearlite range but above M_s, the martensite start temperature. Upper bainite is an aggregate that contains parallel lath-shape units of ferrite, produces the so-called "feathery" appearance in optical microscopy, and is formed above approximately 350 °C (660 °F). Lower bainite, which has an acicular appearance similar to tempered martensite , is formed below approximately 350 °C (660 °F).
- **bainitic hardening**
  - Quench-hardening treatment resulting principally in the formation of bainite .
- **Bakelite**
  - A proprietary name for a phenolic thermosetting resin used as a plastic mounting material for metallographic samples.
- **ball milling**
  - In porcelain enameling, a method of grinding and mixing ceramic materials, with or without liquid, in a dense, ceramic-lined rotating cylinder or conical mill partially filled with grinding media such as pebbles or porcelain balls.
- **bark**
  - The decarburized layer just beneath the scale that results from heating steel in an oxidizing atmosphere.

- **barrel burnishing**
  - The smoothing of surfaces by means of tumbling the work in rotating barrels in the presence of metallic or ceramic shot, and in the absence of abrasive. In ball burnishing, the shot consists of hardened steel balls.
- **barrel finishing**
  - Improving the surface finish of workpieces by processing them in rotating equipment along with abrasive particles that may be suspended in a liquid. The barrel is normally loaded about 60% full with a mixture of parts, media, compound, and water. See also tumbling .
- **barrel plating**
  - (or cleaning). Plating articles in a rotating container, usually a perforated cylinder that operates at least partially submerged in a solution.
- **barrier coat**
  - An exterior coating applied to a composite filament-wound structure to provide protection. In fuel tanks, a coating applied to the inside of the tank to prevent fuel from permeating the side wall.
- **barrier film**
  - The layer of film used during cure to permit removal of air and volatiles from a reinforced plastic or a composite lay-up while minimizing resin loss.
- **barrier layer**
  - In anodizing aluminum, the thin, pore-free, semiconducting aluminum oxide region nearest the metal surface and distinct from the main anodic oxide coating, which has a pore structure.
- **base metal**
  - (1) The original metal to which one or more coatings are applied. Also known as basis metal. (2) The metal present in the largest proportion in an alloy; brass, for example, is a copper-base alloy. (3) A metal that readily oxidizes, or that dissolves to form ions. Contrast with noble metal .
- **basis metal**
  - See base metal .
- **beads**
  - Defects in porcelain enamel caused by coarse enamel particles, spitting of guns, or falloff of accumulation on guns. Also known as lumps.
- **Beilby layer**
  - The altered surface layer formed on a crystalline solid during a wear process or by mechanical polishing that, according to a theory by Sir George Beilby, consists of a material in an amorphous state. It is now generally accepted that an amorphous layer is not formed at a surface except possibly in some special cases; however, the term is still used to denote a surface altered by wear, without any implication as to its actual structure.
- **bending**
  - The straining of material, usually flat sheet or strip metal, by moving it around a straight axis lying in the neutral plane. Metal flow takes place within the plastic range of the metal, so that the bent part retains a permanent set after removal of the applied stress. The cross section of the bend inward from the neutral plane is in compression; the rest of the bend is in tension.
- **bend test**
  - A test for determining relative ductility of metal that is to be formed (usually sheet, strip, plate, or wire) and for determining soundness and toughness of metal (after welding, for example). The specimen is usually bent over a specified diameter through a specified angle for a specified number of cycles. There are four general types of bend test, named according to the manner in which the forces are applied to the specimen to make the bend: free bend, guided bend, semiguided bend, and wrap-around bend. Bend tests can also be used to test the adhesion of metallic or organic coatings.
- **beta rays**
  - Beams of electrons that can be used to cure certain kinds of paints.
- **binder**
  - The paint material that forms the film, so called because it binds the pigment and any additives present into a solid durable film. Also referred to as the resin.
- **bisque**
  - A coating of wet process porcelain enamel that has been dried, but not fired.
- **black annealing**
  - Box annealing or pot annealing ferrous alloy sheet, strip, or wire impart a black color to the oxidized surface. See also box annealing .

- **black carburizing**
  - Simulating the carburizing operation without introducing carbon. This is usually accomplished by using an inert material in place of the carburizing agent, or by applying a suitable protective coating to the ferrous alloy.
- **black oxide**
  - A black finish on a metal produced by immersing it in hot oxidizing salts or salt solutions.
- **black specking**
  - Same as specking .
- **blank nitriding**
  - Simulating the nitriding operation without introducing nitrogen. This is usually accomplished by using an inert material in place of the nitriding agent or by applying a suitable protective coating to the ferrous alloy.
- **blasting or blast cleaning**
  - A process for cleaning or finishing metal objects with an air blast or centrifugal wheel that throws abrasive particles against the surface of the workpiece. Small, irregular particles of metal are used as the abrasive in grit blasting ; sand, in sandblasting ; and steel, in shotblasting .
- **blister**
  - (1) A raised area, often dome shaped, resulting from loss of adhesion between a coating or deposit and the base metal . (2) In porcelain enamel , a defect caused by gas evolution, consisting of a bubble that forms during fusion and remains when the porcelain enamel solidifies. (3) A casting defect, on or near the surface of the metal, resulting from the expansion of gas in a subsurface zone. It is characterized by a smooth bump on the surface of the casting and a hole inside the casting directly below the bump.
- **blistering**
  - The development during firing of enclosed or broken macroscopic vesicles or bubbles in a body, or in a glaze or other coating.
- **bloom**
  - (1) A visible exudation or efflorescence on the surface of an electroplating bath. (2) A bluish fluorescent cast to a painted surface caused by deposition of a thin film of smoke, dust, or oil. (3) A loose, flowerlike corrosion product that forms when certain metals are exposed to a moist environment.
- **blow hole**
  - A void produced by the outgassing of trapped air during cure. (2) A void in a solder connection caused by outgassing or a void in a fired dielectric.
- **blue annealing**
  - Heating hot-rolled ferrous sheet in an open furnace to a temperature within the transformation range, then cooling in air to soften the metal. A bluish oxide surface layer forms.
- **blue brittleness**
  - Brittleness exhibited by some steels after being heated to some temperature within the range of about 205 to 370 °C (400 to 700 °F), particularly if the steel is worked at the elevated temperature. Killed steels are virtually free of this kind of brittleness.
- **blue dip**
  - A solution containing a mercury compound, once widely used to deposit mercury on a metal by immersion, usually prior to silver plating .
- **blue enamel**
  - (1) In dry-process enameling , an area of enamel coating so thin that it appears blue in color. (2) In wet-process enameling , a cover coat applied too thinly to hide the substrate.
- **bluing**
  - (or blueing). Subjecting the scale-free surface of a ferrous alloy to the action of air, steam, or other agents at a suitable temperature, thus forming a thin blue film of oxide and improving the appearance and resistance to corrosion. This term is ordinarily applied to sheet, strip, or finished parts. It is used also to denote the heating of springs after fabrication to improve their properties.
- **blushing**
  - (1) Whitening and loss of gloss of a usually organic coating caused by moisture. Also called blooming. (2) The condensation of atmospheric moisture at the adhesive bond line interface.
- **bobbing compound**
  - A compound used for heavy buffing that usually contains some form of coarse silica such as flint or quartz. Considerably more abrasive than tripoli compound .

- **boiling**
  - A defect visible in fired porcelain enamel that is caused by gas evolution and that results in the formation of blisters , pinholes , specking , dimples , or a spongy surface.
- **bond**
  - (1) In grinding wheels and other relatively rigid abrasive products, the material that holds the abrasive grains together. (2) In an adhesive bonded or diffusion bonded joint, the line along which the faying surfaces are joined together. (3) In thermal spraying, the junction between the material deposited and the substrate , or its strength. See also adhesive bond , mechanical bond , and metallic bond .
- **bond coat**
  - In thermal spraying, a preliminary (or prime) coat of material which improves adherence of the subsequent thermal spray deposit.
- **boriding**
  - Thermochemical treatment involving the enrichment of the surface layer of an object with borides. This surface-hardening process is performed below the Ac_1 temperature (the temperature at which austenite begins to form during heating). Also referred to as boronizing.
- **box annealing**
  - Annealing a metal or alloy in a sealed container under conditions that minimize oxidation. In box annealing a ferrous alloy, the charge is usually heated slowly to a temperature below the transformation range, but sometimes is above or within it, and is then cooled slowly; this process is also called close annealing or pot annealing. See also black annealing .
- **breakout**
  - Fiber separation or break on surface plies at drilled or machined composite material edges.
- **bright annealing**
  - Annealing in a protective medium to prevent discoloration of the bright surface.
- **bright dip**
  - A solution that produces, through chemical action, a bright surface on an immersed metal.
- **brightener**
  - An agent or combination of agents added to an electroplating bath to produce a lustrous deposit.
- **bright finish**
  - A high-quality finish produced on ground and polished rolls. Suitable for electroplating.
- **bright nitriding**
  - Nitriding in a protective medium to prevent discoloration of the bright surface. Compare with blank nitriding .
- **bright plate**
  - An electrodeposit that is lustrous in the as-plated condition.
- **bright-throwing power**
  - The measure of the ability of a plating solution or a specified set of plating conditions to deposit uniformly bright electroplate on an irregularly shaped cathode .
- **Brinelling**
  - (1) Indentation of the surface of a solid body by repeated local impact or impacts, or static overload. Brinelling may occur especially in a rolling-element bearing. (2) Damage to a solid bearing surface characterized by one or more plastically formed indentations brought about by overload. See also false Brinelling .
- **brittle**
  - Permitting little or no plastic deformation prior to fracture.
- **brittle erosion behavior**
  - Erosion behavior having characteristic properties (e.g., little or no plastic flow, the formation of cracks) that can be associated with brittle fracture of the exposed surface. The maximum volume removal occurs at an angle near 90°, in contrast to approximately 25° for ductile erosion behavior .
- **brittle fracture**
  - Separation of a solid accompanied by little or no macroscopic plastic deformation . Typically, brittle fracture occurs by rapid crack propagation with less expenditure of energy than for ductile fracture . Brittle tensile fractures have a bright, granular appearance and exhibit little or no necking. A chevron pattern may be present on the fracture surface, pointing toward the origin of the crack, especially in brittle fractures in flat platelike components. Examples of brittle fracture include transgranular cracking and intergranular cracking .

- **brittleness**
  - The tendency of a material to fracture without first undergoing significant plastic deformation . Contrast with ductility .
- **broaching**
  - Cutting with a tool that consists of a bar having a single edge or a series of cutting edges (teeth) on its surface. The cutting edges of multiple-tooth, or successive single-tooth, broaches increase in size and/or change in shape. The broach cuts in a straight line or axial direction when relative motion is produced in relation to the workpiece, which may also be rotating. The entire cut is made in single or multiple passes over the workpiece to shape the required surface contour.
- **bronzing**
  - (1) Applying a chemical finish to copper or copper-alloy surfaces to alter the color. (2) Plating a copper-tin alloy on various materials.
- **brush plating**
  - A method of plating in which the plating solution is applied with a pad or brush, within which is an anode that is moved over the cathode to be plated. Also called selective plating.
- **brush polishing (electrolytic)**
  - A method of electropolishing in which the electrolyte is applied with a pad or brush in contact with the part to be polished.
- **bubble structure**
  - Size and spatial distribution of voids within fired porcelain enamel .
- **buckle**
  - (1) Bulging of a large, flat face of a casting; in investment casting, caused by dip coat peeling from the pattern. (2) An indentation in a casting, resulting from expansion of the sand, can be termed the start of an expansion defect. (3) A local waviness in metal bar or sheet, usually transverse to the direction of rolling.
- **buffer**
  - A compound or mixture that, when contained in solution, causes the solution to resist change in pH. Each buffer has a characteristic limited range of pH over which it is effective.
- **buffing**
  - Developing a lustrous surface by contacting the work with a rotating buffing wheel .
- **buffing wheel**
  - Buff sections assembled to the required face width for use on a rotating shaft between flanges. Sometimes called a buff.
- **buff sections**
  - Fabric, paper, or leather disks with concentric center holes held together by various types of sewing to provide degrees of flexibility or hardness. These sections are assembled to make wheels for polishing or buffing .
- **building up**
  - Electroplating for the purpose of increasing the dimensions of a workpiece.
- **built-up edge**
  - (1) Chip material adhering to the tool face adjacent to the cutting edge during cutting. (2) Material from the workpiece, especially in machining, which is stationary with respect to the tool. See also wedge formation .
- **bull's-eye structure**
  - The microstructure of malleable or ductile cast iron when graphite nodules are surrounded by a ferrite layer in a pearlitic matrix.
- **burned-in sand**
  - A defect consisting of a mixture of sand and metal cohering to the surface of a casting.
- **burned-on sand**
  - A misnomer usually indicating metal penetration into sand, resulting in a mixture of sand and cast metal adhering to the surface of a casting.
- **burning**
  - (1) Permanently damaging a metal or alloy by heating to cause either incipient melting or intergranular oxidation. (2) During subcritical annealing, particularly in continuous annealing, production of a severely decarburized and grain-coarsened surface layer that results from excessively prolonged heating to an excessively high temperature. (3) In grinding, getting the work hot enough to cause discoloration or to change the microstructure by tempering or

hardening. (4) In sliding contacts, the oxidation of a surface due to local heating in an oxidizing environment. See also metallurgical burn .

- **burnishing**
  - Finish sizing and smooth finishing of surfaces (previously machined or ground) by displacement, rather than removal, of minute surface irregularities with smooth point or line-contact, fixed or rotating tools.
- **burnoff**
  - (1) The unintentional removal of an autocatalytic deposit from a nonconducting substrate, during subsequent electroplating operations, owing to the application of excessive current or a poor contact area. (2) In porcelain enamel , a condition caused by thin application resulting in a black or yellow-green color. The enamel layer may appear transparent. Lack of bubble structure and shinier scale may be associated with this condition.
- **burnt deposit**
  - A rough, noncoherent or otherwise unsatisfactory deposit produced by the application of an excessive current density and usually containing oxides or other inclusions.
- **burr**
  - An undesirable projection of material that results from a cutting, forming, blanking, or shearing operation, especially a rough edge left on sheet steel after stamping or punching.
- **burr hardness**
  - Hardness of the burr in the vicinity of the base of the burr .
- **burr height**
  - The distance a burr projects above the surface of the workpiece.
- **burring**
  - (1) The process of removing burrs (preferred word is deburring). (2) The intentional production of a small flange around holes in a pressworking operation (preferred word is flanging). (3) The act of burr formation.
- **bus (bus bar)**
  - A rigid conducting section, for carrying current to the anode and cathode bars.
- **butler finish**
  - A semilustrous metal finish composed of fine, uniformly distributed parallel lines, usually produced with a soft abrasive buffing wheel ; similar in appearance to the traditional hand-rubbed finish on silver.
- **buttering**
  - A form of surfacing in which one or more layers of weld metal are deposited on the groove face of one member (for example, a high-alloy weld deposit on steel base metal that is to be welded to a dissimilar base metal). The buttering provides a suitable transition weld deposit for subsequent completion of the butt weld (joint).
- **C**
- **calcareous coating or deposit**
  - A layer consisting of a mixture of calcium carbonate and magnesium hydroxide deposited on surfaces being cathodically protected against corrosion , because of the increased pH adjacent to the protected surface.
- **calender**
  - The passing of plastic sheet material between sets of pressure rollers to produce a smooth finish and a desired thickness.
- **calomel half cell (calomel electrode)**
  - A half cell containing a mercury electrode in contact with a solution of potassium chloride of specified concentration that is saturated with mercurous chloride (calomel).
- **calorizing**
  - Imparting resistance to oxidation to an iron or steel surface by heating in aluminum powder at 800 to 1000 °C (1470 to 1830 °F).
- **canning**
  - (1) A dished distortion in a flat or nearly flat sheet metal surface, sometimes referred to as oil canning. (2) Enclosing a highly reactive metal within a relatively inert material for the purpose of hot working without undue oxidation of the active metal.
- **capillary attraction**

- (1) The combined force of adhesion and cohesion that causes liquids, including molten metals, to flow between very closely spaced and solid surfaces, even against gravity. (2) In powder metallurgy, the driving force for the infiltration of the pores of a sintered compact by a liquid.

- **carbide tools**
  - Cutting or forming tools, usually made from tungsten, titanium, tantalum, or niobium carbides, or a combination of them, in a matrix of cobalt, nickel, or other metals. Carbide tools are characterized by high hardnesses and compressive strengths and may be coated to improve wear resistance.
- **carbon edges**
  - Carbonaceous deposits in a wavy pattern along the edges of a steel sheet or strip; also known as snaky edges.
- **carbonitriding**
  - A case hardening process in which a suitable ferrous material is heated above the lower transformation temperature in a gaseous atmosphere of such composition as to cause simultaneous absorption of carbon and nitrogen by the surface and, by diffusion, create a concentration gradient. The heat-treating process is completed by cooling at a rate that produces the desired properties in the workpiece.
- **carbon restoration**
  - Replacing the carbon lost in the surface layer from previous processing of a steel by carburizing this layer to substantially the original carbon level. Sometimes called recarburizing.
- **carburizing**
  - Absorption and diffusion of carbon into solid ferrous alloys by heating, to a temperature usually above Ac_3, in contact with a suitable carbonaceous material. A form of case hardening that produces a carbon gradient extending inward from the surface, enabling the surface layer to be hardened either by quenching directly from the carburizing temperature or by cooling to room temperature, then reaustenitizing and quenching.
- **carrier gas**
  - In thermal spraying, the gas used to carry the powdered materials from the powder feeder or hopper to the gun.
- **case**
  - In heat treating, that portion of a ferrous alloy, extending inward from the surface, whose composition has been altered during case hardening . Typically considered to be the portion of an alloy (a) whose composition has been measurably altered from the original composition, (b) that appears light when etched, or (c) that has a higher hardness value than the core.
- **case hardening**
  - A generic term covering several processes applicable to steel that change the chemical composition of the surface layer by absorption of carbon, nitrogen, or a mixture of the two and, by diffusion, create a concentration gradient. The processes commonly used are carburizing and quench hardening , cyaniding , nitriding , and carbonitriding . The use of the applicable specific process name is preferred.
- **cast film**
  - A film made by depositing a layer of liquid plastic onto a surface and stabilizing this form by the evaporation of solvent, by fusing after deposition, or by allowing a melt to cool. Cast films are usually made from solutions or dispersions .
- **cast replica**
  - In metallography, a reproduction of a surface in plastic made by the evaporation of the solvent from a solution of the plastic or by polymerization of a monomer on the surface. See also replica .
- **catalyst**
  - A chemical used to change the rate of a chemical reaction. Differs from a curing agent in that the catalyst is not itself chemically consumed in the reaction, while a curing agent is. Technically, catalysts that increase reaction rates are called accelerators; those that decrease reaction rates are called inhibitors or retarders.
- **catastrophic wear**
  - Sudden surface damage, deterioration, or change of shape caused by wear to such an extent that the life of the part is appreciably shortened or action is impaired.
- **cathode**

    - The electrode in electrolysis at which positive ions are discharged, negative ions are formed, or other reducing actions occur. Contrast with anode .
- **cathode film**
    - The layer of solution in contact with the cathode that differs in composition from that of the bulk of the solution.
- **cathodic cleaning**
    - Electrolytic cleaning in which the work is the cathode . Also called direct-current cleaning.
- **cathodic corrosion**
    - Corrosion resulting from a cathodic condition of a structure usually caused by the reaction of an amphoteric metal with the alkaline products of electrolysis .
- **cathodic disbondment**
    - The destruction of adhesion between a coating and its substrate by products of a cathodic reaction .
- **cathodic pickling**
    - Electrolytic pickling in which the work is the cathode .
- **cathodic protection**
    - The prevention of corrosion of a metal by electrically connecting it to a sacrificial anode . The anode is itself decomposed, and the object of interest is protected. The sacrificial anode must be replaced periodically. Contrast with anodic protection .
- **cathodic reaction**
    - Electrode reaction equivalent to a transfer of negative charge from the electronic to the ionic conductor. A cathodic reaction is a reduction process. An example common in corrosion is: $Ni^{2+} + 2e^-$ Ni.
- **catholyte**
    - The portion of the electrolyte in the vicinity of the cathode ; in a divided cell the portion of the cathode side of the diaphragm.
- **cation**
    - A positively charged ion that migrates through the electrolyte toward the cathode under the influence of a potential gradient. See also anion and ion .
- **cationic detergent**
    - A detergent that produces aggregates of positively charged ions with colloidal properties.
- **caul**
    - In adhesive bonding, a sheet of material employed singly or in pairs in the hot or cold pressing of assemblies being bonded. A caul is used to protect either the faces of the assembly or the press platens, or both, against marring and staining in order to prevent sticking, facilitate press loading, impart a desired surface texture or finish, and provide uniform pressure distribution. A caul may be made of any suitable material such as aluminum, stainless steel, hardboard, fiberboard, or plastic, the length and width dimensions generally being the same as those of the plates of the press where it is used.
- **caustic dip**
    - A strongly alkaline solution into which metal is immersed for etching, for neutralizing acid, or for removing organic materials such as greases or paints.
- **cavitation**
    - The formation and collapse, within a liquid, of cavities or bubbles that contain vapor or gas or both. In general, cavitation originates from a decrease in the static pressure in the liquid. It is distinguished in this way from boiling, which originates from an increase in the liquid temperature. There are certain situations where it may be difficult to make a clear distinction between cavitation and boiling, and the more general definition that is given here is therefore to be preferred. In order to erode a solid surface by cavitation, it is necessary for the cavitation bubbles to collapse on or close to that surface.
- **cavitation corrosion**
    - A process involving conjoint corrosion and cavitation .
- **cavitation erosion**
    - Progressive loss of original material from a solid surface due to continuing exposure to cavitation .
- **cell**
    - Electrochemical system consisting of an anode and a cathode immersed in an electrolyte . The anode and cathode may be separate metals or dissimilar areas on the same metal. The cell

includes the external circuit, which permits the flow of electrons from the anode toward the cathode.

- **cementite**
  - A hard (800 HV), brittle compound of iron and carbon, known chemically as iron carbide and having the approximate chemical formula Fe_3C. It is characterized by an orthorhombic crystal structure. When it occurs as a phase in steel, the chemical composition will be altered by the presence of manganese and other carbide-forming elements. The highest cementite contents are observed in white cast irons, which are used in applications where high wear resistance is required.
- **centerless grinding**
  - Grinding the outside or inside diameter of a cylindrical piece that is supported on a work support blade instead of being held between centers and that is rotated by a so-called regulating or feed wheel.
- **ceramic-metal coating**
  - A mixture of one or more ceramic materials in combination with a metallic phase applied to a metallic substrate that may or may not require heat treatment prior to service. This term may also be used for coatings applied to nonmetallic substrates, for example, graphite.
- **ceramic process**
  - The production of articles or coatings from essentially inorganic, nonmetallic materials, the article or coating being made permanent and suitable for utilitarian and decorative purposes by the action of heat at temperatures sufficient to cause sintering, solid-state reactions, bonding, or conversion partially or wholly to the glassy state.
- **chafing**
  - Repeated rubbing between two solid bodies that can result in surface damage and/or wear.
- **chafing fatigue**
  - Fatigue initiated in a surface damaged by rubbing against another body. See also fretting .
- **Charpy test**
  - An impact test in which a V-notched, keyhole-notched, or U-notched specimen, supported at both ends, is struck behind the notch by a striker mounted at the lower end of a bar that can swing as a pendulum. The energy that is absorbed in fracture is calculated from the height to which the striker would have risen had there been no specimen and the height to which it actually rises after fracture of the specimen. Contrast with Izod test .
- **chatter marks**
  - Surface imperfections on the work being ground, usually caused by vibrations transferred from the wheel-work interface during grinding.
- **checking**
  - The development of slight breaks in a coating that do not penetrate to the underlying surface. See also craze cracking .
- **chelating agent**
  - (1) An organic compound in which atoms form more than one coordinate bond with metals in solution. (2) A substance used in metal finishing to control or eliminate certain metallic ions present in undesirable quantities.
- **chemical conversion coating**
  - A protective or decorative nonmetallic coating produced in situ by chemical reaction of a metal with a chosen environment. It is often used to prepare the surface prior to the application of an organic coating and to provide some corrosion protection.
- **chemical deposition**
  - The precipitation or plating-out of a metal from solutions of its salts through the introduction of another metal or reagent to the solution.
- **chemical etching**
  - The dissolution of the material of a surface by subjecting it to the corrosive action of an acid or an alkali.
- **chemical milling**
  - A process for the selective and controlled removal of metal from a surface through the use of chemical etchants.
- **chemical polishing**
  - The improvement in surface smoothness of a metal by simple immersion in a suitable solution.
- **chemical vapor deposition (CVD)**

- (1) A coating process, similar to gas carburizing and carbonitriding, whereby a reactant atmosphere gas is fed into a processing chamber where it decomposes at the surface of the workpiece, liberating one material for either absorption by, or accumulation on, the workpiece. A second material is liberated in gas form and is removed from the processing chamber, along with excess atmosphere gas. (2) Process used in manufacture of several composite reinforcements, especially boron and silicon carbide, in which desired reinforcement material is deposited from vapor phase onto a continuous core, for example, boron on tungsten wire (core).

- **chevron pattern**
  - A fractographic pattern of radial marks (shear ledges) that look like nested letters "V;" sometimes called a herringbone pattern. Chevron patterns are typically found on brittle fracture surfaces in parts whose widths are considerably greater than their thicknesses. The points of the chevrons can be traced back to the fracture origin.
- **chipping**
  - Fracturing and breaking away of fragments of a porcelain enamel surface.
- **chips**
  - Pieces of material removed from a workpiece by cutting tools or by an abrasive medium.
- **chlorinated lubricant**
  - A lubricant containing a chlorine compound that reacts with a rubbing surface at elevated temperatures to protect it from sliding damage. See also extreme-pressure lubricant , sulfochlorinated lubricant , and sulfurized lubricant .
- **chlorinated solvent**
  - A liquid organic compound of carbon, hydrogen, and chlorine such as methylene chloride, perchloroethylene, 1,1,1-trichloroethane, and trichloroethylene. These solvents are very effective for degreasing with a minimum fire hazard, but their use is heavily regulated due to their classification as ozone-depleting chemicals.
- **chromadizing**
  - Improving paint adhesion on aluminum or aluminum alloys, mainly aircraft skins, by treatment with a solution of chromic acid. Also called chromidizing or chromatizing. Not to be confused with chromating or chromizing .
- **chromate treatment**
  - A treatment of metal in a solution of a hexavalent chromium compound to produce a conversion coating consisting of trivalent and hexavalent chromium compounds.
- **chromating**
  - The process for producing a conversion coating containing chromium compounds.
- **chromium buffing compound**
  - A buffing compound consisting of fine unfused alumina. Originally developed to color buff chromium-plated parts that had been stained or frosted in the electroplating process.
- **chromium plating**
  - Electrodeposition of chromium on a substrate.
- **chromizing**
  - A surface treatment at elevated temperature, generally carried out in pack, vapor, or salt baths, in which an alloy is formed by the inward diffusion of chromium into the base metal .
- **cladding**
  - (1) A layer of material, usually metallic, that is mechanically or metallurgically bonded to a substrate . Cladding may be bonded to the substrate by any of several processes, such as roll-cladding and explosive forming. (2) A relatively thick layer (>1 mm, or 0.04 in.) of material applied by surfacing for the purpose of improved corrosion resistance or other properties. See also coating , surfacing , and hardfacing .
- **clad metal**
  - A composite metal containing two or more layers that have been bonded together. The bonding may have been accomplished by co-rolling, co-extrusion, welding, diffusion bonding, casting, heavy chemical deposition, or heavy electroplating.
- **cleaning**
  - The removal of grease, oxides, or other foreign material from a surface. See also types of cleaning: alkaline , anodic , cathodic , diphase , electrolytic , emulsion , immersion , soak , solvent , spray , ultrasonic .
- **cleaning-emulsifiable solvent**

- Two-stage cleaning system wherein a concentrate containing organic solvents and surface-active agents is applied to a surface, subsequently emulsified, and removed along with the soil , by water rinsing.

- **clean surface**
  - A surface that is free of foreign material, both visible and invisible.
- **coarse grains**
  - Grains larger than normal for the particular wrought metal or alloy or of a size that produces a surface roughening known as orange peel or alligator skin.
- **coated abrasive**
  - An abrasive product (sandpaper, for example) in which a layer of abrasive particles is firmly attached to a paper, cloth, or fiber backing by means of glue or synthetic-resin adhesive.
- **coating**
  - A relatively thin layer (<1 mm, or 0.04 in.) of material applied by various processes for the purpose of corrosion prevention, resistance to high-temperature scaling, wear resistance, lubrication, or other purposes.
- **coating strength**
  - A measure of the cohesive bond within a coating, as opposed to coating-to-coating substrate bond; the tensile strength of a coating.
- **coating stress**
  - The stresses in a coating resulting, for example, from rapid cooling of molten or semimolten particles as they impact the substrate or from differential thermal expansion.
- **cocoa**
  - In fretting wear , a powdery form of debris, usually consisting of iron oxides, that is expelled from a ferrous metal joint near the location where fretting wear is occurring. Also known as red mud.
- **coefficient of friction**
  - The dimensionless ratio of the friction force (F) between two bodies to the normal force (N) pressing these bodies together: (or f) = (F/N).
- **cohesion**
  - (1) The state in which the particles of a single substance are held together by primary or secondary valence forces. As used in the adhesive field, the state in which the particles of the adhesive (or adherend) are held together. (2) Force of attraction between the molecules (or atoms) within a single phase. Contrast with adhesion .
- **coil breaks**
  - Creases or ridges in sheet or strip that appear as parallel lines across the direction of rolling and that generally extend the full width of the sheet or strip. Most commonly seen in as-annealed carbon steels.
- **cold etching**
  - Etching to reveal microstructure conducted at room temperature and below.
- **cold lap**
  - Wrinkled markings on the surface of an ingot or casting from incipient freezing of the surface and too low a casting temperature.
- **cold rolled sheets**
  - A metal mill product produced from a hot rolled pickled coil that has been given substantial cold reduction at room temperature. The resulting product is usually annealed and temper rolled to make it suitable for most common applications. The usual end product is characterized by improved surface, greater uniformity in thickness, and improved mechanical properties compared with hot rolled sheet.
- **cold shut**
  - (1) A discontinuity that appears on the surface of cast metal as a result of two streams of liquid meeting and failing to unite. (2) A lap on the surface of a forging or billet that was closed without fusion during deformation. (3)Freezing of the top surface of an ingot before the mold is full.
- **cold treatment**
  - Exposing steel to suitable sub-zero temperatures (-85 °C, or -120 °F) for the purpose of obtaining desired conditions or properties such as dimensional or microstructural stability. When the treatment involves the transformation of retained austenite, it is usually followed by tempering.
- **cold-worked structure**

- A microstructure resulting from plastic deformation of a metal or alloy below its recrystallization temperature.

- **collodion replica**
  - In metallography, a replica of a surface cast in nitrocellulose.
- **colloidal particle**
  - An electrically charged particle, generally smaller in size than 200 μm, dispersed in a second continuous phase.
- **colloids**
  - Aggregates of molecules in solution (dispersion) resulting in particles having dimensions in the 0.001 millimicron to 1000 micron range.
- **colonial finish**
  - A surface finish achieved by selectively buffing an oxidized surface, thereby producing lustrous highlights against the oxidized background.
- **color anodizing**
  - In anodizing of aluminum, formation of a colored coating on aluminum where the colored compound, pigment, or dye is incorporated after the coating has been formed and prior to sealing.
- **color buffing**
  - Producing a final high luster by buffing . Sometimes called coloring .
- **color etching**
  - Same as staining and tint etching .
- **coloring**
  - The production of desired colors on metal surfaces by appropriate chemical or electrochemical action. See also color buffing .
- **color oxide**
  - A material used to impart color to a porcelain enamel .
- **columnar structure**
  - A coarse structure of parallel elongated grains formed by unidirectional growth, most often observed in castings, but sometimes seen in structures resulting from diffusional growth accompanied by a solid-state transformation.
- **comet tails (on a polished surface)**
  - A group of comparatively deep unidirectional scratches that form adjacent to a microstructural discontinuity during mechanical polishing. They have the general shape of a comet tail. Comet tails form only when a unidirectional motion is maintained between the surface being polished and the polishing cloth.
- **complex ion**
  - An ion composed of two or more ions or radicals, both of which are capable or independent existence, for example, cuprocyanide $(Cu(CN)_3)^{2-}$.
- **composite coating**
  - A coating on a metal or non-metal that consists of two or more components, one of which is often particulate in form. Example: a cermet composite coating on a cemented carbide cutting tool. Also known as multilayer coating.
- **composite plate**
  - An electrodeposit consisting of layers of at least two different compositions.
- **compound zone**
  - The surface layer of diffusion-treated steels, which is made up of intermetallic compounds such as nitrides or carbides.
- **compressive burr**
  - The burr produced in blanking or piercing operations in which the slug separates from the stock in a compressive stress field. Burrs produced in this manner initially begin as tensile burrs and are typically identified as tensile-plus-compressive burrs .
- **conditioning**
  - The conversion of a surface on a plastic substrate to a suitable state for successful treatment in succeeding steps.
- **conductance**
  - The capacity of a medium, usually expressed in mhos, for transmitting electric current. The reciprocal of resistance.
- **conducting salt**
  - A salt added to the solution in order to increase its conductivity.

- **conformal coating**
  - A coating that covers and exactly fits the shape of the coated object.
- **contact plating**
  - A metal plating process wherein the plating current is provided by galvanic action between the work metal and a second metal, without the use of an external source of current.
- **contact potential**
  - In corrosion technology, the potential difference at the junction of two dissimilar substances.
- **continuity of coating**
  - The degree to which a porcelain enamel or ceramic coating is free of defects , such as bare spots, boiling , blisters , or copperheads , that could reduce its protective properties.
- **controlled cooling**
  - Cooling a metal or alloy from an elevated temperature in a predetermined manner to avoid hardening, cracking, or internal damage, or to produce desired microstructure or mechanical properties.
- **controlled etching**
  - Electrolytic etching with selection of suitable etchant and voltage resulting in a balance between current and dissolved metal ions.
- **controlled rolling**
  - A hot-rolling process in which the temperature of the steel is closely controlled, particularly during the final rolling passes, to produce a fine-grain microstructure.
- **conversion coating**
  - A coating consisting of a compound of the surface metal, produced by chemical or electrochemical treatments of the metal. Examples include chromate coatings on zinc, cadmium, magnesium, and aluminum, and oxide and phosphate coatings on steel. See also chromate treatment and phosphating .
- **copper-accelerated salt-spray (CASS) test**
  - An accelerated corrosion test for some electrodeposits and for anodic coatings on aluminum.
- **copperhead**
  - A reddish spot in a porcelain enamel coating caused by iron pickup during enameling, iron oxide left on poorly cleaned base metal , or burrs on iron or steel base metal that protrude through the coating and are oxidized during firing. Also called pull through.
- **coring**
  - (1) A condition of variable composition between the center and surface of a unit of microstructure (such as a dendrite, grain, carbide particle); results from nonequilibrium solidification, which occurs over a range of temperature. (2) A central cavity at the butt end of a rod extrusion, sometimes called extrusion pipe.
- **Corrodkote test**
  - An accelerated corrosion test for electrodeposits.
- **corrosion**
  - The chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties.
- **corrosion embrittlement**
  - The severe loss of ductility of a metal resulting from corrosive attack, usually intergranular corrosion and often not visually apparent.
- **corrosion fatigue**
  - The process in which a metal fractures prematurely under conditions of simultaneous corrosion and repeated cyclic loading at lower stress levels or fewer cycles than would be required in the absence of the corrosive environment.
- **corrosion protection**
  - Modification of a corrosion system so that corrosion damage is mitigated.
- **corrosion rate**
  - Corrosion effect on a metal per unit of time. The type of corrosion rate used depends on the technical system and on the type of corrosion effect. Thus, corrosion rate may be expressed as an increase in corrosion depth per unit of time (penetration rate, for example, mm/yr) or the mass of metal turned into corrosion products per unit area of surface per unit of time (weight loss, for example, $g/m^2/yr$). The corrosion effect may vary with time and may not be the same at all points of the corroding surface. Therefore, reports of corrosion rates should be accompanied by information on the type, time dependency, and location of the corrosion effect.

- **corrosion resistance**
  - The ability of a material to withstand contact with ambient natural factors or those of a particular, artificially created atmosphere, without degradation or change in properties. For metals, this could be pitting or rusting; for organic materials, it could be crazing .
- **corrosive wear**
  - Wear in which chemical or electrochemical reaction with the environment is significant. See also oxidative wear .
- **corrugations**
  - In metal forming, transverse ripples caused by a variation in strip shape during hot or cold reduction.
- **corundum**
  - A naturally occurring fused aluminum oxide (Al_2O_3) used as an abrasive.
- **coulomb**
  - The quantity of electricity that is transmitted through an electric circuit in 1 s when the current in the circuit is 1 A. The quantity of electricity that will deposit 0.0011180 g of silver.
- **cover coat**
  - A porcelain enamel finish applied to and then fused over a ground coat or applied directly to the metal substrate and then fused.
- **covering power**
  - (1) The ability of a solution to give satisfactory plating at very low current densities, a condition that exists in recesses and pits. This term suggests an ability to cover, but not necessarily to build up, a uniform coating, whereas throwing power suggests the ability to obtain a coating of uniform thickness on an irregularly shaped object. (2) The degree to which a porcelain enamel coating obscures the underlying surface. (3) The ability of a glaze to uniformly and completely cover the surface of the fired ceramic ware.
- **crack**
  - (1) A fracture type discontinuity characterized by a sharp tip and high ratio of length and width to opening displacement. (2) A line of fracture without complete separation.
- **cratering**
  - Depressions on coated surfaces caused by excess lubricant. Cratering results when paint is too thin and later ruptures, leaving pinholes and other voids. Use of less thinner in the coating can reduce or eliminate cratering, as can the use of less lubricant on the part.
- **crater wear**
  - The wear that occurs on the rake face of a cutting tool due to contact with the material in the chip that is sliding along that face.
- **crawling**
  - In porcelain enamel , a condition similar to tearing that occurs when firing a sprayed enamel coating over another coating already fired. It is characterized by the aggregation of the topcoat into balls or irregularly shaped islands during firing, thus exposing the base coat layer.
- **craze cracking**
  - Irregular surface cracking of a metal associated with thermal cycling. This term is used more in the United Kingdom than in the United States, where the term checking is used instead.
- **crazing**
  - (1) A network of fine hairline cracks in a coating. (2) Cracking that occurs in fired glazes or other ceramic coatings due to critical tensile stresses. (3) In porcelain enamel , almost-invisible lines in the finished surface that extend down to the base metal.
- **creep-feed grinding**
  - A subset of surface grinding , creep-feed grinding produces deeper (full) depths of cut at slow traverse rates.
- **crevice corrosion**
  - Localized corrosion of a metal surface at, or immediately adjacent to, an area that is shielded from full exposure to the environment because of close proximity between the metal and the surface of another material.
- **critical current density**
  - In an electrolytic process, a current density at which an abrupt change occurs in an operating variable or in the nature of an electrodeposit or electrode film.
- **critical pigment volume concentration (CPVC)**

- The volume percent of pigment in a coating in which the pigment particles are surrounded by resin so that no free surface pigment exists.

- **cross rolling**
  - Rolling of metal or sheet or plate so that the direction of rolling is about 90° from the direction of a previous rolling.
- **cure**
  - The process by which paint is converted from the liquid to the solid state.
- **current density**
  - The current flowing to or from a unit area of an electrode surface.
- **current efficiency**
  - (1) The ratio of the electrochemical equivalent current density for a specific reaction to the total applied current density . (2) The proportion of current used in a given process to accomplish a desired result; in electroplating, the proportion used in depositing or dissolving metal.
- **curing temperature**
  - The temperature to which a paint film or adhesive is subjected to cure the paint or adhesive.
- **curtain coating**
  - A method of coating that may be employed with low-viscosity resins or solutions, suspensions, or emulsions of resins in which the substrate to be coated is passed through and perpendicular to a freely falling liquid curtain (or waterfall). The flow rate of the falling liquid and the linear speed of the substrate passing through the curtain are coordinated in accordance with the thickness of coating desired.
- **cutting down**
  - Polishing or buffing for the purpose of removing roughness or irregularities.
- **cutting fluid**
  - A fluid used in metal cutting to improve finish, tool life, or dimensional accuracy. On being flowed over the tool and work, the fluid reduces friction, the heat generated, and tool wear, and prevents galling . It conducts the heat away from the point of generation and also serves to wash the chips away.
- **cutoff burr**
  - A projection of material left when the workpiece falls from the stock before the separating cut has been completed.
- **cut wire blasting**
  - Blasting with short, cut lengths of metal wire. See also abrasive blasting .
- **cyaniding**
  - A case-hardening process in which a ferrous material is heated above the lower transformation temperature range in a molten salt containing cyanide to cause simultaneous absorption of carbon and nitrogen at the surface and, by diffusion, create a concentration gradient. Quench hardening completes the process.
- **cylindrical grinding**
  - Grinding the outer cylindrical surface of a rotating part.
- **D**
- **dealloying**
  - The selective corrosion of one or more components of a solid solution alloy. Also called parting or selective leaching . See also decarburization , decobaltification , denickelification , dezincification , and graphitic corrosion .
- **deburring**
  - The removal of burrs, sharp edges, or fins by mechanical, chemical or electrochemical means.
- **decalescence**
  - A phenomenon, associated with the transformation of alpha iron to gamma iron on the heating (superheating) of iron or steel, revealed by the darkening of the metal surface owing to the sudden decrease in temperature caused by the fast absorption of the latent heat of transformation. Contrast with recalescence .
- **decarburization**
  - Loss of carbon from the surface layer of a carbon-containing alloy due to reaction with one or more chemical substances in a medium that contacts the surface. See also dealloying .
- **decobaltification**
  - Corrosion in which cobalt is selectively leached from cobalt-base alloys, such as Stellite, or from cemented carbides. See also dealloying and selective leaching .

- **deep etching**
  - In metallography, macroetching , especially for steels, to determine the overall character of the material, that is, the presence of imperfections, such as seams, forging bursts, shrinkage-void remnants, cracks, and coring.
- **defect**
  - (1) A discontinuity whose size, shape, orientation, or location makes it detrimental to the useful service of the part in which it occurs. (2) A discontinuity or discontinuities which by nature or accumulated effect (for example, total crack length) render a part or product unable to meet minimum applicable acceptance standards or specifications. This term designates rejectability.
- **deflocculating**
  - Thinning the consistency of a slip by adding a suitable electrolyte .
- **degreasing**
  - The removal of grease and oils from a surface. Can be accomplished by immersion in liquid organic solvent, by solvent vapors condensing on the parts being cleaned (vapor degreasing), or by spraying the parts with solvent.
- **delayed fishscaling**
  - See fishscale .
- **delta iron**
  - Solid phase of pure iron that is stable from 1400 to 1539 °C (2550 to 2800 °F) and possesses the body-centered cubic lattice.
- **denickelification**
  - Corrosion in which nickel is selectively leached from nickel-containing alloys. Most commonly observed in copper-nickel alloys after extended service in fresh water. See also dealloying and selective leaching .
- **depletion**
  - Selective removal of one component of an alloy, usually from the surface or preferentially from grain-boundary regions. See also dealloying .
- **deposit corrosion**
  - Corrosion occurring under or around a discontinuous deposit on a metallic surface. Also called poultice corrosion.
- **deposition efficiency**
  - In thermal spraying, the ratio, usually expressed in percent, of the weight of spray deposit to the weight of the material sprayed.
- **deposition rate**
  - In thermal spraying, the weight of material deposited in a unit of time. It is usually expressed as kilograms per hour (kg/h) or pounds per hour (lb/h).
- **descaling**
  - A chemical or mechanical process for removing the thick layer of oxides formed on some metals at elevated temperatures.
- **detergent**
  - A surface active agent that possesses the ability to clean soiled surfaces. See also types of detergents: anionic , cationic , and nonionic .
- **detergent additive**
  - In lubrication technology, a surface-active additive that helps to keep solid particles suspended in an oil.
- **devitrification**
  - In porcelain enamel , a surface defect caused by crystallization of the enamel due to overfiring or contamination, resulting in the loss of the glassy, vitreous appearance of the surface.
- **dezincification**
  - Corrosion in which zinc is selectively leached from zinc-containing alloys leaving a relatively weak layer of copper and copper oxide. Most commonly found in copper-zinc alloys containing less than 85% copper after extended service in water containing dissolved oxygen. See also dealloying and selective leaching .
- **diamond**
  - A highly transparent mineral composed entirely of carbon (allotropic form of carbon) having a cubic structure. The hardest material known, it is used as a gemstone and as an abrasive in cutting and grinding applications. Natural diamonds are produced deep within the earth's crust at extremely high pressures and temperatures. Synthetic diamonds are synthesized by subjecting

carbon, in the form of graphite, to high temperatures and pressures using large special-purpose presses. See also superabrasives .

- **diamondlike film**
  - A hard, noncrystalline carbon film, usually grown by chemical vapor deposition or related techniques, that contains predominantly sp^2 carbon-carbon bonds.
- **diamond wheels**
  - A grinding wheel in which crushed and sized industrial diamonds are held in a resinoid, metal, or vitrified bond.
- **diaphragm**
  - A porous or permeable membrane separating anode and cathode compartments of an electrolytic cell from each other or from an intermediate compartment.
- **dichromate treatment**
  - A chromate conversion coating produced on magnesium alloys in a boiling solution of sodium dichromate.
- **dielectric shield**
  - In a cathodic protection system, an electrically nonconductive material, such as a coating, plastic sheet, or pipe, that is placed between an anode and an adjacent cathode to avoid current wastage and to improve current distribution, usually on the cathode.
- **die lines**
  - Lines or markings on formed, drawn, or extruded metal parts caused by imperfections in the surface of the die.
- **differential coating**
  - A coated product having a specified coating on one surface and a significantly lighter coating on the other surface (such as a hot dip galvanized product or electrolytic tin plate).
- **diffusion**
  - (1) Spreading of a constituent in a gas, liquid, or solid, tending to make the composition of all parts uniform. (2) The spontaneous movement of atoms or molecules to new sites within a material. (3) The movement of a material, such as a gas or liquid, in the body of a plastic. If the gas or liquid is absorbed on one side of a piece of plastic and given off on the other side, the phenomenon is called permeability. Diffusion and permeability are not due to holes or pores in the plastic but are caused by chemical mechanisms.
- **diffusion coating**
  - An alloy coating produced by applying heat to one or more coatings deposited on a base metal .
- **diluent**
  - A usually liquid inert substance added to some other substance or solution so that the volume of the latter substance is increased and its concentration per unit volume is decreased.
- **dimple**
  - In porcelain enamel , a cone-like depression defect in the fired enamel surface, somewhat larger than a pinhole . Also called flux pit.
- **dimpling**
  - (1) The stretching of a relatively small, shallow indentation into sheet metal. (2) In aircraft, the stretching of metal into a conical flange for a countersunk head rivet.
- **dip coating**
  - Applying a plastic coating by dipping the article to be coated into a tank of melted resin or plastisol , then chilling the adhering metal.
- **diphase cleaning**
  - Cleaning by means of solutions that contain a solvent layer and an aqueous layer. Cleaning is effected by both solvent and emulsifying action.
- **dipping**
  - In porcelain enameling, the process of coating a metal shape by immersion in slip, removal, and draining. In dry process enameling, the method of coating by immersing the heated metal shape for a short time in powdered frit .
- **dip plating**
  - Same as immersion coating .
- **direct cleaning**
  - Same as cathodic cleaning .
- **direct fire**

- A method of maturing porcelain enamel so that the products of combustion come in contact with the ware.

- **disbondment**
  - The destruction of adhesion between a coating and the surface coated.
- **disk grinding**
  - Grinding with the flat side of an abrasive disk or segmented wheel. Also called vertical-spindle surface grinding.
- **dispersant additive**
  - In lubrication technology, an additive capable of dispersing cold oil sludge.
- **dispersing agent**
  - A material that increases the stability of a suspension of particles in a liquid medium.
- **dispersion**
  - To break big particles into small particles and suspend them in water so that they can be removed by rinsing. Alkaline silicates and phosphates are beneficial for dispersion.
- **dissolution etching**
  - Development of microstructure by surface removal.
- **divided cell**
  - A cell containing a diaphragm or other means for physically separating the anolyte from the catholyte .
- **double etching**
  - In metallography, use of two etching solutions in sequence. The second etchant emphasizes a particular microstructural feature.
- **drag-in**
  - The water or solution that adheres to the objects introduced into a bath.
- **drag-out**
  - The solution that adheres to the objects removed from a bath.
- **draining**
  - Part of the dipping or flow coating process during which the excess slip flows from suitably positioned ware.
- **drain time**
  - The time required for porcelain enamel slip applied by dipping, slushing, or flow coating to complete movement across the surfaces of a coated part.
- **dredge**
  - The sieve used to apply powdered porcelain enamel frit to the ware during dredging .
- **dredging**
  - In dry process enameling , the application of dry, powdered frit to hot ware by sifting.
- **dressing**
  - The process of eroding the bond matrix in a grinding wheel surface after truing or grinding in order to expose the abrasive grains and thereby improve grinding efficiency.
- **drier**
  - A catalyst added to speed the cure of oil-based paints. Driers are often metal salts of carboxylic acids.
- **drop etching**
  - In metallography, placing of a drop of etchant on the polished surface.
- **droplet erosion**
  - Erosive wear caused by the impingement of liquid droplets on a solid surface. See also erosion .
- **dross**
  - The scum that forms on the surface of molten metal largely because of oxidation but sometimes because of the rising of impurities to the surface.
- **dry etching**
  - In metallography, development of microstructure under the influence of gases.
- **drying cracks**
  - Irregular cracks in dry, unfired porcelain enamel caused by uneven or too rapid drying of the ware. The cracks may or may not heal over during the firing operation.
- **drying oil**
  - A water-insoluble liquid, usually obtained from a plant source, that reacts with oxygen (from the air) to form a cross-linked polymeric film.

- **dry process enameling**
  - A porcelain enameling process in which the metal article is heated to a temperature above the maturing temperature of the coating, usually 870 to 955 °C (1600 to 1750 °F). The coating materials are applied to the hot metal as a dry powder and fired.
- **dry-sand rubber wheel test**
  - In wear testing, a term used to describe a standard abrasive wear testing method in which a stream of dry quartz sand is passed between a rotating rubber wheel and a stationary test coupon that is held against it under specified normal force.
- **dry sliding wear**
  - Sliding wear in which there is no intentional lubricant or moisture introduced into the contact area. See also unlubricated sliding .
- **dry weight**
  - The weight per unit area of bisque .
- **ductile erosion behavior**
  - Erosion behavior having characteristic properties (i.e., considerable plastic deformation) that can be associated with ductile fracture of the exposed solid surface. A characteristic ripple pattern forms on the exposed surface at low values of angle of attack. Contrast with brittle erosion behavior .
- **ductile fracture**
  - Fracture characterized by tearing of metal accompanied by appreciable gross plastic deformation and expenditure of considerable energy. Contrast with brittle fracture .
- **ductility**
  - The ability of a material to deform plastically without fracturing.
- **dummy (or dummy cathode)**
  - A cathode in a plating solution that is not to be made use of after plating. Often used for removal or decomposition of impurities.
- **duplex microstructure**
  - A two-phase structure.
- **dynamic electrode force**
  - The electrode potential measured when current is passing between the electrode and the electrolyte .
- **E**
- **edge strain**
  - Transverse strain lines or Lüders lines ranging from 25 to 300 mm (1 to 12 in.) in from the edges of cold rolled steel sheet or strip. See also Lüders lines .
- **electrical discharge grinding**
  - Grinding by spark discharges between a negative electrode grinding wheel and a positive workpiece separated by a small gap containing a dielectric fluid such as petroleum oil.
- **electrical discharge machining (EDM)**
  - Metal removal by a rapid spark discharge between different polarity electrodes, one on the workpiece and the other the tool, separated by a gap distance of 0.013 to 0.9 mm (0.0005 to 0.035 in.). The gap is filled with dielectrical fluid and metal particles, which are melted, in part vaporized, and expelled from the gap.
- **electrical pitting**
  - The formation of surface cavities by removal of metal as a result of an electrical discharge across an interface.
- **electric arc spraying**
  - A thermal spraying process using as a heat source an electric arc between two consumable electrodes of a coating material and a compressed gas which is used to atomize and propel the material to the substrate.
- **electrochemical cell**
  - An electrochemical system consisting of an anode and a cathode in metallic contact and immersed in an electrolyte . The anode and cathode may be different metals or dissimilar areas on the same metal surface.
- **electrochemical (chemical) etching**
  - General expression for all developments of microstructure through reduction and oxidation (redox reactions).
- **electrochemical corrosion**

- Corrosion that is accompanied by a flow of electrons between cathodic and anodic areas on metallic surfaces.
- **electrochemical discharge machining**
  - Metal removal by a combination of the processes of electrochemical machining and electrical discharge machining . Most of the metal removal occurs via anodic dissolution (i.e., ECM action). Oxide films that form as a result of electrolytic action through an electrolytic fluid are removed by intermittent spark discharges (i.e., EDM action).
- **electrochemical machining (ECM)**
  - Controlled metal removal by anodic dissolution. Direct current passes through a flowing film of conductive solution that separates the workpiece from the electrode/tool. The workpiece is the anode , and the tool is the cathode .
- **electrochemical polishing**
  - An attack-polishing method in which the chemical action of the polishing fluid is enhanced or controlled by the application of an electric current between the specimen and the polishing wheel.
- **electrocorrosive wear**
  - Wear of a solid surface which is accelerated by the presence of a corrosion-inducing electrical potential across the contact interface. This process is usually associated with wear in the presence of a liquid electrolyte in the interface. However, moisture from the air can also facilitate this type of wear when a galvanic wear couple exists and the contacting materials are sufficiently reactive.
- **electrode**
  - A conductor through which current enters or leaves an electrolytic cell , at which there is a change from conduction by electrons to conduction by dry particles of matter, or vice versa.
- **electrodeposition**
  - (1) The deposition of a conductive material from a plating solution by the application of electric current. (2) The deposition of a substance on an electrode by passing electric current through an electrolyte. Electrochemical plating, electroforming , electrorefining , and electrowinning result from electrodeposition.
- **electrode potential**
  - The difference in potential between an electrode and the immediately adjacent electrolyte referred to some standard electrode potential as zero. See also various types of electrode potentials: dynamic , equilibrium , static , and standard .
- **electroforming**
  - The production or reproduction of articles by electrodeposition upon a mandrel or mold that is subsequently separated from the deposit.
- **electrogalvanizing**
  - The electroplating of zinc upon iron or steel.
- **electroless plating**
  - Deposition of a metallic coating by a controlled chemical reduction that is catalyzed by the metal or alloy being deposited.
- **electrolysis**
  - Production of chemical changes by the passage of current through an electrolyte .
- **electrolyte**
  - (1) A conducting medium in which the flow of current is accompanied by movement of matter. Most often an aqueous solution of acids, bases, or salts, but includes many other media, such as fused salts, ionized gases, some solids, and so on. (2) A substance that is capable of forming a conducting liquid medium when dissolved or melted.
- **electrolytic cell**
  - A unit apparatus in which electrochemical reactions are produced by applying electrical energy, or which supplies electrical energy as a result of chemical reactions and which includes two or more electrodes and one or more electrolytes contained in a suitable vessel.
- **electrolytic cleaning**
  - A process of removing soil , scale , or corrosion products from a metal surface by subjecting it as an electrode to an electric current in an electrolytic bath.
- **electrolytic corrosion**
  - Corrosion by means of electrochemical or mechanical action.
- **electrolytic grinding**
  - A combination of grinding and machining wherein a metal-bonded abrasive wheel, usually diamond, is the cathode in physical contact with the anodic workpiece, the contact being made

beneath the surface of a suitable electrolyte. The abrasive particles that produce grinding act as nonconducting spacers permitting simultaneous machining through electrolysis .

- **electrolytic pickling**
  - Pickling in which electric current is used, the work being one of the electrodes.
- **electrolytic polishing**
  - An electrochemical polishing process in which the metal to be polished is made the anode in an electrolytic cell where preferential dissolution at high points in the surface topography produces a specularly reflective surface. Also referred to as electropolishing .
- **electromotive series**
  - A table that lists in order the standard electrode potentials of specified electrochemical reactions.
- **electron-beam curing**
  - A system for curing paint films using the energy of an electron beam. The process lends itself to high-speed curing of paint on flat surfaces. Special paints must be used and personal shielding is required.
- **electron-beam radiation**
  - Radiation generated from high-energy electrons that is used in cross-linking coating systems.
- **electrophoresis**
  - The movement of colloidal particles produced by the application of an electric potential.
- **electroplating**
  - The application of a metallic coating on a surface by means of electrolytic action.
- **electropolishing**
  - A technique commonly used to prepare metallographic specimens, in which a high polish is produced making the specimen the anode in an electrolytic cell , where preferential dissolution at high points smooths the surface. Also referred to as electrolytic polishing .
- **electrorefining**
  - The process of anodically dissolving a metal from a pure anode and depositing it cathodically in a purer form.
- **electrostatic spray**
  - The process by which paint particles are electrically charged and attracted to a substrate bearing an opposite charge.
- **electrowinning**
  - The production of metals by electrolysis with insoluble anodes in solutions derived from ores or other materials.
- **elongated grain**
  - A grain with one principal axis slightly longer than either of the other two.
- **embeddability**
  - The ability of a bearing material to embed harmful foreign particles and reduce their tendency to cause scoring or abrasion.
- **embedded abrasive**
  - Fragments of abrasive particles forced into the surface of a workpiece during grinding , abrasion, or polishing.
- **embossing**
  - (1) Technique used to create depressions of a specific pattern in plastic film and sheeting. Such embossing in the form of surface patterns can be achieved on molded parts by the treatment of the mold surface with photoengraving or another process. (2) Raising a design in relief against a surface.
- **embrittlement**
  - The severe loss of ductility or toughness or both, of a material, usually a metal or alloy. Many forms of embrittlement can lead to brittle fracture . Many forms can occur during thermal treatment or elevated-temperature service (thermally induced embrittlement). In addition, steels and other metals and alloys can be embrittled by environmental conditions (environmentally assisted embrittlement).
- **emery**
  - Naturally occurring abrasive containing 57 to 75% aluminum oxide and a remainder of iron oxide and impurities.
- **emulsifying agent**
  - A substance that increases the stability of an emulsion .
- **emulsion**

- A class of collodial dispersions containing two or more immiscible liquids such as oil in water. Emulsions are usually unstable and will separate into their components unless a stabilizing agent is present.

- **emulsion cleaning**
  - Cleaning by means of solutions containing organic solvents, water, and emulsifying agents .
- **enamel**
  - A broad classification of free-flowing clear or pigmented varnishes, treated oils, or other forms of organic coatings that usually dry to a hard, glossy or semiglossy finish.
- **end-quench hardenability test**
  - Same as Jominy test .
- **entrance burr**
  - Burr formed on the surface at which the cutting tool or its teeth enters the workpiece.
- **environmental cracking**
  - Brittle fracture of a normally ductile material in which the corrosive effect of the environment is a causative factor. Environmental cracking is a general term that includes corrosion fatigue , high-temperature hydrogen attack , hydrogen blistering, hydrogen embrittlement , liquid metal embrittlement, solid metal embrittlement, stress-corrosion cracking , and sulfide stress cracking . The following terms have been used in the past in connection with environmental cracking, but are becoming obsolete: caustic embrittlement, delayed fracture, season cracking, static fatigue, stepwise cracking, sulfide corrosion cracking, and sulfide stress-corrosion cracking. See also embrittlement .
- **equiaxed grain structure**
  - A structure in which the grains have approximately the same dimensions in all directions.
- **equilibrium electrode potential**
  - A static electrode potential when the electrode and the electrolyte are in equilibrium with respect to a specified electrochemical reaction.
- **erosion**
  - (1) Loss of material from a solid surface due to relative motion in contact with a fluid that contains solid particles. Erosion in which the relative motion of particles is nearly parallel to the solid surface is called abrasive erosion. Erosion in which the relative motion of the solid particles is nearly normal to the solid surface is called impingement erosion or impact erosion. (2) Progressive loss of original material from a solid surface due to mechanical interaction between that surface and a fluid, a multicomponent fluid, and impinging liquid, or solid particles. (3) Loss of material from the surface of an electrical contact due to an electrical discharge (arcing). See also cavitation erosion , electrical pitting , and erosion-corrosion .
- **erosion-corrosion**
  - A conjoint action involving corrosion and erosion in the presence of a moving corrosive fluid, leading to the accelerated loss of material.
- **erosion (erosive) wear**
  - See erosion .
- **etch**
  - (1) A roughened surface produced by chemical or electrochemical means. (2) To dissolve unevenly a part of the surface of a metal.
- **etchant**
  - (1) A chemical solution used to etch a metal to reveal structural details. (2) A solution used to remove, by chemical reaction, the unwanted portion of material from a printed circuit board. (3) Hydrofluoric acid or other agent used to attack the surface of glass for marking or decoration.
- **etch cleaning**
  - Removing soil by dissolving away some of the underlying metal.
- **etch cracks**
  - Shallow cracks in hardened steel containing high residual surface stresses, produced by etching in an embrittling acid.
- **etching (pitting)**
  - The localized attack of metal surfaces. Controlled etching of metals improves the adhesion of organic coatings. By contrast, uncontrolled etching of metals by an acid can cause damage by weakening the crystal structure.
- **etch rinsing**

- Pouring etchant over a tilted surface until the desired degree of attack is achieved. Used for etchants with severe gas formation.

- **eutectoid**
  - (1) An isothermal reversible reaction in which a solid solution is converted into two or more intimately mixed solids on cooling, the number of solids formed being the same as the number of components in the system. (2) An alloy having the composition indicated by the eutectoid point on a phase diagram. (3) An alloy structure of intermixed solid constituents formed by a eutectoid reaction.
- **evaporative deposition**
  - The techniques of condensing a thin film of material on a substrate. The entire process takes place in a high vacuum. The source material may be radioactively heated by bombardment with electrons (electron-beam radiation) or may be heated by thermal-conduction techniques.
- **exempt solvents**
  - Solvents that are not subject to air pollution legislation. Many alcohols, esters, some ketones, and mineral spirits are exempt. Aromatic and some ethylenic compounds are not exempt, and their use as solvents is therefore subject to regulation.
- **exit burr**
  - Burr formed on the surface at which the cutting tool or its teeth leaves the workpiece.
- **extreme-pressure lubricant**
  - A lubricant that imparts increased load-carrying capacity to rubbing surfaces under severe operating conditions. Extreme-pressure lubricants usually contain sulfur, halogens, or phosphorus. The term antiscuffing lubricant has been suggested as a replacement for extreme-pressure lubricant.
- **extrusion coating**
  - Using a resin to coat a substrate by extruding a thin film of molten resin and pressing it onto or into the substrate, or both, without the use of an adhesive.
- **extrusion pipe**
  - Same as coring (2).
- **F**
- **false Brinelling**
  - (1) Damage to a solid bearing surface characterized by indentations not caused by plastic deformation resulting from overload, but thought to be due to other causes such as fretting corrosion . (2) Local spots appearing when the protective film on a metal is broken continually by repeated impacts, usually in the presence of corrosive agents. The appearance is generally similar to that produced by Brinelling but corrosion products are usually visible. It may result from fretting corrosion. This term should be avoided when a more precise description is possible. False Brinelling (race fretting) can be distinguished from true Brinelling because in false Brinelling, surface material is removed so that original finishing marks are removed. The borders of a false Brinell mark are sharply defined, whereas a dent caused by a rolling element does not have sharp edges and the finishing marks are visible in the bottom of the dent.
- **fatigue**
  - The phenomenon leading to fracture under repeated or fluctuating stresses having a maximum value less than the ultimate tensile strength of the material.
- **fatigue striation**
  - Parallel lines frequently observed in electron microscope fractographs or fatigue fracture surfaces. The lines are transverse to the direction of local crack propagation; the distance between successive lines represents the advance of the crack front during the one cycle of stress variation.
- **fatigue wear**
  - (1) Removal of particles detached by fatigue arising from cyclic stress variations. (2) Wear of a solid surface caused by fracture arising from material fatigue. See also spalling .
- **feather burr**
  - A very fine or thin burr .
- **feather edge**
  - Same as feather burr except that feather edge can also refer to the ends of a lead-in or lead-out thread, which is a very thin machined ridge. Sometimes called a wire edge or whisker-type burr .
- **feed lines**
  - Linear marks on a machined or ground surface that are spaced at intervals equal to the feed per revolution or per stroke.

- **feed rate**
  - In thermal spraying, the rate at which material passes through the gun in a unit of time. A synonym for spray rate.
- **ferrite**
  - (1) A solid solution of one or more elements in body-centered cubic iron. Unless otherwise designated (for instance, as chromium ferrite), the solute is generally assumed to be carbon. On some equilibrium diagrams, there are two ferrite regions separated by an austenite area. The lower area is alpha ferrite; the upper, delta ferrite. If there is no designation, alpha ferrite is assumed. (2) An essentially carbon-free solid solution in which alpha iron is the solvent, and which is characterized by a body-centered cubic crystal structure. Fully ferritic steels are only obtained when the carbon content is quite low. The most obvious microstructural features in such metals are the ferrite grain boundaries.
- **ferrograph**
  - An instrument used to determine the size distribution of wear particles in lubricating oils of mechanical systems. The technique relies on the debris being capable of being attracted to a magnet.
- **filiform corrosion**
  - Corrosion that occurs under some coatings in the form of randomly distributed threadlike filaments.
- **film strength**
  - The relative resistance of a bisque to mechanical damage.
- **final polishing**
  - A polishing process in which the primary objective is to produce a final surface suitable for microscopic examination.
- **fine grinding**
  - See microgrinding .
- **fineness of enamel**
  - A measurement of the degree to which a frit has been milled in wet or dry form, usually expressed in grams residue retained on a certain type of mesh screen from a 50 cm^3 or a 100 g sample.
- **finish allowance**
  - (1) The amount of excess metal surrounding the intended final configuration of a formed part; sometimes called forging envelope, machining allowance, or cleanup allowance. (2) Amount of stock left on the surface of a casting for machining.
- **finish grinding**
  - The final grinding action on a workpiece, of which the objectives are surface finish and dimensional accuracy.
- **firing**
  - The controlled heat treatment of ceramic ware in a kiln or furnace to develop the desired final properties.
- **firing time**
  - The period during which the ware remains in the firing zone of the furnace to mature a ceramic or porcelain enamel coating.
- **fishscale**
  - A scaly appearance in a porcelain enamel coating in which the evolution of hydrogen from the base metal (iron or steel) causes loss of adhesion between the enamel and the base metal. Individual scales are usually small, but have been observed in sizes up to 25 mm (1 in.) or more in diameter. The scales are somewhat like blisters that have cracked part way around the perimeter but still remain attached to the coating around the rest of the perimeter. Delayed fishscaling occurs after the final porcelain enamel processing.
- **fixed-feed grinding**
  - Grinding in which the wheel is fed into the work, or vice versa, by given increments or at a given rate.
- **flaking**
  - (1) The removal of material from a surface in the form of flakes or scalelike particles. (2) A form of pitting resulting from fatigue. See also spalling .
- **flame cleaning**
  - Cleaning metal surfaces of scale , rust, dirt, and moisture by use of a gas flame.

- **flame hardening**
  - A process for hardening the surfaces of hardenable ferrous alloys in which an intense flame is used to heat the surface layers above the upper transformation temperature, whereupon the workpiece is immediately quenched.
- **flame spraying**
  - Thermal spraying in which a coating material is fed into an oxyfuel gas flame, where it is melted. Compressed gas may or may not be used to atomize the coating material and propel it onto the substrate. The sprayed material is originally in the form of wire or powder. Related terms are powder flame spraying and wire flame spraying . The term flame spraying is usually used when referring to a combustion-spraying process, as differentiated from plasma spraying .
- **flash coat**
  - A thin metallic coating usually less than 0.05 mm (0.002 in.) in thickness.
- **flash (or flash plate)**
  - A very thin electrodeposit, less than 2.5 μm (0.1 mil) thick. See also strike .
- **flash time**
  - The time between paint application and baking. Usually a considerable quantity of solvent is lost during this interval, and this solvent loss prevents popping problems in the oven.
- **flat honing**
  - A low-velocity abrading process, similar to honing , that uses a large, flat honing surface to simultaneously finish a large number of flat parts.
- **flocculate**
  - To aggregate into larger particles, to increase in size to the point where precipitation occurs.
- **flocculating**
  - In porcelain enameling, thickening the consistency of a slip by adding a suitable electrolyte .
- **flocking**
  - A method of coating by spraying finely dispersed textile powders or fibers.
- **floppers**
  - On metals, lines or ridges that are transverse to the direction of rolling and generally confined to the section midway between the edges of a coil as rolled.
- **flotation**
  - The rising of soil particles to the surface of cleaning baths for removal by skimming.
- **flow brightening**
  - (1) Melting of an electrodeposit, followed by solidification, especially of tin plate. See also reflowing . (2) Fusion (melting) of a chemically or mechanically deposited metallic coating on a substrate , particularly as it pertains to soldering.
- **flow coating**
  - The process of coating a metal shape by causing the slip to flow over its surface and then allowing the excess slip to drain.
- **flow lines**
  - (1) Texture showing the direction of metal flow during hot or cold working. Flow lines can often be revealed by etching the surface or a section of a metal part. (2) In mechanical metallurgy, paths followed by minute volumes of metal during deformation.
- **fluidized-bed coating**
  - A method of applying a thermoplastic or thermosetting resin coating to a heated article that is immersed in a dense-phase fluidized bed of powdered resin and thereafter heated in an oven to provide a smooth, pinhole -free coating.
- **fluorescent penetrant inspection**
  - Inspection using a fluorescent liquid that will penetrate any surface opening; after the surface has been wiped clean, the location of any surface flaws may be detected by the fluorescence, under ultraviolet light, of back-seepage of the fluid.
- **flux**
  - A substance that promotes fusion in a given ceramic mixture.
- **flux pit**
  - See dimple .
- **foam blanket**
  - An additive that forms a layer on the surface of electroplating baths that have poor anode /cathode efficiency and prevents any mist or spray from escaping.
- **foil**

- Metal in sheet form less than 0.15 mm (0.006 in.) thick.
- **forged structure**
  - The macrostructure through a suitable section of a forging that reveals direction of working.
- **form grinding**
  - Grinding with a wheel having a contour on its cutting face that is a mating fit to the desired form.
- **Formvar replica**
  - A reproduction of a surface in a plastic Formvar film (used for the preparation of replicas or for specimen-supporting membranes).
- **free cyanide**
  - (1) True: The actual concentration of cyanide radical, or equivalent alkali cyanide, not combined in complex ions with metals in solution. (2) Calculated: The concentration of cyanide, or alkali cyanide, present in solution in excess of that calculated as necessary to form a specified complex ion with a metal or metals present in solution. (3) Analytical: The free cyanide content of a solution, as determined by a specified analytical method.
- **fretting**
  - A type of wear that occurs between tight-fitting surfaces subjected to cyclic relative motion of extremely small amplitude. Usually, fretting is accompanied by corrosion , especially of the very fine wear debris. Also referred to as fretting corrosion and false Brinelling (in rolling-element bearings).
- **fretting corrosion**
  - (1) The accelerated deterioration at the interface between contacting surfaces as the result of corrosion and slight oscillatory movement between the two surfaces. (2) A form of fretting in which chemical reaction predominates. Fretting corrosion is often characterized by the removal of particles and subsequent formation of oxides, which are often abrasive and so increase the wear. Fretting corrosion can involve other chemical reaction products, which may not be abrasive.
- **fretting wear**
  - Wear arising as a result of fretting .
- **friction**
  - The resisting force tangential to the common boundary between two bodies when, under the action of an external force, one body moves or tends to move relative to the surface of the other. The term friction is also used, incorrectly, to denote coefficient of friction . It is vague and imprecise unless accompanied by the appropriate modifiers, such as dry friction or kinetic friction. See also static coefficient of friction .
- **frit**
  - In porcelain enamel , the small friable particles produced by quenching a molten glassy material.
- **fused coating**
  - A metallic coating (usually tin or solder alloy) that has been melted and solidified, forming a metallurgical bond to the base metal .
- **fused spray deposit**
  - A self-fluxing spray deposit which is deposited by conventional thermal spraying and subsequently fused using either a heating torch or a furnace. The coatings are usually made of nickel and cobalt alloys to which hard particles, such as tungsten carbide, may be added for increased wear resistance.
- **fusing**
  - The melting of a metallic coating (usually electrodeposited) by means of a heat-transfer medium, followed by solidification.
- **fusion spray**
  - In thermal spraying, the process in which the coating is completely fused to the base metal , resulting in a metallurgically bonded, essentially void-free coating.
- **G**
- **galling**
  - (1) A condition whereby excessive friction between high spots results in localized welding with subsequent spalling and a further roughening of the rubbing surfaces of one or both of two mating parts. (2) A severe form of scuffing associated with gross damage to the surfaces or failure. Galling has been used in many ways; therefore, each time the term is encountered its meaning must be ascertained from the specific context of the usage. See also scoring and scuffing .

- **galvanic anode**
  - A metal which, because of its relative position in the galvanic series , provides sacrificial protection to metals that are more noble in the series, when coupled in an electrolyte . See also cathodic protection .
- **galvanic cell**
  - (1) An electrolytic cell capable of producing electrical energy by electrochemical action.
- **galvanic corrosion**
  - Corrosion associated with the current of a galvanic cell consisting of two dissimilar conductors in an electrolyte or two similar conductors in dissimilar electrolytes. Where the two dissimilar metals are in contact, the resulting reaction is referred to as couple action.
- **galvanic series**
  - A list of metals and alloys arranged according to their relative potentials in a given environment. Compare with electromotive series .
- **galvanizing**
  - Application of a coating of zinc to a metal surface using any of various processes.
- **galvanneal**
  - To produce a zinc-iron alloy coating on iron or steel by keeping the coating molten after hot-dip galvanizing until the zinc alloys completely with the base metal .
- **garnet**
  - A generic name for a related group of mineral silicates that have the general chemical formula $A_3B_2(SiO_4)_3$, where *A* can be calcium, magnesium, manganese, or ferrous iron, and *B* can be aluminum, ferric iron, chromium, or titanium. Garnet is used for coating abrasive paper or cloth, for bearing pivots in watches, for electronics, and the finer specimens for gemstones. The hardness of garnet varies from Mohs 6 to 8 (1360 Knoop), the latter being used for abrasive applications.
- **gas atomization**
  - An atomization process whereby molten metal is broken up into particles by a rapidly moving inert gas stream. The resulting particles are nearly spherical with attached satellites.
- **gaseous corrosion**
  - Corrosion with gas as the only corrosive agent and without any aqueous phase on the surface of the metal. Also called dry corrosion. See also hot corrosion and sulfidation .
- **gas holes**
  - Holes in castings or welds that are formed by gas escaping from molten metal as it solidifies. Gas holes may occur individually, in clusters, or throughout the solidified metal.
- **gas lubrication**
  - A system of lubrication in which the shape and relative motion of the sliding surfaces cause the formation of a gas film having sufficient pressure to separate the surfaces.
- **gas porosity**
  - Fine holes or pores within a metal that are caused by entrapped gas or by the evolution of dissolved gas during solidification.
- **gassing**
  - The occurrence of surface defects such as poor gloss or blisters on fired enamel ware caused by bubbles from contamination or poor firing conditions.
- **gear (form) grinding**
  - Removal of material to obtain correct gear tooth form by grinding . This is one of the more exact methods of finishing gears.
- **gelatin replica**
  - A reproduction of a surface prepared in a film composed of gelatin. See also replica .
- **general corrosion**
  - (1) A form of deterioration that is distributed more or less uniformly over a surface. (2) Corrosion dominated by uniform thinning that proceeds without appreciable localized attack. See also uniform corrosion .
- **ghost lines**
  - Lines running parallel to the rolling direction that appear in a sheet metal panel when it is stretched. These lines may not be evident unless the panel has been sanded or painted. Not to be confused with leveler lines .
- **glass**
  - A term sometimes used for porcelain enamel or frit .

- **glass electrode**
    - A half cell in which the potential measurements are made through a glass membrane.
- **glaze**
    - (1) A ceramic coating matured to the glassy state on a formed ceramic article, or the material or mixture from which the coating is made. (2) In tribology, a ceramic or other hard, smooth surface film produced by sliding.
- **glazing**
    - Dulling the abrasive grains in the cutting face of a wheel during grinding .
- **gloss**
    - The shine or luster of a porcelain enamel or a painted surface.
- **gold filled**
    - Covered on one or more surfaces with a layer of gold alloy to form a clad or composite material. Gold-filled dental restorations are an example of such materials.
- **gouging abrasion**
    - A form of high-stress abrasion in which easily observable grooves or gouges are created on the surface. See also abrasion , and low-stress abrasion .
- **graded abrasive**
    - An abrasive powder in which the sizes of the individual particles are confined to certain specified limits. See also grit size .
- **graded coating**
    - A thermal spray coating consisting of several successive layers of different materials; for example, starting with 100% metal, followed by one or more layers of metal-ceramic mixtures, and finishing with 100% ceramic.
- **grain**
    - An individual crystal in a polycrystalline material; it may or may not contain twinned regions and subgrains.
- **grain boundary**
    - A narrow zone in a metal or ceramic corresponding to the transition from one crystallographic orientation to another, thus separating one grain from another; the atoms in each grain are arranged in an orderly pattern.
- **grain-boundary etching**
    - In metallography, the development of intersections of grain faces with the polished surface. Because of severe, localized crystal deformation, grain boundaries have higher dissolution potential than grains themselves. Accumulation of impurities in grain boundaries increases this effect.
- **grain coarsening**
    - A heat treatment that produces excessively large austenitic grains in metals.
- **grain-contrast etching**
    - In metallography, the development of grain surfaces lying in the polished surface of the microsection. These become visible through differences in reflectivity caused by reaction products on the surface or by differences in roughness.
- **grain flow**
    - Fiber-like lines on polished and etched sections of forgings caused by orientation of the constituents of the metal in the direction of working during forging. Grain flow produced by proper die design can improve required mechanical properties of forgings. See also flow lines and forged structure .
- **grain growth**
    - (1) An increase in the average size of the grains in polycrystalline material, usually as a result of heating at elevated temperature. (2) In polycrystalline materials, a phenomenon occurring fairly close below the melting point in which the larger grains grow still larger while the smallest ones gradually diminish and disappear. See also recrystallization .
- **graining**
    - The process of vigorously stirring or agitating a partially solidified material to develop large grains having a thin oxide coating.
- **grain refinement**
    - The manipulation of the solidification process to cause more (and therefore smaller) grains to be formed and/or to cause the grains to form in specific shapes. The term refinement is usually used to denote a chemical addition to the metal but can refer to control of the cooling rate.

- **grain size**
  - (1) For metals, a measure of the areas or volumes of grains in a polycrystalline material, usually expressed as an average when the individual sizes are fairly uniform. In metals containing two or more phases, grain size refers to that of the matrix unless otherwise specified. Grain size is reported in terms of number of grains per unit area or volume, in terms of average diameter, or as a grain-size number derived from area measurements. (2) For grinding wheels, see preferred term grit size .
- **graphitic corrosion**
  - Corrosion of gray iron in which the iron matrix is selectively leached away, leaving a porous mass of graphite behind; it occurs in relatively mild aqueous solutions and on buried pipe and fittings.
- **graphitization**
  - The formation of graphite in iron or steel. Where graphite is formed during solidification, the phenomenon is termed primary graphitization; where formed later by heat treatment, secondary graphitization.
- **greaseless compounds**
  - A variety of buffing compounds in which the abrasive is blended with water and gelatin glue rather that tallow, wax, or oil.
- **green rot**
  - A form of high-temperature attack on stainless steels, nickel-chromium alloys and nickel-chromium-iron alloys subjected to simultaneous oxidation and carburization. Basically, attack occurs first by precipitation of chromium as chromium carbide, then by oxidation of the carbide particles.
- **grindability**
  - A value that represents the efficiency of the grinding process. Grindability = (G-ratio)/(specific energy), where G-ratio = (volume of material removed)/(volume of the grinding wheel used) and specific energy = (grinding power)/(material removal rate).
- **grinding**
  - Removing material from a workpiece with a grinding wheel or abrasive belt. See also various grinding techniques: surface , creep-feed , cylindrical , internal , centerless , gear (form) , and thread .
- **grinding stress**
  - Residual stress , generated by grinding, in the surface layer of work. It may be tensile or compressive, or both.
- **grit blasting**
  - Abrasive blasting with small irregular pieces of steel, malleable cast iron, or hard nonmetallic materials.
- **grit size**
  - Nominal size of abrasive particles in a grinding wheel, corresponding to the number of openings per linear inch in a screen through which the particles can pass.
- **groove**
  - In thermal spraying, a method of surface roughening in which grooves are made and the original surface roughened and spread. Also called rotary roughening.
- **ground coat**
  - (1) A porcelain enamel applied directly to the base metal to function as an intermediate layer between the metal and the cover coat. (2) On sheet steel, a porcelain enamel coating containing adherence-promoting agents that may be used either as an intermediate layer between the metal and the cover coat or as a single coat over the base metal.
- **H**
- **hairline craze**
  - Multiple fine surface separation cracks in composites that exceed 6 mm (in.) in length and do not penetrate in depth the equivalent of a full ply of reinforcement. See also crazing .
- **half cell**
  - An electrode immersed in a suitable electrolyte . It may be designed to yield a known constant potential, in which case unknown potentials may be measured against it; for example, the calomel half cell .
- **hanging burr**

- Loose or flexible portions of a burr that are not firmly attached to the workpiece (i.e., hanging from the workpiece). Sometimes called a flag.
- **hard chromium**
  - Chromium electrodeposited for engineering purposes (such as to increase the wear resistance of sliding metal surfaces) rather than as a decorative coating. It is usually applied directly to base metal and is customarily thicker (>1.2 μm, or 0.05 mils) than a decorative deposit, but not necessarily harder.
- **hard coating**
  - In anodizing aluminum, an anodic oxide coating on aluminum with a higher apparent density and thickness and a greater resistance to wear than conventional coatings.
- **hardenability**
  - The relative ability of a ferrous alloy to form martensite when quenched from a temperature above the upper critical temperature. Hardenability is commonly measured as the distance below a quenched surface at which the metal exhibits a specific hardness (50 HRC, for example) or a specific percentage of martensite in the microstructure.
- **hardening**
  - Increasing hardness of metals by suitable treatment, usually involving heating and cooling. When applicable, the following more specific terms should be used: age hardening , case hardening , flame hardening , induction hardening , precipitation hardening and quench hardening .
- **hardfacing**
  - The application of a hard, wear-resistant material to the surface of a component by welding, spraying, or allied welding processes to reduce wear or loss of material by abrasion, impact, erosion, galling , and cavitation . See also surfacing .
- **hardfacing alloys**
  - Wear-resistant materials available as bare welding rod, flux-coated rod, long-length solid wires, long-length tubular wires, or powders that are deposited by hardfacing . Hardfacing materials include a wide variety of alloys, ceramics, and combinations of these materials. Conventional hardfacing alloys are normally classified as steels or low-alloy ferrous materials, chromium white irons, high-alloy ferrous materials, carbides, nickel-base alloys, or cobalt-base alloys.
- **hardness**
  - A measure of the resistance of a material to surface indentation or abrasion; may be thought of as a function of the stress required to produce some specified type of surface deformation. There is no absolute scale for hardness; therefore, to express hardness quantitatively, each type of test has its own scale of arbitrarily defined hardness. Indentation hardness can be measured by Brinell, Rockwell, Vickers , Knoop, and Scleroscope hardness tests.
- **hardness profile**
  - Hardness as a function of distance from a fixed reference point (usually from the surface).
- **Haring cell**
  - A rectangular box of nonconducting material, with principal and auxiliary electrodes so arranged as to permit estimation of throwing power or electrode polarizations and potentials between them.
- **heat-affected zone**
  - That portion of the base metal that was not melted during brazing, cutting, or welding, but whose microstructure and mechanical properties were altered by the heat.
- **heat checking**
  - A process in which fine cracks are formed on the surface of a body in sliding contact due to the buildup of excessive frictional heat.
- **healed-over scratch**
  - A scratch in a metallic object that occurred in an earlier mill operation and was partially masked in subsequent rolling. It may open up during forming.
- **heat mark**
  - Extremely shallow depression or groove in the surface of a plastic visible because of a sharply defined rim or a roughened surface.
- **hiding power**
  - The ability of a paint to mask the color or pattern of a surface. Usually expressed as ft^2/gal or m^2/L.
- **highlighting**

- Buffing or polishing selected areas of a complex shape to increase the luster or change the color of those areas.

- **highly deformed layer**
  - In tribology, a layer of severely plastically deformed material that results from the shear stresses imposed on that region during sliding contact. See also Beilby layer and white etching layer .
- **high-solids paint**
  - Paint containing 35 to 80% solids. These products have become popular because of the reduction in solvent emissions associated with their use.
- **high-stress abrasion**
  - A form of abrasion in which relatively large cutting forces are imposed on the particles or protuberances causing the abrasion, and that produces significant cutting and deformation of the wearing surface. In metals, high-stress abrasion can result in significant surface strain hardening. This form of abrasion is common in mining and agricultural equipment, and in highly loaded bearings where hard particles are trapped between mating surfaces. See also low-stress abrasion .
- **high-temperature hydrogen attack**
  - A loss of strength and ductility of steel by high-temperature reaction of absorbed hydrogen with carbides in the steel resulting in decarburization and internal fissuring.
- **hinge area**
  - The juncture of a hanging burr with the more rigidly adhered portion of a burr .
- **Hohman A-6 wear machine**
  - A widely used type of wear and friction testing machine in which a rotating ring specimen is squeezed between two diametrically opposed rub blocks. This design is said to eliminate shaft flexure such as that found in other machines whose load application from the rub block to the ring is from one side only. Block geometry can be changed from flat to conforming or V-block. This type of machine is designed for use with either lubricated or unlubricated specimens.
- **holidays**
  - Discontinuities in a coating (such as porosity, cracks, gaps, and similar flaws) that allow areas of base metal to be exposed to any corrosive environment that contacts the coated surface.
- **homogeneous carburizing**
  - Use of a carburizing process to convert a low-carbon ferrous alloy to one of uniform and higher carbon content throughout the section.
- **honing**
  - A low-speed finishing process used chiefly to produce uniform high dimensional accuracy and fine finish, most often on inside cylindrical surfaces. In honing, very thin layers of stock are removed by simultaneously rotating and reciprocating a bonded abrasive stone or stick that is pressed against the surface being honed with lighter force than is typical of grinding .
- **hot corrosion**
  - An accelerated corrosion of metal surfaces that results from the combined effect of oxidation and reactions with sulfur compounds and other contaminants, such as chlorides, to form a molten salt on a metal surface that fluxes, destroys, or disrupts the normal protective oxide. See also gaseous corrosion .
- **hot dip**
  - Covering a surface by dipping the surface to be coated into a molten bath of the coating material. See also hot dip coating .
- **hot dip coating**
  - A metallic coating obtained by dipping the base metal into a molten metal.
- **hot etching**
  - In metallography, development and stabilization of the microstructure at elevated temperature in etchants or gases.
- **hot shortness**
  - A tendency for some alloys to separate along grain boundaries when stressed or deformed at temperatures near the melting point. Hot shortness is caused by a low-melting constituent, often present only in minute amounts, that is segregated at grain boundaries.
- **Hull cell**
  - A trapezoidal box of nonconducting material with electrodes arranged to permit observation of cathodic or anodic effects over a wide range of current densities.
- **hydrogen damage**

- A general term for the embrittlement , cracking, blistering , and hydride formation that can occur when hydrogen is present in some metals.
- **hydrogen embrittlement**
  - A process resulting in a decrease of the toughness or ductility of a metal due to the presence of atomic hydrogen. Hydrogen embrittlement has been recognized classically as being of two types. The first, known as internal hydrogen embrittlement, occurs when the hydrogen enters molten metal which becomes supersaturated with hydrogen immediately after solidification. The second type, environmental hydrogen embrittlement, results from hydrogen being absorbed by solid metals. This can occur during elevated-temperature thermal treatments and in service during electroplating, contact with maintenance chemicals, corrosion reactions, cathodic protection , and operating in high-pressure hydrogen. In the absence of residual stress or external loading, environmental hydrogen embrittlement is manifested in various forms, such as blistering , internal cracking, hydride formation, and reduced ductility. With a tensile stress or stress-intensity factor exceeding a specific threshold, the atomic hydrogen interacts with the metal to induce subcritical crack growth leading to fracture. In the absence of a corrosion reaction (polarized cathodically), the usual term used is hydrogen-assisted cracking (HAC) or hydrogen stress cracking (HSC). In the presence of active corrosion, usually as pits or crevices (polarized anodically), the cracking is generally called stress-corrosion cracking (SCC), but should more properly be called hydrogen-assisted stress-corrosion cracking (HSCC). Thus, HSC and electrochemically anodic SCC can operate separately or in combination. In some metals, such as high-strength steels, the mechanism is believed to be all, or nearly all, HSC. The participating mechanism of HSC is not always recognized and may be evaluated under the generic heading of SCC.
- **hydrophilic**
  - (1) Tending to absorb water. (2) Tending to concentrate in the aqueous phase.
- **hydrophobic**
  - (1) Tending to repel water. (2) Lacking an affinity for water.
- **I**
- **identification etching**
  - Etching to expose particular microconstituents; all others remain unaffected.
- **immersion cleaning**
  - Cleaning in which the work is immersed in a liquid solution.
- **immersion coating**
  - A coating produced in a solution by chemical or electrochemical action without the use of external current.
- **immersion etching**
  - Method in which a microsection is dipped face up into etching solution and is moved around during etching. This is the most common etching method.
- **immersion plate**
  - A metallic deposit produced by a displacement reaction in which one metal displaces another from solution, for example: $Fe + Cu^{2+} \rightarrow Cu + Fe^{2+}$.
- **immersion plating**
  - Depositing a metallic coating on a metal immersed in a liquid solution, without the aid of an external electric current. Also called dip plating.
- **impact wear**
  - Wear of a solid surface resulting from repeated collisions between that surface and another solid body. The term erosion (erosive) wear is preferred in the case of multiple impacts and when the impacting body or bodies are very small relative to the surface being impacted.
- **impingement**
  - A process resulting in a continuing succession of impacts between liquid or solid particles and a solid surface. In preferred usage, impingement also connotes that the impacting particles are smaller than the solid surface, and that the impacts are distributed over the surface or a portion of the surface. If all impacts are superimposed on the same point or zone, then the term repeated impact is preferred.
- **impingement attack**
  - Corrosion associated with turbulent flow of liquid. May be accelerated by entrained gas bubbles. See also erosion-corrosion .
- **impregnation**

- (1) Treatment of porous castings with a sealing medium to stop pressure leaks. (2) The process of filling the pores of a sintered compact, usually with a liquid such as a lubricant. (3) The process of mixing particles of a nonmetallic substance in a cemented carbide matrix, as in diamond-impregnated tools.
- **impression replica**
  - A surface replica made by impression. See also replica .
- **inclusions**
  - (1) A physical and mechanical discontinuity occurring within a material or part, usually consisting of solid, encapsulated foreign material. Inclusions are often capable of transmitting some structural stresses and energy fields, but to a noticeably different degree than from the parent material. (2) Particles of foreign material in a metallic matrix. The particles are usually compounds, such as oxides, sulfides, or silicates, but may be of any substance that is foreign to (and essentially insoluble in) the matrix. See also stringer .
- **induction hardening**
  - A surface-hardening process in which only the surface layer of a suitable ferrous workpiece is heated by electromagnetic induction to above the upper critical temperature and immediately quenched.
- **inhibitor**
  - A substance used to reduce the rate of a chemical or electrochemical reaction, commonly corrosion or pickling .
- **inorganic**
  - Being or composed of matter other than hydrocarbons and their derivatives, or matter that is not of plant or animal origin.
- **interdendritic corrosion**
  - Corrosive attack that progresses preferentially along interdendritic paths. This type of attack results from local differences in composition, such as coring commonly encountered in alloy castings.
- **interface**
  - The boundary between any two phases. Among the three phases (gas, liquid, and solid), there are five types of interfaces: gas-liquid, gas-solid, liquid-liquid, liquid-solid, and solid-solid.
- **intergranular corrosion**
  - Corrosion occurring preferentially at grain boundaries , usually with slight or negligible attack on the adjacent grains. See also interdendritic corrosion .
- **intergranular cracking**
  - Cracking or fracturing that occurs between the grains or crystals in a polycrystalline aggregate. Also called intercrystalline cracking. Contrast with transgranular cracking .
- **intergranular fracture**
  - Brittle fracture of a polycrystalline material in which the fracture is between the grains, or crystals, that form the material. Also called intercrystalline fracture. Contrast with transgranular fracture .
- **intergranular stress-corrosion cracking (IGSCC)**
  - Stress-corrosion cracking in which the cracking occurs along grain boundaries .
- **internal grinding**
  - Grinding an inside of a rotating workpiece by use of a wheel spindle that rotates and reciprocates through the length or depth of the hole being ground.
- **internal oxidation**
  - The formation of isolated particles of corrosion products beneath the metal surface. This occurs as the result of preferential oxidation of certain alloy constituents by inward diffusion of oxygen, nitrogen, sulfur, and so forth. Also called subscale formation.
- **internal shrinkage**
  - A void or network of voids within a casting caused by inadequate feeding of that section during solidification.
- **interrupted-current plating**
  - Plating in which the flow of current is discontinued for periodic short intervals to decrease anode polarization and elevate the critical current density . It is most commonly used in cyanide copper plating.
- **intumescence**

- The swelling or bubbling of a coating usually because of heating (term currently used in space and fire protection applications).
- **ion**
  - An electrified portion of matter of atomic or molecular dimensions.
- **ion beam assisted deposition**
  - An ion implantation technique in which ion beams are combined with physical vapor deposition .
- **ion beam mixing**
  - An ion implantation technique in which deposited layers (electroplating, sputtering) tens or hundreds of nanometers thick are mixed and bonded to the substrate by an argon or xenon ion beam.
- **ion beam sputtering**
  - An ion implantation technique in which an ion beam of argon or xenon directed at a target sputters material from the target to a substrate ; the sputtered material arrives at the substrate with enough energy to promote good adhesion of the coating to substrate.
- **ion carburizing**
  - A method of surface hardening in which carbon ions are diffused into a workpiece in a vacuum through the use of high-voltage electrical energy. Synonymous with plasma carburizing or glow-discharge carburizing.
- **ion etching**
  - Surface removal by bombarding with accelerated ions in vacuum (1 to 10 kV).
- **ion implantation**
  - The process of modifying the physical or chemical properties of the near surface of a solid (target) by embedding appropriate atoms into it from a beam of ionized particles. The properties to be modified may be electrical, optical, or mechanical, and they may relate to the semiconducting behavior of the material or its corrosion behavior. The solid may be crystalline, polycrystalline, or amorphous and need not be homogeneous. Related techniques are also used in conjunction with ion implantation to increase the ratio of material introduced into the substrate per unit area, to provide appropriate mixtures of materials, or to overcome other difficulties involved in surface modification by ion implantation alone. See also specific techniques: ion beam sputtering , ion beam mixing , plasma ion deposition , and ion beam assisted deposition .
- **ion nitriding**
  - A method of surface hardening in which nitrogen ions are diffused into a workpiece in a vacuum through the use of high-voltage electrical energy. Synonymous with plasma nitriding or glow-discharge nitriding.
- **ion plating**
  - A generic term applied to atomistic film deposition processes in which the substrate surface and/or the depositing film is subjected to a flux of high-energy particles (usually gas ions) sufficient to cause changes in the interfacial region or film properties. Such changes may be in film adhesion to the substrate, film morphology, film density, film stress, or surface coverage by the depositing film material.
- **ion-scattering spectrometry**
  - A technique to elucidate composition and structure of the outermost atomic layers of a solid material, in which principally mono-energetic, singly charged, low-energy (less than 10 keV) probe ions are scattered from the surface and are subsequently detected and recorded as a function of the energy.
- **isocorrosion diagram**
  - A graph or chart that shows constant corrosion behavior with changing solution (environment) composition and temperature.
- **Izod test**
  - A type of impact test in which a V-notched specimen, mounted vertically, is subjected to a sudden blow delivered by the weight at the end of a pendulum arm. The energy required to break off the free end is a measure of the impact strength or toughness of the material. Contrast with Charpy test .
- **J**
- **jet vapor deposition**
  - A vacuum deposition method in which evaporated atoms or molecules are "seeded" into a supersonic jet flow of inert gas into a rapidly pumped vacuum chamber. The jet flow transports the atoms and molecules to the substrate surface, where they are deposited.

- **Jominy test**
  - A laboratory procedure for determining the hardenability of a steel or other ferrous alloy. Hardenability is determined by heating a standard specimen above the upper critical temperature, placing the hot specimen in a fixture so that a stream of cold water impinges on one end, and, after cooling to room temperature is completed, measuring the hardness near the surface of the specimen at regularly spaced intervals along its length. The data are normally plotted as hardness versus distance from the quenched end. Also called the end-quench hardenability test.
- K
- **karat**
  - A 24th part by weight; thus 18-karat gold is 18/24 pure.
- **knife coating**
  - A method of coating a substrate (usually paper or fabric) in which the substrate, in the form of a continuous moving web, is coated with a material, the thickness of which is controlled by an adjustable knife or bar set at a suitable angle to the substrate.
- **knife-line attack**
  - Intergranular corrosion of an alloy, usually stabilized stainless steel, along a line adjoining or in contact with a weld after heating into the sensitization temperature range.
- **knurling**
  - Impressing a design into a metallic surface, usually by means of small, hard rollers that carry the corresponding design on their surfaces.
- L
- **lacquer**
  - (1) A coating formulation based on thermoplastic film-forming material dissolved in organic solvent. The coating dries primarily by evaporation of the solvent. Typical lacquers include those based on lac, nitrocellulose, other cellulose derivatives, vinyl resins, acrylic resins, and so forth. (2) In lubrication, a deposit resulting from the oxidation and/or polymerization of fuels and lubricants when exposed to high temperatures. Softer deposits are described as varnishes or gums.
- **lamination**
  - In porcelain enamel , a defect resulting from bloating of a sheet steel piece during firing due to a separation in the steel structure.
- **lap**
  - A surface imperfection, with the appearance of a seam , caused by hot metal, fins, or sharp corners being folded over and then being rolled or forged into the surface but without being welded.
- **lapping**
  - Rubbing two surfaces together, with or without abrasives, for the purpose of obtaining extreme dimensional accuracy or superior surface finish .
- **laser surface processing**
  - The use of lasers with continuous outputs of 0.5 to 10 kW to modify the metallurgical structure of a surface and to tailor the surface properties without adversely affecting the bulk properties. The surface modification can take the following three forms. The first is transformation hardening in which a surface is heated so that thermal diffusion and solid-state transformations can take place. The second is surface melting, which results in a refinement of the structure due to the rapid quenching from the melt. The third is surface (laser) alloying, in which alloying elements are added to the melt pool to change the composition of the surface. The novel structures produced by laser surface melting and alloying can exhibit improved electrochemical and tribological behavior.
- **latent solvent**
  - A liquid that cannot itself dissolve a binder but increases the tolerance of the paint for a diluent.
- **lath martensite**
  - Martensite formed partly in steels containing less than approximately 1.0% C and solely in steels containing less than approximately 0.5% C as parallel arrays of packets of lath-shape units 0.1 to 0.3 μm (4 to 12 μin.) thick.
- **lay**
  - Direction of predominant surface pattern remaining after cutting, grinding , lapping , or other processing.
- **ledeburite**

- The eutectic of the iron-carbon system, the constituents of which are austenite and cementite . The austenite decomposes into ferrite and cementite on cooling below Ar_1, the temperature at which transformation of austenite to ferrite or ferrite plus cementite is completed during cooling.

- **leveler lines**
  - Lines on sheet or strip running transverse to the direction of roller leveling. These lines may be seen upon stoning or light sanding after leveling (but before drawing) and can usually be removed by moderate stretching.
- **leveling action**
  - Ability of a plating solution to produce a plated surface smoother than that of the substrate .
- **linishing**
  - A method of finishing by grinding on a continuous abrasive belt.
- **liquid carburizing**
  - Surface hardening of steel by immersion into a molten bath consisting of cyanides and other salts.
- **liquid honing**
  - Producing a finely polished finish by directing an air-ejected chemical emulsion containing fine abrasives against the surface to be finished.
- **liquid nitriding**
  - A method of surface hardening in which ferrous metal parts are exposed to molten nitrogen-bearing fused-salt baths containing cyanates, cyanides, or both at subcritical temperatures. A typical commercial bath is a mixture of sodium and potassium salts. The anions are 30 to 40% cyanate, 1 to 5% cyanide, and the balance carbonate. The operating temperature for these salt baths is 510 to 595 °C (950 to 1100 °F).
- **liquid nitrocarburizing**
  - A nitrocarburizing process utilizing molten liquid salt baths below the lower critical temperature. Liquid nitrocarburizing processes are used to improve wear resistance and fatigue properties of steels and cast irons. See liquid nitriding .
- **liquid penetrant inspection**
  - A type of nondestructive inspection that locates discontinuities that are open to the surface of a metal by first allowing a penetrating dye or fluorescent liquid to infiltrate the discontinuity, removing the excess penetrant, and then applying a developing agent that causes the penetrant to seep back out of the discontinuity and register as an indication. Liquid penetrant inspection is suitable for both ferrous and nonferrous materials, but is limited to the detection of open surface discontinuities in nonporous solids.
- **localized corrosion**
  - Corrosion at discrete sites, for example, crevice corrosion , pitting , and stress-corrosion cracking .
- **long-term etching**
  - Etching times of a few minutes to hours.
- **lower critical temperature**
  - The temperature below which ferrite is the stable phase. Also called the A_1 temperature.
- **low-stress abrasion**
  - A form of abrasion in which relatively low contact pressures on the abrading particles or protuberances cause only fine scratches and microscopic cutting chips to be produced. See also high-stress abrasion .
- **lubricant**
  - Any substance interposed between two surfaces in relative motion for the purpose of reducing the friction or wear between them. This definition implies intentional addition of a substance to an interface; however, species such as oxides and tarnishes on certain metals can also act as lubricants even though they were not added to the system intentionally.
- **lubricious (lubricous)**
  - Relating to a substance or surface condition that tends to produce relatively low friction.
- **Lüders lines**
  - Elongated surface markings or depressions in sheet metal, often visible with the unaided eye, caused by discontinuous (inhomogeneous) yielding. Also known as Lüders bands, Hartmann lines, Piobert lines, or stretcher strains .
- **lumps**
  - See beads .
- **luster finish**

- A bright as-rolled finish, produced on ground metal rolls; it is suitable for decorative painting or plating, but usually must undergo additional surface preparation after forming.

- **M**
- **macroetching**
  - Etching a metal surface to accentuate gross structural details, such as grain flow , segregation, porosity, or cracks, for observation by the unaided eye or at magnifications to 25×.
- **machining**
  - Removing material from a part, usually using a cutting tool, and usually using a power-driven machine.
- **mandrel**
  - A form used as a cathode in electroforming ; a mold or matrix.
- **man-made (synthetic) diamond**
  - A manufactured diamond, darker, blockier, and considered to be more friable than most natural diamonds.
- **mask**
  - A device for protecting a surface from the effects of blasting and/or coating. Masks are generally either reusable or disposable.
- **mass finishing**
  - A group of finishing methods that involve loading of components to be finished into a container together with some abrasive media, water, and compound, and then applying some action to the container in order to cause the media and parts to rub against one another, thereby improving the surface of the components. Mass finishing processes include barrel finishing , tumbling , and vibratory finishing .
- **material removal rate**
  - In grinding , the volume of material removed in a unit of time. Material removal rate = work speed × depth of cut × width of cut.
- **matte finish**
  - (1) A metal finish produced by using a sand blast or acid dip, creating a frosted and nonreflective surface that is free of parallel lines. (2) In porcelain enamel , a slightly roughened surface lacking in luster.
- **mechanical activation**
  - The acceleration or initiation of a chemical reaction by mechanical exposure of a nascent solid surface. Metal cutting (machining) is an effective method of exposing large areas of fresh surface.
- **mechanical bond**
  - The adherence of a thermal sprayed deposit to a roughened surface by the mechanism of particle interlocking.
- **mechanical cleaning**
  - Process for removing dirt, scale, or other deposits from surfaces through the use of mechanical means such as abrasive blasting .
- **mechanical plating**
  - A process whereby hard, small spherical objects (such as glass shot) are tumbled against a metallic surface in the presence of finely divided metal powder (such as zinc dust) and appropriate chemicals for the purpose of covering such surfaces with metal.
- **mechanical polishing**
  - A process that yields a specularly reflecting surface entirely by the action of machining tools, which are usually the points of abrasive particles suspended in a liquid among the fibers of a polishing cloth.
- **mechanical wear**
  - Removal of material due to mechanical processes under conditions of sliding, rolling, or repeated impact. The term mechanical wear includes adhesive wear , abrasive wear , and fatigue wear . Compare with corrosive wear and thermal wear .
- **metallic bond**
  - The principal bond between metal atoms, which arises from the increased spatial extension of valence-electron wave functions when an aggregate of metal atoms is brought close together. An example is the bond formed between base metals and filler metals in all welding processes.
- **metallic wear**

- Typically, wear due to rubbing or sliding contact between metallic materials that exhibits the characteristics of severe wear, for example, significant plastic deformation , material transfer, and indications that cold welding of asperities possibly has taken place as part of the wear process. See also adhesive wear and severe wear .
- **metallizing**
  - (1) Application of an electrically conductive metallic layer to the surface of nonconductors. (2) The application of metallic coatings by nonelectrolytic procedures such as spraying of molten metal and deposition from the vapor phase.
- **metallurgical bond**
  - Adherence of a coating to the base material characterized by diffusion, alloying, or intermolecular or intergranular attraction at the interface between the coating and the base material.
- **metallurgical burn**
  - Modification of the microstructure near the contact surface due to frictional temperature rise.
- **metal penetration**
  - A surface condition in castings in which metal or metal oxides have filled voids between sand grains without displacing them.
- **metal shadowing**
  - The enhancement of contrast in a microscope by vacuum deposition of a dense metal onto the specimen at an angle generally not perpendicular to the surface of the specimen. See also shadowing .
- **metal spraying**
  - Coating metal objects by spraying molten metal against their surfaces. See also thermal spraying and flame spraying .
- **microfinishing grinding**
  - See microgrinding .
- **microgrinding**
  - A precision grinding process that uses extremely fine abrasive (50 μm and finer). Also known as fine grinding and microfinishing grinding.
- **microstructure**
  - The structure of an object, organism, or material as revealed by a microscope at magnifications greater than 25×.
- **microthrowing power**
  - The ability of a plating solution or a specified set of plating conditions to deposit metal in pores or scratches.
- **mil**
  - One thousandth of an inch 0.001 = 25.4 μm.
- **mild wear**
  - A form of wear characterized by the removal of material in very small fragments. Mild wear is an imprecise term, frequently used in research, and contrasted with severe wear . In fact, the phenomena studied usually involve the transition from mild to severe wear and the factors that influence this transition. Mild wear may be appreciably greater than can be tolerated in practice. With metallic sliders, mild wear debris usually consists of oxide particles. See also normal wear and severe wear .
- **mill addition**
  - Any material added to the ball milling charge of a frit .
- **mill finish**
  - A nonstandard (and typically nonuniform) surface finish on mill products that are delivered without being subjected to a special surface treatment (other than a corrosion-preventive treatment) after the final working or heat-treating step.
- **milling**
  - Using a rotary tool with one or more teeth that engage the workpiece and remove material as the workpiece moves past the rotating cutter.
- **mill scale**
  - The heavy oxide layer that forms during the hot fabrication or heat treatment of metals.
- **minimized spangle**
  - A hot dip galvanized coating of very small grain size, which makes the spangle less visible when the part is subsequently painted.
- **mirror-finish grinding**

- A class of grinding processes in which extremely fine abrasive particles are used to achieve reflective surfaces of precise geometry. These methods are used in finishing such items as molds and dies used for making contact lenses and optical components.

- **mold coating**
  - (1) Coating to prevent surface defects on permanent mold castings and die castings. (2) Coating on sand molds to prevent metal penetration and to improve metal finish. Also called mold facing or mold dressing.
- **molecular beam epitaxy**
  - A vacuum deposition process used to form epitaxial films on semiconductor materials.
- **molten metal flame spraying**
  - A thermal spraying process variation in which the metallic material to be sprayed is in the molten condition. See also flame spraying .
- **molten salt bath**
  - Same as salt bath .
- **morphology**
  - The characteristic shape, form, or surface texture or contours of the crystals, grains , or particles of (or in) a material, generally on a microscopic scale.
- **motor-generator (MG set)**
  - A machine that consists of one or more motors mechanically coupled to one or more generators. In plating , such a machine in which the generator delivers dc of appropriate amperage and voltage.
- **multilayer coating**
  - Same as composite coating .
- **multiple etching**
  - Sequential etching of a microsection, with specific reagents attacking distinct microconstituents.
- **N**
- **negative replica**
  - A method of reproducing a surface obtained by the direct contact of the replicating material with the specimen. Using this technique, the contour of the replica surface is reversed with respect to that of the original. See also replica .
- **neutralization**
  - The balancing of acidity and alkalinity by interaction. In the context of cleaning, the removal of acid soils by alkalines and alkaline soils by acids.
- **nitriding**
  - Introducing nitrogen into the surface layer of a solid ferrous alloy by holding at a suitable temperature (below Ac_1 for ferritic steels) in contact with a nitrogenous material, usually ammonia or molten salt of appropriate composition. Quenching is not required to produce a hard case. See also aerated bath nitriding , bright nitriding , liquid nitriding , and nitrocarburizing .
- **nitrocarburizing**
  - Any of several processes in which both nitrogen and carbon are absorbed into the surface layers of a ferrous material from a molten salt or gaseous atmosphere at temperatures below the lower critical temperature and, by diffusion, create a concentration gradient. Nitrocarburizing is performed primarily to provide an antiscuffing surface layer and to improve fatigue resistance. Compare with carbonitriding .
- **noble metal**
  - A metal that does not readily tend to furnish ions, and therefore does not dissolve readily, nor easily enter into such reactions as oxidation, etc. Contrast with base metal .
- **nodular pearlite**
  - Pearlite that has grown as a colony with an approximately spherical morphology.
- **nonionic detergent**
  - A detergent that produces aggregates of electrically neutral molecules with colloidal properties.
- **normal wear**
  - Loss of material within the design limits expected for the specific intended application. The concept of normal wear depends on economic factors, such as the expendability of a worn part.
- **notch sensitivity**
  - The extent to which the sensitivity of a material to fracture is increased by the presence of a stress concentration, such as a notch, a sudden change in cross section, a crack, or a scratch. Low notch

sensitivity is usually associated with ductile materials, and high notch sensitivity is usually associated with brittle materials.

- **nucleation**
  - In plating of plastics, the preplating step in which a catalytic material, often a palladium or gold compound, is absorbed on a surface of the plastic substrate to act as sites for initial stages of deposition.
- **O**
- **oblique evaporation shadowing**
  - The condensation of evaporated material onto a substrate that is inclined to the direct line of the vapor stream to produce shadows. See also shadowing .
- **oil-based paints**
  - Paints with films that form solids by the air-induced cross-linking of certain unsaturated plant oils known as drying oils. Oxygen is consumed in the process.
- **one-coat ware**
  - (1) Workpieces finished in a single coat of porcelain enamel . Also known as one-coat work. (2) Sometimes a contraction of one-cover-coat ware in which the finish consists of a single cover coat applied over the ground coat.
- **opacifier**
  - A material that imparts or increases the diffuse reflectance of porcelain enamel .
- **opacity**
  - In porcelain enamel , the property of reflecting light diffusely and nonselectively.
- **orange peel**
  - (1) In painting, a pebbled film surface caused by too rapid drying after spraying, by failure of the coating material to exhibit the desired leveling effects, or by uneven flow (application) in roller coating techniques. (2) In porcelain enamel , a surface condition characterized by an irregular waviness that resembles an orange skin in texture; sometimes considered a defect. (3) A surface roughening in the form of a pebble-grained pattern that occurs when a metal of unusually coarse grain size is stressed beyond its elastic limit. Also called pebbles and alligator skin.
- **organic solvent**
  - See chlorinated solvent .
- **organic zinc-rich paint**
  - Coating containing zinc powder pigment and an organic resin.
- **overfiring**
  - In porcelain enamel , a condition sometimes occurring during firing when the temperature of the furnace is too high or the ware is left in the furnace for a greater length of time than necessary.
- **overpickling**
  - Using pickling solutions of greater strength or at higher temperature than recommended, or allowing the workpiece to remain in the pickling tanks for a greater length of time than necessary. Overpickling can lead to blistering of subsequently applied porcelain enamel finishes.
- **oxidation**
  - A reaction in which electrons are removed from a reactant. Sometimes, more specifically the combination of a reactant with oxygen. Contrast with reduction .
- **oxidation reduction**
  - To change the valence state of oxide scale and rust to soluble forms for removal from metal surfaces. Rust is chemically changed in this way to a more soluble form, easily dissolved by acids.
- **oxidative wear**
  - (1) A corrosive wear process in which chemical reaction with oxygen or oxidizing environment predominates. (2) A type of wear resulting from the sliding action between two metallic components that generates oxide films on the metal surfaces. These oxide films prevent the formation of a metallic bond between the sliding surfaces, resulting in fine wear debris and low wear rates.
- **oxide film replica**
  - A thin film of an oxide of the specimen to be examined. The replica is prepared by air, oxygen, chemical, or electrochemical oxidation of the parent metal and is subsequently freed mechanically or chemically for examination. See also replica .
- **oxidized steel surface**

- Surface having a thin, tightly adhering oxidized skin (from straw to blue in color), which forms when steel is heated in an oxidizing atmosphere.

- **oxidizing agent**
  - A compound that causes oxidation, thereby itself being reduced.
- **oxygen deficiency**
  - A form of crevice corrosion in which galvanic corrosion proceeds because oxygen is prevented from diffusing into the crevice.
- **P**
- **pack carburizing**
  - A method of surface hardening of steel in which parts are packed in a steel box with a carburizing compound and heated to elevated temperatures. Common carburizing compounds contain 10 to 20% alkali or alkaline earth metal carbonates (for example, barium carbonate, $BaCO_3$) bound to hardwood charcoal or to coke by oil, tar, or molasses. This process has been largely supplanted by gas and liquid carburizing processes.
- **pack cementation**
  - A coating process akin to pack carburizing that involves packing the parts to be coated into a retort with a carefully blended mixture of powders and then exposing the pack under hermetically sealed conditions or an inert atmosphere to elevated temperatures. Pack cementation is principally used for the application of aluminum diffusion coatings and ceramic coatings.
- **paint**
  - A material that when applied as a liquid to a surface forms a solid film for the purpose of decoration and/or protection. Generally, a paint contains a binder(s), solvent(s), and a pigment(s). Often other materials are present to give special properties to the paint film. Examples of such additives are rust inhibitors, light stabilizers, and softening agents (plasticizers).
- **passivation**
  - (1) A reduction of the anodic reaction rate of an electrode involved in corrosion . (2) The process in metal corrosion by which metals become passive. (3) The changing of a chemically active surface of a metal to a much less reactive state. Contrast with activation . (4) The formation of an insulating layer directly over a semiconductor surface to protect the surface from contaminants, moisture, and so forth.
- **passivator**
  - A type of corrosion inhibitor that appreciably changes the potential of a metal to a more noble (positive) value.
- **passive**
  - (1) A metal corroding under the control of a surface reaction product. (2) The state of the metal surface characterized by low corrosion rates in a potential region that is strongly oxidizing for the metal.
- **passive-active cell**
  - A corrosion cell in which the anode is a metal in the active state and the cathode is the same metal in the passive state.
- **passivity**
  - A condition in which a piece of metal, because of an impervious covering of oxide or other compound, has a corrosion rate much less than that of the metal in the active state.
- **patina**
  - The coating, usually green, that forms on the surface of metals such as copper and copper alloys exposed to the atmosphere. Also used to describe the appearance of a weathered surface of any metal.
- **pearlite**
  - A metastable lamellar aggregate of ferrite and cementite resulting from the transformation of austenite at temperatures above the bainite range.
- **peeling**
  - The detaching of one layer of a coating from another, or from the base metal , because of poor adherence.
- **periodic reverse plating**
  - A method of plating in which the current is reversed periodically. The cycles are usually no longer than a few minutes and may be much less.
- **pH**

- The negative logarithm of the hydrogen-ion activity or hydrogen-ion concentration in gram equivalents per liter that is used in expressing both acidity and alkalinity on a scale of values running from 0 to 14; 0 to 7 represents acidity; 7 neutrality, and 7 to 14 alkalinity.

- **phosphate coating**
  - Same as phosphating .
- **phosphating**
  - Forming an adherent phosphate coating on a metal by immersion in a suitable aqueous phosphate solution. Also called phosphatizing. See also conversion coating .
- **photoresist**
  - (1) A radiation-sensitive material which, when properly applied to a variety of substrates and then properly exposed and developed, masks portions of the substrate with a high degree of integrity. (2) A photosensitive coating that is applied to a laminate and subsequently exposed through a photo tool (film) and developed to create a pattern that can be either plated or etched.
- **physical vapor deposition (PVD)**
  - A coating process whereby the deposition species are transferred and deposited in the form of individual atoms or molecules. The most common PVD methods are sputtering and evaporation. Sputtering, which is the principal PVD process, involves the transport of a material from a source (target) to a substrate by means of the bombardment of the target by gas ions that have been accelerated by a high voltage. Atoms from the target are ejected by momentum transfer between the incident ions and the target. These ejected particles move across the vacuum chamber to be deposited on the substrate. Evaporation, which was the first PVD process used, involves the transfer of material to form a coating by physical means alone, essentially vaporization. The streaming vapor is generated by melting and evaporating a coating material source bar, by an electron beam in a vacuum chamber. Because both of these methods are line-of-sight processes, it is necessary to use specially shaped targets or multiple evaporation sources and to rotate or move the substrate uniformly to expose all areas. PVD coatings are used to improve the wear, friction, and hardness properties of cutting tools and as corrosion-resistant coatings.
- **pickle**
  - See pickling .
- **pickle stain**
  - Discoloration of metal due to chemical cleaning without adequate washing and drying.
- **pickling**
  - The chemical removal of surface oxides (scale) from iron and steel by immersion in an aqueous acid solution. The most common pickling solutions for carbon steels are sulfuric and hydrochloric acids.
- **pickup**
  - (1) Transfer of metal from tools to part or from part to tools during a forming operation. (2) Small particles of oxidized metal adhering to the surface of a mill product. (3) The amount of slip retained per unit area on dipped porcelain enamel ware.
- **pigment**
  - Small particles added to the paint to influence properties such as color, corrosion resistance , and mechanical strength.
- **pinhole porosity**
  - Porosity consisting of numerous small gas holes distributed throughout a metal; found in weld metal, castings, and electrodeposited metal.
- **pinhole**
  - A porcelain enamel surface defect caused by gas evolution and characterized by a small hole resembling a pin prick that may extend to the base metal .
- **pit**
  - A porcelain enamel surface defect similar to a dimple but slightly smaller.
- **pitting**
  - (1) Forming small sharp cavities in a surface by corrosion , wear, or other mechanically assisted degradation. (2) Localized corrosion of a metal surface, confined to a point or small area, that takes the form of cavities.
- **planishing**
  - Producing a smooth finish on metal by a rapid succession of blows delivered by highly polished dies or by a hammer designed for the purpose, or by rolling in a planishing mill.
- **plasma**

- A gas of sufficient energy so that a large fraction of the species present is ionized and thus conducts electricity. Plasmas may be generated by the passage of a current between electrodes, by induction, or by a combination of these methods.

- **plasma-assisted chemical vapor deposition**
  - A chemical vapor deposition process that uses low-pressure glow-discharge plasmas to promote the chemical deposition reactions. Also called plasma-enhanced chemical vapor deposition.
- **plasma ion deposition**
  - An ion implantation technique in which ion beams are used to create coatings having special phases, especially ion beam formed carbon coatings in the diamond phase or ion beam formed boron nitride coatings.
- **plasma spraying**
  - A thermal spraying process in which the coating material is melted with heat from a plasma torch that generates a nontransferred arc; molten powder coating material is propelled against the base metal by the hot, ionized gas issuing from the torch.
- **plastic deformation**
  - The permanent (inelastic) distortion of materials under applied stresses that strain the material beyond its elastic limit.
- **plasticizer**
  - A lower molecular weight material added to polymeric materials such as paints, plastics, or adhesives to improve the flexibility.
- **plastic replica**
  - In fractography and metallography, a reproduction in plastic of the surface to be studied. It is prepared by evaporation of the solvent from a solution of plastic, polymerization of a monomer, or solidification of a plastic on the surface.
- **plastisol**
  - A suspension of a finely divided resin in a plasticizer that can be converted to a continuous film by the application of heat. Distinct from baking enamels etc. in that substantially all the original mixture becomes a part of the film; there is no significant evaporation of solvent. The films are usually much thicker than obtainable from coatings that depend on the evaporation of a volatile solvent.
- **plate martensite**
  - Martensite formed partly in steel containing more than approximately 0.5% C and solely in steel containing more than approximately 1.0% C that appears as lenticular-shape plates (crystals).
- **plating**
  - Forming an adherent layer of metal on an object; often used as a shop term for electroplating . See also electrodeposition and electroless plating .
- **plating rack**
  - A fixture used to hold work and conduct current to it during electroplating .
- **plowing**
  - In tribology, the formation of grooves by plastic deformation of softer of two surfaces in relative motion.
- **plunge grinding**
  - Grinding wherein the only relative motion of the wheel is radially toward the work.
- **plymetal**
  - Sheet consisting of bonded layers of dissimilar metals.
- **Poisson burr**
  - A burr formed predominantly by the phenomenon that is responsible for Poisson's ratio. Sometimes called a flow-type burr.
- **polarization**
  - The change in the potential of a electrode during electrolysis , such that the potential of an anode always becomes more noble and that of a cathode less noble than their respective static potentials. Equal to the difference between the static electrode potential and the dynamic electrode potential .
- **polished surface**
  - A surface prepared for metallographic inspection that reflects a large proportion of the incident light in a specular manner.
- **polishing**

- The smoothing of a metal surface by means of the action of abrasive particles attached by adhesive to the surface of wheels or endless belts usually driven at a high speed.

- **polishing wear**
  - An extremely mild form of wear for which the mechanism has not been clearly identified, but that may involve extremely fine-scale abrasion, plastic smearing of micro-asperities, and/or tribochemical material removal.
- **polymers**
  - A high molecular weight organic compound, natural or synthetic, with a structure that can be represented by a repeated small unit, the mer. Synthetic polymers are formed by addition or condensation polymerization of monomers. When two or more dissimilar monomers are involved, the product is called a copolymer. The lengths of polymer chains, usually measured by molecular weight, have very significant effects on the performance properties of plastics and profound effects on processability.
- **pop-off**
  - Loss of small portions of a porcelain enamel coating. The usual cause is outgassing of hydrogen or other gases from the base metal during firing , but pop-off may also occur because of oxide particles or other debris on the surface of the base metal. Usually, the pits are minute and cone shaped, but when pop-off is the result of severe fishscale the pits may be much larger and irregular.
- **porcelain**
  - A glazed or unglazed vitreous ceramic whiteware used for technical purposes. This term designates such products as electrical, chemical, mechanical, structural, and thermal wares when they are vitreous. This term is frequently used as a synonym for china.
- **porcelain enamel**
  - A substantially vitreous or glassy, inorganic coating (borosilicate glass) bonded to metal by fusion at a temperature above 425 °C (800 °F). Porcelain enamels are applied primarily to components made of sheet iron or steel, cast iron, aluminum, or aluminum-coated steels.
- **pore**
  - (1) A small opening, void, interstice, or channel within a consolidated solid mass or agglomerate, usually larger than atomic or molecular dimensions. (2) A minute cavity in a powder metallurgy compact, sometimes added intentionally. (3) A minute perforation in an electroplated coating.
- **porosity**
  - (1) Fine holes or pores within a solid; the amount of these pores is expressed as a percentage of the total volume of the solid. (2) Cavity-type discontinuities in weldments formed by gas entrapment during solidification. (3) A characteristic of being porous, with voids or pores resulting from trapped air or shrinkage in a casting. See also gas porosity and pinhole porosity .
- **positive replica**
  - A replica whose contours correspond directly to the surface being replicated. Contrast with negative replica .
- **post-nucleation**
  - The step where, if necessary, the catalyst is converted to its final form when plating on plastic substrates. This is the final step prior to electroless plating .
- **poultice corrosion**
  - Same as deposit corrosion .
- **powder adhesion**
  - In dry process enameling , the ability of an electrostatic powder to remain attached by static attraction to a grounded substrate.
- **powder flame spraying**
  - A thermal spraying process variation in which the material to be sprayed is in powder form. See also flame spraying .
- **precipitation**
  - The consolidation of soil particles (the opposite of dispersion) in a cleaning bath, permitting their removal as sludge and prolonging bath life. The hardness of water can be reduced by precipitation with soda ash or trisodium phosphate.
- **precipitation (deposit) etching**
  - Development of microstructure in a metallographic specimen through formation of reaction products at the surface of the microsection. See also staining .
- **precipitation hardening**

- Hardening in metals caused by the precipitation of a constituent from a supersaturated solid solution. See also age hardening and aging .

- **precision grinding**
  - Machine grinding to specified dimensions and low tolerances.
- **precoated metal products**
  - Mill products that have a metallic, organic, or conversion coating applied to their surfaces before they are fabricated into parts.
- **preshadowed replica**
  - A replica for fractographic or metallographic inspection that is formed by the application of shadowing material to the surface to be replicated. It is formed before the thin replica film is cast or otherwise deposited on the surface. See also shadowing .
- **primary boiling**
  - The evolution of gas during the initial firing of porcelain enamel ; sometimes considered a defect.
- **primer**
  - A coating applied to a surface prior to the application of a paint topcoat or adhesive to improve the performance of the bond.
- **primes**
  - Metal products, principally sheet and plate, of the highest quality and free from blemishes or other visible imperfections.
- **proeutectoid carbide**
  - Primary crystals of cementite formed directly in ferrous alloys from the decomposition of austenite exclusive of that cementite resulting from the eutectoid reaction. See also eutectoid .
- **proeutectoid ferrite**
  - Primary crystals of ferrite formed directly in ferrous alloys from the decomposition of austenite exclusive of that ferrite resulting from the eutectoid reaction. See also eutectoid .
- **proeutectoid phase**
  - Particles of a phase in ferrous alloys that precipitate during cooling after austenitizing but before the eutectoid transformation takes place. See also eutectoid .
- **protective atmosphere**
  - (1) A gas envelope surrounding the part to be brazed, welded, or thermal sprayed, with the gas composition controlled with respect to chemical composition, dew point, pressure, flow rate, and so forth. Examples are inert gases, combusted fuel gases, hydrogen, and vacuum. (2) The atmosphere in a heat treating or sintering furnace designed to protect the parts or compacts from oxidation, nitridation, or other contamination from the environment.
- **pull through**
  - See copperhead .
- **Q**
- **quantitative metallography**
  - Determination of specific characteristics of a microstructure by quantitative measurements on micrographs or metallographic images. Quantities so measured include volume concentration of phases, grain size, particle size, mean free path between like particles or secondary phases, and surface area to volume ratio of microconstituents, particles, or grains.
- **quench-age embrittlement**
  - Embrittlement of low-carbon steels resulting from precipitation of solute carbon at existing dislocations and from precipitation hardening of the steel caused by differences in the solid solubility of carbon in ferrite at different temperatures. Quench-age embrittlement usually is caused by rapid cooling of the steel from temperatures slightly below Ac_1 (the temperature at which austenite begins to form), and can be minimized by quenching from lower temperatures.
- **quench hardening**
  - (1) Hardening suitable alpha-beta alloys (most often certain copper or titanium alloys) by solution treating and quenching to develop a martensitic-like structure. (2) In ferrous alloys, hardening by austenitizing and then cooling at a rate such that a substantial amount of austenite transforms to martensite.
- **R**
- **rack**
  - Same as plating rack .
- **rain erosion**

- A form of liquid impingement erosion in which the impinging liquid particles are raindrops. This form of erosion is of particular concern to designers and material selectors for external surfaces of rotary-wing and fixed-wing aircraft. See also erosion .

- **rattail**
  - A surface imperfection on a casting, occurring as one or more irregular lines, caused by expansion of sand in the mold. Compare with buckle (2).
- **reactive evaporation**
  - A vacuum deposition process in which trace amounts of an active gas are added to the vacuum chamber; the gas reacts with an evaporating material in the chamber, promoting deposition of the material on a substrate.
- **real area of contact**
  - Same as actual contact area .
- **reamer**
  - A rotary cutting tool with one or more cutting elements (teeth), used for enlarging a hole to desired size and contour. It is supported principally by the metal around the hole it cuts.
- **reaming**
  - An operation in which a previously formed hole is sized and contoured accurately by using a rotary cutting tool (reamer) with one or more cutting elements (teeth). The principal support for the reamer during the cutting action is supplied by the workpiece.
- **reboiling**
  - In porcelain enamel , gas evolution occurring and recurring during repeated firing of the ground coat; sometimes considered a defect.
- **recalescence**
  - (1) The increase in temperature that occurs after undercooling, because the rate of liberation of heat during transformation of a material exceeds the rate of dissipation of heat. (2) A phenomenon, associated with the transformation of gamma iron to alpha iron on cooling (supercooling) of iron or steel, that is revealed by the brightening (reglowing) of the metal surface owing to the sudden increase in temperature caused by the fast liberation of the latent heat of transformation. Contrast with decalescence .
- **reclain**
  - Porcelain enamel overspray that is removed from the spray booth and reconditioned for use.
- **recrystallization**
  - (1) The formation of a new, strain-free grain structure from that existing in cold-worked metal, usually accomplished by heating. (2) The change from one crystal structure to another, as occurs on heating or cooling through a critical temperature. (3) A process, usually physical, by which one crystal species is grown at the expense of another or at the expense of others of the same substance but smaller in size.
- **rectification**
  - The conversion of alternating current into direct current.
- **rectifier**
  - A device that converts alternating current into direct current by virtue of a characteristic permitting appreciable flow of current in only one direction.
- **reduction**
  - A reaction in which electrons are added to a reactant. More specifically, the addition of hydrogen or the abstraction of oxygen. Such a reaction takes place, for example, at the cathode in electrolysis . Contrast with oxidation .
- **reflector sheet**
  - A clad product consisting of a facing layer of high-purity aluminum capable of taking a high polish, for reflecting heat or light, and a base of commercially pure aluminum or an aluminum-manganese alloy, for strength and formability.
- **reflowing**
  - Melting of an electrodeposit followed by solidification. The surface has the appearance and physical characteristics of a hot dipped surface (especially tin or tin alloy plates). Also called flow brightening .
- **Rehbinder effect**
  - Modification of the mechanical properties at or near the surface of a solid, attributable to interaction with a surfactant .
- **relieving**

- The removal of material from selected portions of a colored metal surface by mechanical means to achieve a multicolored effect.

- **replica**
  - A reproduction of a surface in a material. It is usually accomplished by depositing a thin film of suitable material, such as a plastic, onto the specimen surface. This film is subsequently extracted and examined by optical microscopy, scanning electron microscopy , or transmission electron microscopy , the latter being the most common. Replication techniques can be classified as either surface replication or extraction replication. Surface replicas provide an image of the surface topography of a specimen, while extraction replicas lift particles from the specimen. See also atomic replica , cast replica , collodion replica , Formvar replica , gelatin replica , impression replica , negative replica , oxide film replica , plastic replica , positive replica , preshadowed replica , tape replica method (faxfilm) , and vapor-deposited replica .
- **residual stress**
  - (1) The stress existing in a body at rest, in equilibrium, at uniform temperature, and not subjected to external forces. Often caused by the forming or thermal processing curing process. (2) An internal stress not depending on external forces resulting from such factors as cold working, phase changes, or temperature gradients. (3) Stress present in a body that is free of external forces or thermal gradients. (4) Stress remaining in a structure or member as a result of thermal or mechanical treatment or both. Stress arises in fusion welding primarily because the weld metal contracts on cooling from the solidus to room temperature.
- **resinoid wheel**
  - A grinding wheel bonded with a synthetic resin.
- **resist**
  - (1) Coating material used to mask or protect selected areas of a substrate from the action of an etchant , solder, or plating . (2) A material applied to a part of a cathode or plating rack to render the surface nonconductive.
- **reverse cleaning**
  - Same as anodic cleaning .
- **rinsability**
  - The relative ease with which a substance can be removed from a metal surface with a liquid such as water.
- **ripple (dc)**
  - Regular modulations in the dc output wave of a rectifier unit, or a motor-generator set, originating from the harmonics of the ac input system in the case of a rectifier, or from the harmonics of the induced voltage of a motor-generator set.
- **ripple formation**
  - Formation of periodic ridges and valleys transverse to the direction of motion on a solid surface. Also referred to as rippling.
- **robber**
  - An extra cathode or cathode extension that reduces the current density on what would otherwise be a high-current-density area on work being electroplated.
- **Rochelle copper**
  - (1) A copper electrodeposit obtained from copper cyanide plating solution to which Rochelle salt (sodium potassium tartrate) has been added for grain refinement , better anode corrosion, and cathode efficiency. (2) The solution from which a Rochelle copper electrodeposit is obtained.
- **rolling-contact wear**
  - Wear to a solid surface that results from rolling contact between that surface and another solid surface or surfaces.
- **rollover burr**
  - Burr formed by a cutter when it exits over a surface and allows the chip to be rolled away from the cutter, rather than sheared.
- **root mean square (rms)**
  - A term describing the surface roughness of a machined surface, R_q, calculated as the square root of the average of the squared distance of the surface from the mean line. See also surface roughness .
- **rosette graphite**
  - Arrangement of graphite flakes in which the flakes extend radially from the center of crystallized areas in gray cast iron.

- **rotary roughening**
  - A method of surface roughening prior to thermal spraying wherein a revolving roughening tool is pressed against the surface being prepared, while either the work, or the tool, or both, move.
- **rouge finish**
  - A highly reflective finish produced with rouge (finely divided, hydrated iron oxide) or other very fine abrasive, similar in appearance to the bright polish or mirror finish on sterling silver utensils.
- **rough grinding**
  - Grinding where surface generation occurs at a rapid rate, and tolerances or surface features are less critical compared to the production rate. Usually followed by a subsequent operation.
- **roughness**
  - (1) Relatively finely spaced surface irregularities, the heights, widths, and directions of which establish the predominant surface pattern. (2) The microscopic peak-to-valley distances of surface protuberances and depressions. See also surface roughness .
- **rough-polishing process**
  - A polishing process having the primary objective of removing the layer of significant damage produced during earlier machining and abrasion stages of a metallographic preparation sequence. A secondary objective is to produce a finish of such quality that a final polish can be produced easily. See also final polishing .
- **running-in**
  - The process by which machine parts improve in conformity, surface topography, and frictional compatibility during the initial stage of use. Chemical processes, including formation of an oxide skin, and metallurgical processes, such as strain hardening, may contribute.
- **rust**
  - A visible corrosion product consisting of hydrated oxides of iron. Applicable only to ferrous alloys. See also white rust .
- **S**
- **sacrificial protection**
  - The form of corrosion protection wherein one metal corrodes in preference to another, thereby protecting the latter from corrosion.
- **sagging**
  - (1) A defect characterized by a wavy line or lines appearing on those surfaces of porcelain enamel that have been fired in a vertical position. (2) A defect characterized by irreversible downward bending in a porcelain enamel article insufficiently supported during the firing cycle.
- **salt bath**
  - A molten, usually anhydrous inorganic solution used for heat treating or surface diffusion treatments wherein nitrogen, carbon, or other elements are diffused into the work. Specialized compositions are used for removal of scale , refractory materials, and organic materials from work surfaces.
- **sandblasting**
  - Abrasive blasting with sand. See also blasting or blast cleaning and compare with shotblasting .
- **sanitary ware**
  - Porcelain enamel ware such as sinks, lavatories, and bathtubs.
- **saponification**
  - The conversion of insoluble fats and fatty acids to water-soluble soaps by alkalies. The cleaning of buffing compounds from metallic surfaces can be achieved by saponification.
- **satin finish**
  - A diffusely reflecting surface finish on metals, lustrous but not mirrorlike. One type is a butler finish .
- **scab**
  - A defect on the surface of a casting that appears as a rough, slightly raised surface blemish, crusted over by a thin porous layer of metal, under which is a honeycomb or cavity that usually contains a layer of sand; defect common to thin-wall portions of the casting or around hot areas of the mold.
- **scale**
  - Surface oxidation, consisting of partially adherent layers of corrosion products, left on metals by heating or casting in air or in other oxidizing atmospheres.
- **scaling**

- (1) Forming a thick layer of oxidation products on metals at high temperature. Scaling should be distinguished from rusting, which involves the formation of hydrated oxides. See also rust . (2) Depositing water-insoluble constituents on a metal surface, as in cooling tubes and water boilers.
- **scanning Auger microscopy (SAM)**
    - An analytical technique that measures the lateral distribution of elements on the surface of a material by recording the intensity of their Auger electrons versus the position of the electron beam.
- **scanning electron microscopy (SEM)**
    - An analytical technique in which an image is formed on a cathode-ray tube whose raster is synchronized with the raster of a point beam of electrons scanned over an area of the sample surface. The brightness of the image at any point is proportional to the scattering by or secondary emissions from the point on the sample being struck by the electron beam.
- **scanning laser acoustic microscopy (SLAM)**
    - A high-resolution, high-frequency (10 to 500 MHz) ultrasonic inspection technique that produces images of features in a sample throughout its entire thickness. In operation, ultrasound is introduced to the bottom surface of the sample by a piezoelectric transducer, and the transmitted wave is detected on the top side by a rapidly scanning laser beam.
- **scanning transmission electron microscopy (STEM)**
    - An analytical technique in which an image is formed on a cathode-ray tube whose raster is synchronized with the raster of a point beam of electrons scanned over an area of the sample. The brightness of the image at any point is proportional to the number of electrons that are transmitted through the sample at the point where it is struck by the beam.
- **scoring**
    - (1) The formation of severe scratches in the direction of sliding. Scoring may be due to local solid-phase welding or to abrasion. In the United States, the term scuffing is sometimes used as a synonym for scoring. Minor damage should be called scratching rather than scoring. (2) In tribology, a severe form of wear characterized by the formation of extensive grooves and scratches in the direction of sliding. (3) The act of producing a scratch or narrow groove in a surface by causing a sharp instrument to move along that surface. (4) The marring or scratching of any formed metal part by metal pickup on the punch or die. (5) The reduction in thickness of a material along a line to weaken it intentionally along that line.
- **scouring**
    - (1) A wet or dry cleaning process involving mechanical scrubbing. (2) A wet or dry mechanical finishing operation, using fine abrasive and low pressure, carried out by hand or with a cloth or wire wheel to produce satin or butler -type finishes.
- **scratch**
    - A groove produced in a solid surface by the cutting and/or plowing action of a sharp particle or protuberance moving along that surface.
- **scratch brush finish**
    - A finish on nonferrous metals produced by buffing that shows a combination of coarse lines with a slight underlying luster.
- **scratch-resistant coatings**
    - Coating applied to glass surfaces to reduce the effects of frictive damage. Examples are SnO_2 or TiO_2 coatings applied to glass containers.
- **screen test**
    - A standard test for fineness of porcelain enamel slip or powder.
- **scuffing**
    - Same as scoring .
- **scumming**
    - A defect characterized by areas of poor gloss on the surface of a porcelain enamel that can be caused by uneven heat distribution in the furnace, overfiring, or underfiring.
- **sealed (anodic) coating**
    - In anodizing aluminum, an anodic oxide coating on aluminum that has been treated in aqueous or steam medium resulting in reduced porosity of the coating.
- **sealing of anodic coating**
    - A process which, by absorption, chemical reaction, or other mechanism, increases the resistance of an anodic coating to staining and corrosion , improves the durability of colors produced in the coating, or imparts other desirable properties.

- **seam**
  - (1) On a metal surface, an unwelded fold or lap that appears as a crack, usually resulting from a discontinuity. (2) A surface defect on a casting related to but of lesser degree than a cold shut . (3) A ridge on the surface of a casting caused by a crack in the mold face.
- **secondary gas**
  - In thermal spraying, the gas constituting the minor constituent of the arc gas fed to the gun to produce the plasma. The primary arc gas, usually argon or nitrogen, is supplemented with secondary gases such as nitrogen, helium, and/or hydrogen, in order to increase the temperature of the plasma.
- **secondary ion mass spectroscopy (SIMS)**
  - An analytical technique that measures the masses of ions emitted from the surface of a material when exposed to a beam of incident ions. The incident ions are usually monoenergetic and are all of the same species, for example, 5-keV Ne^+ ions.
- **sectioning**
  - The removal of a conveniently sized, representative specimen from a larger sample for metallographic inspection. Sectioning methods include shearing, sawing (using hacksaws, band saws, and diamond wire saws), abrasive cutting, and electrical discharge machining.
- **segregation (coring) etching**
  - Development of segregation (coring) mainly in macrostructures and microstructures of castings.
- **seizing**
  - The stopping of a moving part by a mating surface as a result of excessive friction.
- **selective leaching**
  - Corrosion in which one element is preferentially removed from an alloy, leaving a residue (often porous) of the elements that are more resistant to the particular environment. Also called dealloying or parting. See also decarburization , decobaltification , denickelification , dezincification , and graphitic corrosion .
- **selective plating**
  - Same as brush plating .
- **self-fluxing alloys**
  - In thermal spraying, certain materials that "wet" the substrate and coalesce when heated to their melting point, without the addition of a fluxing agent.
- **self-limiting characteristic**
  - Characteristic of electrostatic powders to build only a limited amount of surface film during application due to the buildup of a layer of charged particles that will repel particles of like charge. See also back emission .
- **sensitization**
  - (1) The absorption of a reducing agent, often a stannous compound, on the surface of a plastic substrate . (2) The effect caused by a sensitizing heat treatment .
- **sensitizing heat treatment**
  - A heat treatment, whether accidental, intentional, or incidental (as during welding), that causes precipitation of constituents at grain boundaries , often causing the alloy to become susceptible to intergranular corrosion or intergranular stress-corrosion cracking .
- **sequestration and chelation**
  - To inactivate calcium, magnesium, and iron salts in water so that they will not interfere with cleaning. Chelated alkaline compounds can remove oxides and rust from steel surfaces, eliminating the need for acids that may react with the metal to cause hydrogen embrittlement.
- **serial sectioning**
  - A metallographic technique in which an identified area on a section surface is observed repeatedly after successive layers of known thickness have been removed from the surface. It is used to construct a three-dimensional morphology of structural features. See also sectioning .
- **set**
  - A flow property of porcelain enamel slip affecting the rate of draining, residual thickness, and uniformity of coating.
- **setting-up agent**
  - An electrolyte used to increase the measured pickup of a slip . Also known as set-up agent.
- **severe wear**
  - A form of wear characterized by removal of material in relatively large fragments. Severe wear is an imprecise term, frequently used in research, and contrasted with mild wear. In fact, the

phenomena studied usually involve the transition from mild to severe wear and the factors that influence that transition. With metals, the fragments are usually predominantly metallic rather than oxidic. Severe wear is frequently associated with heavy loads and/or adhesive contact. See also mild wear and normal wear .

- **shadow angle**
  - In shadowing of replicas, the angle between the line of motion of the evaporated atoms and the surface being shadowed. See also replica and shadowing .
- **shadow cast replica**
  - A replica that has been shadowed. See also replica and shadowing .
- **shadowing**
  - Directional deposition of carbon or a metallic film on a plastic replica so as to highlight features to be analyzed by transmission electron microscopy . Most often used to provide maximum detail and resolution of the features of fracture surfaces. See also metal shadowing , oblique evaporation shadowing , and shadow angle .
- **shadow mask**
  - A thermal spraying process variation in which an area is partially shielded during the thermal spraying operation, thus permitting some overspray to produce a feathering at the coating edge.
- **shales**
  - Abrasive particles of platelike shape. The term is applied particularly to diamond abrasives.
- **shaving**
  - (1) As a finishing operation, the accurate removal of a thin layer of a work surface by straightline motion between a cutter and the surface. (2) Trimming parts such as stampings, forgings, and tubes to remove uneven sheared edges or to improve accuracy.
- **sheet**
  - A flat-rolled metal product of some maximum thickness and minimum width arbitrarily dependent on the type of metal. It has a width-to-thickness ratio greater than about 50. Generally, such flat products under 6.5 mm (in.) thick are called sheets, and those 6.5 mm (in.) thick and over are called plates. Occasionally, the limiting thickness for steel to be designated as sheet steel is No. 10 Manufacturer's Standard Gage for sheet steel, which is 3.42 mm (0.1345 in.) thick.
- **shelf roughness**
  - Roughness on upward-facing surfaces where undissolved solids have settled on parts during a plating operation.
- **shelling**
  - (1) A term used in railway engineering to describe an advanced phase of spalling . (2) A mechanism of deterioration of coated abrasive products in which entire abrasive grains are removed from the cement coating that held the abrasive to the backing layer of the product.
- **shielding**
  - (1) A material barrier that prevents radiation or a flowing fluid from impinging on an object or a portion of an object. (2) In an electron-optical instrument, the protection of the electron beam from distortion due to extraneous electric and magnetic fields. Because the metallic column of the microscope is at ground potential, it provides electrostatic shielding. (3) Placing an object in an electrolytic bath so as to alter the current distribution on the cathode . A nonconductor is called a shield; a conductor is called a robber , a thief, or a guard.
- **short-term etching**
  - In metallographic preparation of specimens, etching times of seconds to a few minutes.
- **shot**
  - (1) Small, spherical particles of metal. (2) The injection of molten metal into a die casting die. The metal is injected so quickly that it can be compared to the shooting of a gun.
- **shotblasting**
  - Blasting with metal shot ; usually used to remove deposits or mill scale more rapidly or more effectively than can be done by sandblasting .
- **shot peening**
  - A method of cold working metals in which compressive stresses are induced in the exposed surface layers of parts by the impingement of a stream of shot , directed at the metal surface at high velocity under controlled conditions. It differs from blast cleaning in primary purpose and in the extent to which it is controlled to yield accurate and reproducible results. Although shot

peening cleans the surface being peened, this function is incidental. The major purpose of shot peening is to increase fatigue strength. Shot for peening usually is made of iron, steel, or glass.

- **shrinkage cavity**
  - A void left in cast metal as a result of solidification shrinkage. Shrinkage cavities can appear as either isolated or interconnected irregularly shaped voids.
- **sieve analysis**
  - A method of determining particle size distribution, usually expressed as the weight percentage retained upon each of a series of standard screens of decreasing mesh size.
- **sigma-phase embrittlement**
  - Embrittlement of iron-chromium alloys (most notably austenitic stainless steels) caused by precipitation at grain boundaries of the hard, brittle intermetallic sigma phase during long periods of exposure to temperatures between approximately 560 and 980 °C (1050 and 1800 °F). Sigma-phase embrittlement results in severe loss in toughness and ductility, and can make the embrittled material susceptible to intergranular corrosion .
- **siliconizing**
  - Diffusing silicon into solid metal, usually low-carbon steels, at an elevated temperature in order to improve corrosion or wear resistance.
- **size**
  - In composites manufacturing, a treatment consisting of starch, gelatin, oil, wax, or other suitable ingredients applied to yarn or fibers at the time of formation to protect the surface and aid the process of handling and fabrication or to control the fiber characteristics. The treatment contains ingredients that provide surface lubricity and binding action, but unlike a finish, contains no coupling agent. Before final fabrication into a composite, the size is usually removed by heat cleaning, and a finish is applied.
- **skid-polishing process**
  - A mechanical polishing process in which the surface of the metallographic specimen to be polished is made to skid across a layer of paste, consisting of the abrasive and the polishing fluid, without contacting the fibers of the polishing cloth.
- **skin**
  - A thin outside metal layer, not formed by bonding as in cladding or electroplating, that differs in composition, structure, or other characteristics from the main mass of metal.
- **skin lamination**
  - In flat-rolled metals, a surface rupture resulting from the exposure of a subsurface lamination by rolling.
- **skinning**
  - The formation of a thin, tough film on the surface of a liquid paint film, usually due to reaction with the air or to rapid solvent loss.
- **slab**
  - A flat-shaped semifinished rolled metal ingot with a width not less than 250 mm (10 in.) and a cross-sectional area not less than 105 cm^2 (16 $in.^2$).
- **slip**
  - A suspension of finely divided ceramic material in liquid.
- **sliver**
  - An imperfection consisting of a very thin elongated piece of metal attached by only one end to the parent metal into whose surface it has been worked.
- **sludge**
  - An accumulation of insoluble materials and reaction products that collects in cleaning and processing tanks.
- **slump test**
  - A test used to determine the consistency of slip in which measurement is made of the spreading of a specified volume of slip over a flat plate.
- **slurry**
  - A suspension of solids in water.
- **slurry erosion**
  - Erosion produced by the movement of a slurry past a solid surface.
- **smearing**
  - Mechanical removal of material from a surface, usually involving plastic shear deformation, and redeposition of the material as a thin layer on one or both surfaces. See also transfer .

- **smelt**
  - A batch or lot of frit .
- **smut**
  - A reaction product sometimes left on the surface of a metal after pickling , electroplating, or etching .
- **soak cleaning**
  - Immersion cleaning without the use of current, usually in alkaline solution.
- **soil**
  - Undesirable material on a surface that is not an integral part of the surface. Oil, grease, and dirt can be soils; a decarburized skin and excess hard chromium are not soils. Loose scale is soil; hard scale may be an integral part of the surface and, hence, not soil.
- **solid lubricant**
  - Any solid used as a powder or thin film on a surface to provide protection from damage during relative movement and to reduce friction and wear. Examples include molybdenum disulfide, graphite, polytetra-fluoroethylene (PTFE), and mica.
- **soluble oil**
  - A mineral oil containing additives that enable it to form a stable emulsion with water. Soluble oils are used as cutting or grinding fluids.
- **solvency**
  - The property of removal of soils by dissolving in a cleaning solution. For example, oils and fats are soluble in some solvents.
- **solvent**
  - A usually liquid substance capable of dissolving or dispersing other substances. See chlorinated solvent .
- **solvent cleaning**
  - Cleaning by means of organic solvents.
- **sour gas**
  - A gaseous environment containing hydrogen sulfide and carbon dioxide in hydrocarbon reservoirs. Prolonged exposure to sour gas can lead to hydrogen damage , sulfide-stress cracking , and/or stress-corrosion cracking in ferrous alloys.
- **spalling**
  - (1) Separation of particles from a surface in the form of flakes. The term spalling is commonly associated with rolling-element bearings and with gear teeth. Spalling is usually a result of subsurface fatigue and is more extensive than pitting. (2) In tribology, the separation of macroscopic particles from a surface in the form of flakes or chips, usually associated with rolling-element bearings and gear teeth, but also resulting from impact events. (3) The spontaneous chipping, fragmentation, or separation of a surface or surface coating. (4) A chipping or flaking of a surface due to any kind of improper heat treatment or material dissociation.
- **spangle**
  - The characteristic crystalline form in which a hot dipped zinc coating solidifies on steel strip.
- **specking**
  - Discoloration of an enamel surface due to foreign particles, dirt, or scale embedding themselves in the enamel. May also be caused by base coat migration up through the cover coat in two coat/one fire powder systems. Also known as black specking.
- **spotting out**
  - The delayed appearance of spots and blemishes on plated or finished surfaces that is most prevalent on porous base metals or substrates .
- **spray angle**
  - In thermal spraying, the angle of particle approach, measured from the surface of the substrate to the axis of the spray nozzle.
- **spray cleaning**
  - Cleaning by means of spraying.
- **spray deposit**
  - A coating applied by any of the thermal spray methods. See also thermal spraying .
- **sputter deposition**
  - Same as sputtering .
- **sputtering**

- The bombardment of a solid surface with a flux of energetic particles (ions) that results in the ejection of atomic species. The ejected material may be used as a source for deposition. See also physical vapor deposition .
- **stabilizing gas**
  - In plasma spraying, the arc gas, which is ionized to form the plasma. Introduced into the arc chamber tangentially, the relatively cold gas chills the outer surface of the arc stream, tending to constrict the arc, raise its temperature, and force it out of the front anode nozzle in a steady, relatively unfluctuating stream.
- **stain**
  - On an enameled surface, an iridescent spot caused by the action of fruit juice or chemicals.
- **staining**
  - Precipitation etching that causes contrast by distinctive staining of microconstituents; different interference colors originate from surface layers of varying thickness. Also known as color etching.
- **standard electrode potential**
  - An equilibrium electrode potential for an electrode in contact with an electrolyte in which all of the components of a specified chemical reaction are in their standard states. The standard for state for an ionic constituent is unit ion activity.
- **stardusting**
  - An extremely fine form of roughness on the surface of a metal deposit.
- **star marks**
  - A defect that sometimes occurs in sheet steel or iron porcelain enamel cover coats where the dried ware is set down too hard on the firing fixture points and the enamel coating is fractured.
- **stars**
  - In porcelain enamel , a defect in the fired surface that appears as a series of small hairlines radiating from a common center. Similar to star marks . Typical of porcelain enamel powder systems.
- **starting sheet**
  - A thin sheet of metal used as the cathode in electrolyte refining.
- **static coefficient of friction**
  - The coefficient of friction corresponding to the maximum friction force that must be overcome to initiate macroscopic motion between two bodies.
- **static electrode potential**
  - The electrode potential measured when no net current is flowing between the electrode and the electrolyte .
- **steadite**
  - A hard structural constituent of cast iron that consists of a binary eutectic of ferrite , containing some phosphorus in solution, and iron phosphide (Fe_3P). The eutectic consists of 10.2% P and 89.8% Fe. The melting temperature is 1050 °C (1920 °F).
- **stereophotogrammetry**
  - A method of generating topographic maps of fracture surfaces by the use of a stereoscopic microscope interfaced to a microcomputer that calculates the three-dimensional coordinates of the fracture surface and produces the corresponding profile map, contour plot, or carpet plot.
- **stippled finish**
  - A pebbly textured porcelain enamel , often multicolored.
- **stopping off**
  - (1) The application of a resist to any part of an electrode: cathode , anode , or plating rack . (2) Depositing a metal (copper, for example) in localized areas to prevent carburization, decarburization , or nitriding in those areas.
- **strain etching**
  - Metallographic etching that provides information on deformed and undeformed areas if present side by side. In strained areas, more compounds are precipitated.
- **stray current**
  - Current through paths other than the intended circuit, such as through heating coils or the tank.
- **stray-current corrosion**
  - Corrosion resulting from direct current flow through paths other than the intended circuit. For example, by an extraneous current in the earth.
- **stress-corrosion cracking (SCC)**

- A cracking process that requires the simultaneous action of a corrodent and sustained tensile stress. This excludes corrosion-reduced sections that fail by fast fracture. It also excludes intercrystalline or transcrystalline corrosion, which can disintegrate an alloy without applied or residual stress. Stress-corrosion cracking may occur in combination with hydrogen embrittlement .

- **stress relieving**
  - Heating to a suitable temperature, holding long enough to reduce residual stresses, and then cooling slowly enough to minimize the development of new residual stresses.
- **stretcher strains**
  - Elongated markings that appear on the surface of some sheet materials when deformed just past the yield point. These markings lie approximately parallel to the direction of maximum shear stress and are the result of localized yielding. See also Lüders lines .
- **strike**
  - (1) A thin electrodeposited film of metal to be overlaid with other plated coatings. (2) A plating solution of high covering power and low efficiency designed to electroplate a thin, adherent film of metal.
- **striking**
  - Electrodepositing, under special conditions, a very thin film of metal that will facilitate further plating with another metal or with the same metal under different conditions.
- **stringer**
  - In wrought materials, an elongated configuration of microconstituents or foreign material aligned in the direction of working. The term is commonly associated with elongated oxide or sulfide inclusions in steel.
- **strip**
  - (1) A process or solution used for the removal of a coating from a base metal or an undercoat . (2) To remove a coating from the base metal or undercoat.
- **submicron powder**
  - Any powder whose particles are smaller than 1 μm.
- **substrate**
  - (1) The material, workpiece, or substance on which a coating is deposited. (2) A material upon the surface of which an adhesive-containing substance is spread for any purpose, such as bonding or coating. A broader term than adherend . (3) In electronic devices, a body, board, or layer of material on which some other active or useful material(s) or component(s) may be deposited or laid; for example, electronic circuitry laid on an alumina ceramic board. (4) In catalysts , the formed, porous, high-surface area carrier on which the catalytic agent is widely and thinly distributed for reasons of performance and economy.
- **substrate temperature**
  - In thermal spraying, the temperature attained by the base material as the coating is applied. Proper control of the substrate temperature by intermittent spraying or by the application of external cooling will minimize stresses caused by substrate and coating thermal expansion differences.
- **subsurface corrosion**
  - Formation of isolated particles of corrosion products beneath a metal surface. This results from the preferential reactions of certain alloy constituents to inward diffusion of oxygen, nitrogen, or sulfur.
- **sulfidation**
  - The reaction of a metal or alloy with a sulfur-containing species to produce a sulfur compound that forms on or beneath the surface of the metal or alloy.
- **sulfide stress cracking (SSC)**
  - Brittle fracture by cracking under the combined action of tensile stress and corrosion in the presence of water and hydrogen sulfide. See also environmental cracking .
- **sulfochlorinated lubricant**
  - A lubricant containing chlorine and sulfur compounds, which react with a rubbing surface at elevated temperatures to form a protective film. There may be a synergistic effect, producing a faster reaction than with sulfur or chlorine additives alone.
- **sulfurized lubricant**
  - A lubricant containing sulfur or a sulfur compound that reacts with a rubbing surface at elevated temperatures to form a protective film. The shear strength of the sulfide film formed on ferrous

materials is lower than that of the metal but greater than that of the film formed by reaction with a chlorinated lubricant .

- **superabrasives**
  - Exceptionally hard and abrasion-resistant synthetic materials used for a wide variety of abrasive or cutting applications. Synthetic diamond and cubic boron nitride (CBN) are the two superabrasives used for grinding applications. Diamond is the hardest material known, and CBN is the second hardest.
- **superfines**
  - The portion of a metal powder that is composed of particles smaller than a specified size, usually 10 m.
- **superfinishing**
  - An abrasive process utilizing either a curved bonded honing stick (stone) for a cylindrical workpiece or a cup wheel for flat and spherical work. A large contact area, 30% approximately, exists between workpiece and abrasive. The object of superfinishing is to remove surface fragmentation and to correct inequalities in geometry, such as grinding feed marks and chatter marks. Also known as microhoning. See also honing .
- **surface active agent**
  - A substance that affects markedly the interfacial or surface tension of solutions even when present in very low concentrations.
- **surface alterations**
  - Irregularities or changes on the surface of a material due to machining or grinding operations. The types of surface alterations associated with metal removal practices include mechanical (for example, plastic deformation , hardness variations, cracks, etc.), metallurgical (for example, phase transformations, twinning, recrystallization , and untempered or overtempered martensite), chemical (for example, intergranular attack, embrittlement , and pitting), thermal (heat-affected zone, recast, or redeposited metal, and resolidified material), and electrical surface alterations (conductivity change or resistive heating).
- **surface damage**
  - In tribology, damage to a solid surface resulting from mechanical contact with another substance, surface, or surfaces moving relatively to it and involving the displacement or removal of material. In certain contexts, wear is a form of surface damage in which material is progressively removed. In another context, surface damage involves a deterioration of function of a solid surface even though there is no material loss from that surface. Surface damage may therefore precede wear.
- **surface finish**
  - (1) The geometric irregularities in the surface of a solid material. Measurement of surface finish shall not include inherent structural irregularities unless these are the characteristics being measured. (2) Condition of a surface as a result of a final treatment. See also roughness .
- **surface grinding**
  - Producing a flat surface with a rotating grinding wheel as the workpiece passes under.
- **surface hardening**
  - A generic term covering several processes applicable to a suitable ferrous alloy that produces a surface layer that is harder or more wear resistant than the core. The processes commonly used are carbonitriding , carburizing , induction hardening , flame hardening , nitriding , and nitrocarburizing . Use of the applicable specific process name is preferred.
- **surface integrity**
  - A technology that involves the specification and manufacture of unimpaired or enhanced surfaces through the control of the many possible alterations produced in a surface layer during manufacture. Surface integrity is achieved by the proper selection and control of manufacturing processes and the ability to estimate their effects on the significant engineering properties of work materials. See also surface alterations .
- **surface modification**
  - The alteration of surface composition or structure by the use of energy or particle beams. Elements may be added to influence the surface characteristics of the substrate by the formation of alloys, metastable alloys or phases, or amorphous layers. Surface-modified layers are distinguished from conversion or coating layers by their greater similarity to metallurgical alloying versus chemically reacted, adhered, or physically bonded layers. However, surface structures are produced that differ significantly from those obtained by conventional

metallurgical processes. This latter characteristic further distinguishes surface modification from other conventional processes, such as amalgamation or thermal diffusion. Two types of surface modification methods commonly employed are ion implantation and laser surface processing .

- **surface roughness**
  - Fine irregularities in the surface texture of a material, usually including those resulting from the inherent action of the production process. Surface roughness is usually reported as the arithmetic roughness average, R_a, and is given in micrometers or microinches.
- **surface tension**
  - That property, due to molecular forces, that exists in the surface film of all liquids and tends to prevent the liquid from spreading.
- **surface texture**
  - The roughness, waviness , lay , and flaws associated with a surface.
- **surface void**
  - A void which is located at the surface of a material and is a consequence of processing, that is, a surface reaction layer, as distinguished from a volume distributed flaw such as a pore or inclusion .
- **surfacing**
  - The deposition of filler metal (material) on a base metal (substrate) to obtain desired properties or dimensions. See also buttering , cladding , coating , and hardfacing .
- **surfactant**
  - (1) A chemical substance characterized by a strong tendency to form adsorbed interfacial films when in solution, emulsion, or suspension, thus producing effects such as low surface tension, penetration, boundary lubrication, wetting , and dispersing. (2) A compound that affects interfacial tensions between two liquids. It usually reduces surface tension. See also Rehbinder effect .
- **synthetic cold rolled sheet**
  - A hot rolled pickled sheet given a sufficient final temper pass to impart a surface approximating that of cold rolled steel.
- **T**
- **tape replica method (faxfilm)**
  - A method of producing a replica by pressing the softened surface of tape or plastic sheet material onto the surface to be replicated.
- **taper section**
  - A section cut obliquely (acute angle) through a surface and prepared metallographically. The angle is often chosen to increase the vertical magnification of surface features by a factor of 5 or 10. Taper sectioning is usually carried out for microstructural examination of coated metal specimens.
- **tarnish**
  - (1) The dulling, staining , or discoloration of metals due to superficial corrosion . (2) The film so formed.
- **tear burr**
  - Burr formed by the sides of a cutter as the cutter tears a chip from the workpiece. Also a ragged form of the Poisson burr caused by a built-up edge on the cutting tool.
- **tearing**
  - A defect in the surface of porcelain enamel characterized by short breaks or cracks that have been healed.
- **temper**
  - (1) In heat treatment, reheating hardened steel or hardened cast iron to some temperature below the eutectoid temperature for the purpose of decreasing hardness and increasing toughness. The process also is sometimes applied to normalized steel. (2) In tool steels, temper is sometimes used, but inadvisedly, to denote the carbon content. (3) In nonferrous alloys and in some ferrous alloys (steels that cannot be hardened by heat treatment), the hardness and strength produced by mechanical or thermal treatment, or both, and characterized by a certain structure, mechanical properties, or reduction in area during cold working.
- **temper color**
  - A thin, tightly adhering oxide skin (only a few molecules thick) that forms when steel is tempered at a low temperature, or for a short time, in air or a mildly oxidizing atmosphere. The color,

which ranges from straw to blue depending on the thickness of the oxide skin, varies with both tempering time and temperature.

- **tempered layer**
  - A surface or subsurface layer in a steel specimen that has been tempered by heating during some stage of the metallographic preparation sequence (usually grinding) . When observed in a section after etching , the layer appears darker than the base material.
- **tempered martensite**
  - The decomposition products that result from heating martensite below the ferrite-austenite transformation temperature. Under the optical microscope, darkening of the martensite needles is observed in the initial stages of tempering. Prolonged tempering at high temperatures produces spheroidized carbides in a matrix of ferrite . At the higher resolution of the electron microscope, the initial stage of tempering is observed to result in a structure containing a precipitate of fine iron carbide particles. At approximately 260 °C (500 °F), a transition occurs to a structure of larger and elongated cementite particles in a ferrite matrix. With further tempering at higher temperatures, the cementite particles become spheroidal, decrease in number, and increase in size.
- **tempered martensite embrittlement**
  - Embrittlement of high-strength alloy steels caused by tempering in the temperature range of 205 to 370 °C (400 to 700 °F); also called 350 °C or 500 °F embrittlement. Tempered martensite embrittlement is thought to result from the combined effects of cementite precipitation on prior-austenite grain boundaries or interlath boundaries and the segregation of impurities at prior-austenite grain boundaries. It differs from temper embrittlement in the strength of the material and the temperature exposure range. In temper embrittlement, the steel is usually tempered at a relatively high temperature, producing lower strength and hardness, and embrittlement occurs upon slow cooling after tempering and during service at temperatures within the embrittlement range. In tempered martensite embrittlement, the steel is tempered within the embrittlement range, and service exposure is usually at room temperature.
- **temper embrittlement**
  - Embrittlement of low-alloy steels caused by holding within or cooling slowly through a temperature range (generally 300 to 600 °C, or 570 to 1110 °F) just below the transformation range. Embrittlement is the result of the segregation at grain boundaries of impurities such as arsenic, antimony, phosphorus, and tin; it is usually manifested as an upward shift in ductile-to-brittle transition temperature. Temper embrittlement can be reversed by retempering above the critical temperature range, then cooling rapidly. Compare with tempered martensite embrittlement .
- **tempering**
  - In heat treatment, reheating hardened steel to some temperature below the eutectoid temperature to decrease hardness and/or increase toughness.
- **temper rolling**
  - Light cold rolling of sheet steel to improve flatness, to minimize the formation of stretcher strains , and to obtain a specified hardness or temper.
- **tensile burr**
  - The burr produced in blanking or piercing operations in which the slug separates from the stock as a result of tensile stresses.
- **tensile-plus-compressive burr**
  - The burr produced in blanking or piercing operations in which the slug separates from the stock in a stress field that is initially tensile, but changes to compressive at actual separation. This burr is usually associated with small die clearances and short die life.
- **terne**
  - An alloy of lead containing 3 to 15% Sn, used as a hot dip coating for steel sheet or plate. The term long terne is used to describe terne-coated sheet, whereas short terne is used for terne-coated plate. Terne coatings, which are smooth and dull in appearance (terne means dull or tarnished in French), give the steel better corrosion resistance and enhance its ability to be formed, soldered, or painted.
- **thermal embrittlement**
  - Intergranular fracture of maraging steels with decreased toughness resulting from improper processing after hot working. Thermal embrittlement occurs upon heating above 1095 °C (2000 °F) and then slow cooling through the temperature range of 980 to 815 °C (1800 to 1500 °F), and

has been attributed to precipitation of titanium carbides and titanium carbonitrides at austenite grain boundaries during cooling through the critical temperature range.

- **thermal etching**
  - Heating a specimen (usually a ceramic) in air, vacuum, or inert gases in order to delineate the grain structure. Used primarily in high-temperature microscopy.
- **thermal fatigue**
  - Fracture resulting from the presence of temperature gradients that vary with time in such a manner as to produce cyclic stresses in a structure. See also craze cracking .
- **thermal spraying**
  - A group of coating or welding processes in which finely divided metallic or nonmetallic materials are deposited in a molten or semimolten condition to form a coating. The coating material may be in the form of powder, ceramic rod, wire, or molten materials. See also electric arc spraying , flame spraying , plasma spraying , and powder flame spraying .
- **thermal spray powder**
  - A metal, carbide, or ceramic powder mixture designed for use with hardfacing and thermal spraying operations.
- **thermal wear**
  - Removal of material due to softening, melting, or evaporation during sliding or rolling. Thermal shock and high-temperature erosion may be included in the general description of thermal wear. Wear by diffusion of separate atoms from one body to the other, at high temperatures, is also sometimes denoted as thermal wear.
- **thermogalvanic corrosion**
  - Corrosion resulting from an electrochemical cell caused by a thermal gradient.
- **thermomechanical working**
  - A general term covering a variety of metal forming processes combining controlled thermal and deformation treatments to obtain synergistic effects, such as improvement in strength without loss of toughness. Same as thermal-mechanical treatment.
- **thermoplastic**
  - A type of polymer that softens and melts when heated and then resolidifies upon cooling. Thermoplastics generally have linear or branched structures.
- **thermoreactive deposition/diffusion process (TRD)**
  - A method of coating steels with a hard, wear-resistant layer of carbides, nitrides, or carbonitrides. In the TRD process, the carbon and nitrogen in the steel substrate diffuse into a deposited layer with a carbide-forming or nitride-forming element such as vanadium, niobium, tantalum, chromium, molybdenum, or tungsten. The diffused carbon or nitrogen reacts with the carbide- and nitride-forming elements in the deposited coating so as to form a dense and metallurgically bonded carbide or nitride coating at the substrate surface.
- **thermosetting**
  - A type of polymer that does not soften appreciably when heated. Thermosets may char when heated in air. They are generally cross-linked polymers.
- **thick-film circuit**
  - A circuit that is fabricated by the deposition of materials having between 5 and 20 μm (0.2 and 0.8 mil) thickness, such as screen-printed cermet pastes on a ceramic substrate, which are fired in a kiln to create permanent conductive patterns. Compare with thin-film circuit .
- **thick-film lubrication**
  - A condition of lubrication in which the film thickness of the lubricant is appreciably greater than that required to cover the surface asperities when subjected to the operating load, so that the effect of the surface asperities is not noticeable. Also known as full-film lubrication. See also thin-film lubrication .
- **thief**
  - A racking device or nonfunctional pattern area used in the electroplating process to provide a more uniform current density on plated parts. Thieves absorb the unevenly distributed current on irregularly shaped parts, thereby ensuring that the parts will receive an electroplated coating of uniform thickness.
- **thin-film circuit**
  - A circuit fabricated by the deposition of material several thousand angstroms thick (such as a circuit fabricated by vapor deposition). Compare with thick-film circuit .
- **thin-film lubrication**

- A condition of lubrication in which the film thickness of the lubricant is such that the friction and wear between the surfaces is determined by the properties of the surfaces as well as the viscosity of the lubricant. Under thin-film conditions, the coefficient of friction is often 10 to 100 times greater than under thick-film conditions and wear is no longer negligible. Compare with thick-film lubrication .

- **thread grinding**
  - Thread cutting by use of suitably formed grinding wheel.
- **threading and knurling**
  - A method of surface roughening in which spiral threads are prepared, followed by upsetting with a knurling tool.
- **throwing power**
  - The ability of an electrodeposit to coat recessed areas of an irregularly shaped cathode , usually measured by noting the coating distance up a cylindrical tube that is coated in an electrodeposition bath. Compare with covering power .
- **tiger stripes**
  - Continuous bright lines on sheet or strip in the rolling direction.
- **tint etching**
  - Immersing metallographic specimens in specially formulated chemical etchants in order to produce a stable film on the specimen surface. When viewed under an optical microscope, these surface films produce colors that correspond to the various phases in the alloy. Also known as color etching.
- **titania**
  - A white water-insoluble powder of composition TiO_2 that is produced commercially from the minerals ilmenite and rutile. Used in paints and cosmetics and as an ingredient in porcelain enamels , ceramic whiteware, and ophthalmic glasses. Pure TiO_2 is also used as thin- or thick-film semiconductors.
- **titanium carbide**
  - Very hard, heat-resistant ceramic materials of the composition TiC used in cermets and tungsten carbide cutting tools. Chemical vapor deposited TiC coatings are also used to extend the life of cemented carbide cutting tools.
- **titanium nitride**
  - A hard, high-melting-point ceramic (2950 °C, or 5342 °F) of the composition TiN that is used in cermets and as a coating material for cemented carbide cutting tools. See also carbide tools .
- **tolerance**
  - The specified permissible deviation from a specified nominal dimension, or the permissible variation in size or other quality characteristic of a part.
- **topcoat**
  - Usually the final paint film applied to a surface.
- **topography**
  - The configuration of a surface including its relief and the position of its natural and man-made features.
- **total cyanide**
  - Cyanide content of an electroplating bath (including both simple and complex ions).
- **toughness**
  - Ability of a material to absorb energy and deform plastically before fracturing. Toughness is proportional to the area under the stress-strain curve from the origin to the breaking point. In metals, toughness is usually measured by the energy absorbed in a notch impact test.
- **T-peel strength**
  - The average load per unit width of adhesive bond line required to produce progressive separation of two bonded, flexible adherends, under standard test conditions.
- **transcrystalline cracking**
  - Cracking or fracturing that occurs through or across a crystal. Also termed intracrystalline cracking.
- **transfer**
  - In tribology, the process by which material from one sliding surface becomes attached to another surface, possibly as the result of interfacial adhesion. Transfer is usually associated with adhesion, but the possibility of mechanical interlocking adherence, without adhesive bonding, exists in certain occurrences. Material may also back transfer to the surface from which it came.

- **transfer efficiency**
  - In powder coating, the rate at which a powder is deposited on a target per unit of time divided by the gun output.
- **transferred arc**
  - A plasma arc established between the electrode and the workpiece during plasma arc welding, cutting, and thermal spraying.
- **transgranular cracking**
  - Cracking or fracturing that occurs through or across a crystal or grain. Also called transcrystalline cracking. Contrast with intergranular cracking .
- **transgranular fracture**
  - Fracture through or across the crystals or grains of a material. Also called transcrystalline fracture or intracrystalline fracture. Contrast with intergranular fracture .
- **transition diagram**
  - In tribology, a plot of two or more experimental or operating variables that indicates the boundaries between various regimes of wear or surface damage. The IRG transition diagram is a plot of normal force (ordinate) versus sliding velocity (abscissa), and is used to identify three regions with differing lubrication effectiveness. Various plots have been called transition diagrams, and the context of usage must be established.
- **transmission electron microscopy (TEM)**
  - An analytical technique in which an image is formed by an electron beam directly on a photographic film of phosphor-coated plate. Image contrast is formed by the scattering of electrons out of the beam. TEM is used for very high magnification characterization of metals, ceramics, minerals, polymers, and biological materials.
- **traverse speed**
  - The lineal velocity at which the torch is passed across the substrate during the thermal spraying operation.
- **trees**
  - Branched or irregular projections formed on a cathode during electrodeposition , especially at edges and other areas of high current density .
- **tribology**
  - (1) The science and technology of interacting surfaces in relative motion and of the practices related thereto. (2) The science concerned with the design, friction, lubrication, and wear of contacting surfaces that move relative to each other (as in bearings, cams, or gears, for example).
- **tribosurface**
  - Any solid surface whose intermittent, repeated, or continuous contact with another surface or surfaces, in relative motion, results in friction, wear, and/or surface damage. The surface of a body subjected to a catastrophic collision would not generally be considered a tribosurface because significant damage to the entire body is involved.
- **trimming**
  - The mechanical shearing of flash from molded and forged parts.
- **tripoli compound**
  - A buffing compound containing approximately 75% free or crystalline silica.
- **truing**
  - The removal of the outside layer of abrasive grains on a grinding wheel for the purpose of restoring its face.
- **trunk**
  - The thick base of a burr .
- **tuberculation**
  - The formation of localized corrosion products scattered over the surface in the form of knoblike mounds called tubercles. The formation of tubercles is usually associated with biological corrosion.
- **tumble grinding**
  - Various surfacing operations ranging from deburring and polishing to honing and microfinishing metallic parts before and after plating.
- **tumbling**
  - Rotating workpieces, usually castings or forgings, in a barrel partly filled with metal slugs or abrasives, to remove sand, scale , or fins. It may be done dry, or with an aqueous solution added to the contents of the barrel. See also barrel finishing .

- **turning**
  - Removing material by forcing a single-point cutting tool against the surface of a rotating workpiece. The tool may or may not be moved toward or along the axis of rotation while it cuts away material.
- **U**
- **ultrahard tool materials**
  - Very hard, wear-resistant materials--specifically, polycrystalline diamond and polycrystalline cubic boron nitride--that are fabricated into solid or layered cutting tool blanks for machining applications. See also superabrasives .
- **ultraprecision finishing**
  - Machining processes used to alter surface characteristics such as finish, waviness, roundness, etc., without substantial removal of the work material. Examples include lapping and polishing of optical lenses, computer chips, or magnetic heads, and honing of cylinder liners.
- **ultrasonic cleaning**
  - Immersion cleaning aided by ultrasonic waves that cause microagitation and microcavitation.
- **ultrasonic C-scan inspection**
  - A method for displaying the relative attenuation of ultrasonic waves across the surface (plan view) of a structural component. An ultrasonic transducer is used to scan the surface of a material mechanically in an *x-y* raster scan mode while generating and receiving waves. Either the material is immersed in a water bath or columns of water are provided between the transducer and the material as a medium for ultrasonic energy transmissions. The received wave signals are electronically conditioned and measured to determine relative energy losses of the wave as it progresses through the material at each particular location on the specimen. Ultrasonic C-scan has been used extensively to determine both the initial integrity of a manufactured part and the void content, and to follow the initiation and progression of damage resulting from environmental loading.
- **ultrasonic impact grinding**
  - Material removal by means of an abrasive slurry and the ultrasonic vibration of a nonrotating tool. The abrasive slurry flows through a gap between the workpiece and the vibrating tool. Material removal occurs when the abrasive particles, suspended in the slurry, are struck on the downstroke of the vibrating tool. The velocity imparted to the abrasive particles causes microchipping and erosion as the particles impinge on the workpiece. See also ultrasonic machining .
- **ultrasonic inspection**
  - A nondestructive method in which beams of high-frequency sound waves are introduced into materials for the detection of surface and subsurface flaws in the material. The sound waves travel through the material with some attendant loss of energy (attenuation) and are reflected at interfaces. The reflected beam is displayed and then analyzed to define the presence and location of flaws or discontinuities. Most ultrasonic inspection is done at frequencies between 0.1 and 25 MHz--well above the range of human hearing, which is about 20 Hz to 20 kHz.
- **ultrasonic machining**
  - A process for machining of hard, brittle, nonmetallic materials that involves the ultrasonic vibration of a rotating diamond core drill or milling tool. Rotary ultrasonic machining is similar to the conventional drilling of glass and ceramic with diamond core drills, except that the rotating core drill is vibrated at an ultrasonic frequency of 20 kHz. Rotary ultrasonic machining does not involve the flow of an abrasive slurry through a gap between the workpiece and the tool. Instead, the tool contacts and cuts the workpiece, and a liquid coolant, usually water, is forced through the bore of the tube to cool and flush away the removed material. See also ultrasonic impact grinding .
- **ultraviolet radiation**
  - High-energy short-wavelength radiation used in coatings to cross link primarily acrylic and methacrylic systems by means of free-radical reactions.
- **undercoat**
  - A deposited coat of material that acts as a substrate for a subsequent thermal spray deposit. See also bond coat .
- **underfilm corrosion**
  - Corrosion that occurs under organic films in the form of randomly distributed threadlike filaments or spots. In many cases this is identical to filiform corrosion .

- **underfiring**
  - Firing a porcelain enamel coating at a lower temperature than that recommended, allowing an insufficient length of time in the furnace, or applying too heavy a layer of the enamel. Likely to cause blisters or boiling of the ground coat through the cover coat, or the enamel ground coat may fishscale before the cover coat can be applied and fired.
- **uniform corrosion**
  - (1) A type of corrosion attack (deterioration) uniformly distributed over a metal surface. (2) Corrosion that proceeds at approximately the same rate over a metal surface. Also called general corrosion .
- **unlubricated sliding**
  - Sliding without lubricant but not necessarily under completely dry conditions. Unlubricated sliding is often used to mean "not intentionally lubricated," but surface species such as naturally formed surface oxides and other interfacial contaminants may act in a lubricious manner in nominally lubricated sliding.
- **upper critical temperature**
  - The temperature above which austenite is the stable phase. Also called the A_3 temperature.
- **UV stabilizers**
  - Chemicals added to paint to absorb the ultraviolet radiation present in sunlight. Ultraviolet radiation decomposes the polymer molecules in a paint film, and thus UV stabilizers are used to prolong paint life.
- **V**
- **vacuum carburizing**
  - A high-temperature gas carburizing process using furnace pressures between 13 and 67 kPa (0.1 to 0.5 torr) during the carburizing portion of the cycle. Steels undergoing this treatment are austenitized in a rough vacuum, carburized in a partial pressure of hydrocarbon gas, diffused in a rough vacuum, and then quenched in either oil or gas. Both batch and continuous furnaces are used.
- **vacuum deposition**
  - Deposition of a metal film onto a substrate in a vacuum by metal evaporation techniques.
- **vacuum metallizing**
  - A process in which surfaces are thinly coated by exposing them to a metal vapor under vacuum.
- **vacuum nitrocarburizing**
  - A subatmospheric nitrocarburizing process using a basic atmosphere of 50% ammonia/50% methane, containing controlled oxygen additions of up to 2%.
- **vapor degreasing**
  - See degreasing .
- **vapor-deposited replica**
  - A replica formed of a metal or a salt by the condensation of the vapors of the material onto the surface to be replicated.
- **vapor-phase lubrication**
  - A type of lubrication in which one or more gaseous reactants are supplied to the vicinity of the surface to be lubricated and which subsequently react to form a lubricious deposit on that surface.
- **vapor plating**
  - Deposition of a metal or compound on a heated surface by reduction or decomposition of a volatile compound at a temperature below the melting points of the deposit and the base material. The reduction is usually accomplished by a gaseous reducing agent such as hydrogen. The decomposition process may involve thermal dissociation or reaction with the base material. Occasionally used to designate deposition on cold surfaces by vacuum evaporation. See also vacuum deposition .
- **varnish**
  - (1) In lubrication, a deposit resulting from the oxidation and/or polymerization of fuels, lubricating oils, or organic constituents of bearing materials. Harder deposits are described as lacquers , softer deposits are described as gums. (2) A transparent surface coating which is applied as a liquid and then changes to a hard solid; all varnishes are solutions of resinous materials in a solvent.
- **vehicle**
  - The combination of a paint binder and solvents or diluents, which are used to put the binder in a liquid, usable form.

- **veining**
  - A subboundary structure in a metal that can be delineated because of the presence of a greater than average concentration of precipitate or solute atoms.
- **vibratory cavitation**
  - Cavitation caused by the pressure fluctuations within a liquid, induced by the vibration of a solid surface immersed in the liquid.
- **vibratory finishing**
  - A process for deburring and surface finishing in which the product and an abrasive mixture are placed in a container and vibrated.
- **vibratory polishing**
  - A mechanical polishing process in which a metallographic specimen is made to move around the polishing cloth by imparting a suitable vibratory motion to the polishing system. See also polishing .
- **Vickers hardness test**
  - A microindentation hardness test employing a 136° diamond pyramid indenter (Vickers) and variable loads, enabling the use of one hardness scale for all ranges of hardness--from very soft lead to tungsten carbide. Also known as diamond pyramid hardness test.
- **VI improver**
  - An additive, usually a polymer , that reduces the variation of viscosity with temperature, thereby increasing the viscosity index of an oil.
- **viscosity**
  - The property of a liquid that enables it to resist flow, often measured by the time required for a given volume of liquid to flow through a small hole in the bottom of a cup under controlled conditions. A thick liquid-like molasses has a high viscosity.
- **visual examination**
  - The qualitative observation of physical characteristics, observed by using the unaided eye or perhaps aided by the use of a simple hand-held lens (up to 10×).
- **void**
  - (1) A shrinkage cavity produced in castings or weldments during solidification. (2) A term generally applied to paints to describe holidays , holes, and skips in a film.
- **volatile organic compounds (VOC)**
  - Volatile organic materials, such as solvents, that are present in many coating products.
- **volatiles**
  - Materials, such as water and alcohol, in a sizing or resin formulation, that are capable of being driven off as a vapor at room temperature or at slightly elevated temperature. See also size .
- **W**
- **Wallner lines**
  - A distinct pattern of intersecting sets of parallel lines, sometimes producing a set of V-shaped lines, sometimes observed when viewing brittle fracture surfaces at high magnification in an electron microscope. Wallner lines are attributed to interaction between a shock wave and a brittle crack front propagating at high velocity. Sometimes Wallner lines are misinterpreted as fatigue striations .
- **warpage**
  - (1) Deformation other than contraction that develops in a casting between solidification and room temperature. (2) The distortion that occurs during annealing, stress relieving, and high-temperature service.
- **water break test**
  - A test to determine if a surface is chemically clean by the use of a drop of water, preferably distilled water. If the surface is clean, the water will break and spread; a contaminated surface will cause the water to bead.
- **water marks**
  - Defects in a fired porcelain enamel surface due to water (perspiration) dropping on the dried enamel or not being thoroughly removed from crevices in the workpiece during the drying step after pickling or cleaning. Similar defects may also be caused by too much water in an enamel slip or poor suspension of the enamel slip. Also called water lines or water streaks.
- **waviness**
  - A wavelike variation from a perfect surface, generally much larger and wider than the roughness caused by tool or grinding marks. See also roughness .

- **wear**
  - Damage to a solid surface, generally involving progressive loss of material, due to a relative motion between that surface and a contacting surface or substance. Compare with surface damage .
- **wear debris**
  - Particles that become detached in a wear process.
- **wear scar**
  - The portion of a solid surface that exhibits evidence that material has been removed from it due to the influence of one or more wear processes.
- **weathering steels**
  - Copper-bearing high-strength low-alloy steels that exhibit high resistance to atmospheric corrosion in the unpainted condition.
- **wedge effect**
  - The establishment of a pressure wedge in a lubricant. See also wedge formation (2).
- **wedge formation**
  - (1) In sliding metals, the formation of a wedge or wedges of plastically sheared metal in local regions of interaction between sliding surfaces. This type of wedge is also known as a prow. It is similar to a built-up edge . (2) In hydrodynamic lubrication, the establishment of a pressure gradient in a fluid flowing into a converging channel. This is also known as wedge effect .
- **weld decay**
  - Intergranular corrosion , usually of stainless steels or certain nickel-base alloys, that occurs as the result of sensitization in the heat-affected zone during the welding operation.
- **wet blasting**
  - A process for cleaning or finishing by means of a slurry of abrasive in water directed at high velocity against the workpieces. Many different kinds and sizes of abrasives can be used in wet blasting. Sizes range from 20-mesh (very coarse) to 5000-mesh (which is much finer than face powder). Among the types of abrasives used are: organic or agricultural materials such as walnut shells and peach pits; novaculite, which is a soft type (6 to 6.5 Mohs hardness) of silica (99.46% silica); silica, quartz, garnet, and aluminum oxide; other refractory abrasives; and glass beads.
- **wet etching**
  - In metallography, revealing the microstructure in metals through the use of liquids, such as acids, bases, neutral solutions, or mixtures of solutions.
- **wet milling**
  - The grinding of porcelain enamel materials with sufficient liquid to form a slurry .
- **wet process enameling**
  - A method of porcelain enameling in which slip is applied to a metal article at ambient temperature, dried, and fired.
- **wetting**
  - The penetration of soil by the cleaning solution. Soap and/or wetting agents wetting increase the wetting action of water or solvents on a surface or soil by reducing surface tension. This wetting action helps in dislodging and removing soil.
- **wetting agent**
  - A substance that reduces the surface tension of a liquid, thereby causing it to spread more readily on a solid surface.
- **whiskers**
  - Metallic filamentary growths, often microscopic, sometimes formed during electrodeposition and sometimes spontaneously during storage or service, after finishing. Common on electrical contacts plated with zinc or cadmium.
- **white-etching layer**
  - A surface layer in a steel that, as viewed in a section after etching, appears whiter than the base metal . The presence of the layer may be due to a number of causes, including plastic deformation induced by machining, or surface rubbing, heating during a metallographic preparation stage to such an extent that the layer is austenitized and then hardened during cooling, and diffusion of extraneous elements into the surface.
- **white layer**
  - Surface layer on nitrided steels that is made up of intermetallic compounds, which do not etch and appear white in light microscopy.
- **white rust**

- Zinc oxide; the powder product of corrosion of zinc or zinc-coated surfaces.

- **wiped coat**
  - A hot dipped galvanized coating from which virtually all free zinc is removed by wiping prior to solidification, leaving only a thin zinc-iron alloy layer.
- **wipe solvent cleaning**
  - A method for removing contaminants from a surface by wetting a clean cloth with a solvent , wiping the surface to be cleaned, and then removing the residual solvent from the surface with a clean, dry cloth.
- **wiping**
  - In tribology, the smearing or removal of material from one point, often followed by the redeposition of the material at another point, on the surface of two bodies in sliding contact. The smeared metal is usually softened or melted.
- **wire flame spraying**
  - A thermal spraying process variation in which the material to be sprayed is in wire or rod form. See also flame spraying .
- **X**
- **x-ray tomography**
  - A method of imaging the internal structure of materials in which an x-ray beam is passed through the sample in multiple directions. The density throughout the sample is reconstructed by a computer from the transmitted x-ray signal.
- **x-ray topography**
  - A technique that comprises topography and x-ray diffraction. The term topography refers to a detailed description and mapping of physical (surface) features in a region. In the context of the x-ray diffraction, topographic methods are used to survey the lattice structure and imperfections in crystalline materials.
- **Z**
- **Zincrometal**
  - A steel coil-coated product consisting of a mixed-oxide underlayer containing zinc particles and a zinc-rich organic (epoxy) topcoat. It is weldable, formable, paintable, and compatible with commonly used adhesives. Zincrometal is used to protect outer body panels in automobiles from corrosion.
- **zinc worms**
  - Surface imperfections, characteristic of high-zinc brass castings, that occur when zinc vapor condenses at the mold/metal interface, where it is oxidized and then becomes entrapped in the solidifying metals.

Abbreviations, Symbols, and Tradenames

Abbreviations and Symbols

- ***a***
  - area
- **A**
  - austenite; ampere
- ***A***
  - cross-sectional area; contact area
- Å
  - angstrom
- **ac**
  - alternating current
- **ABS**
  - acrylonitrile butadiene styrene
- **AC**
  - air cool
- **Ac_1**
  - temperature at which austenite begins to form during heating

- **Ac_3**
  - temperature at which transformation of ferrite to austenite is completed during heating
- **AC_{cm}**
  - in hypereutectoid steel, temperature at which cementite completes solution in austenite
- **A_e**
  - surface area
- **Ae_{cm}, Ae_1, Ae_3**
  - equilibrium transformation temperatures in steel
- **AEM**
  - analytical electron microscope/microscopy
- **AES**
  - Auger electron spectroscopy; acoustic emission spectroscopy
- **AESF**
  - American Electroplaters and Surface Finishers Society
- **AFM**
  - atomic force microscope
- **AG**
  - aged; alternating grinding
- **AGMA**
  - American Gear Manufacturers Association
- **AISI**
  - American Iron and Steel Institute
- **Ams**
  - Amsler circumferential, rotating disk-on-disk machine
- **AMS**
  - Aerospace Material Specification; acoustic material signature
- **ANSI**
  - American National Standards Institute
- **APCVD**
  - atmospheric-pressure chemical vapor desposition
- **API**
  - American Petroleum Institute
- **Ar_1**
  - temperature at which transformation to ferrite or to ferrite plus cementite is completed on cooling
- **Ar_3**
  - temperature at which transformation of austenite to ferrite begins on cooling
- **Ar_{cm}**
  - temperature at which cementite begins to precipitate from austenite on cooling
- **ARE**
  - activated reactive evaporation
- **ARIP**
  - activated reactive ion plating
- **ARP**
  - Aerospace Recommended Practice
- **ASLE**
  - American Society of Lubrication Engineers (former name of STLE)
- **ASM**
  - American Society for Metals (now ASM International)
- **ASME**
  - American Society of Mechanical Engineers
- **ASTM**
  - American Society for Testing and Materials
- **at.%**
  - atomic percent
- **atm**
  - atmospheres (pressure)
- **AWS**

- American Welding Society
- **B**
    - bainite
- ***B***
    - gaseous reaction product
- **bal**
    - balance
- **BARE**
    - biased activated reactive evaporation
- **bcc**
    - body-centered cubic
- **bct**
    - body-centered tetragonal
- **Bé**
    - Baumé (specific-gravity scale)
- **BUE**
    - built-up edge
- ***c***
    - edge length in crystal structure; speed of light; specific heat; constant; conductivity
- **C**
    - cementite; coulomb; heat capacity
- ***C***
    - constant; velocity of light; shock wave velocity
- **CAD/CAM**
    - computer-aided design/computer-aided manufacturing
- **CAE**
    - corrosion-affected erosion
- **CANMET**
    - Canada Center for Mineral and Energy Technology
- **CBED**
    - convergent-beam electron diffraction
- **CBN**
    - cubic boron nitride
- **CCT**
    - continuous-cooling transformation
- **cd**
    - candela
- **CE**
    - carbon equivalent
- **CERCLA**
    - Comprehensive Environmental Response, Compensation, and Liability Act
- C_f
    - bearing friction factor
- **CFC**
    - chlorofluorocarbon
- **CFG**
    - creep feed grinding
- **CFR**
    - Code of Federal Regulations
- **cgs**
    - centimeter-gram-second (system of units)
- **CI**
    - compression ignition
- **CLA**
    - center-line average
- **cm**
    - centimeter

- **CMA**
  - cylindrical mirror analyzer
- **CMOS**
  - complementary metal-oxide semiconductor
- **CNC**
  - computer numerical control
- **cP**
  - centipoise
- **CSOM**
  - confocal scanning optical microscope
- **cSt**
  - centistokes
- **CTE**
  - coefficient of thermal expansion
- **CVD**
  - chemical vapor deposition
- **CVI**
  - chemical vapor infiltration
- **CVN**
  - Charpy V-notch (impact test or specimen)
- **cw**
  - continuous wave
- **d**
  - day
- ***d***
  - used in mathematical expressions involving a derivative (denotes rate of change); depth; diameter; interatomic distance
- ***D***
  - diameter; penetration depth
- ***da*/*dN***
  - fatigue crack growth rate
- **dB**
  - decibel
- D_B
  - ball diameter of Brinell hardness tester
- **DBT**
  - ductile-to-brittle transition
- **dc**
  - direct current
- **dhcp**
  - double hexagonal close-packed
- **diam**
  - diameter
- **DIBS**
  - dual-ion-beam sputtering
- **DIN**
  - Deutsche Industrie-Normen (German Industrial Standards)
- **DLC**
  - diamondlike carbon
- ***dL*/*dX***
  - loading rate
- **dpa**
  - displacements per incident atom
- **DPH**
  - diamond pyramid hardness (Vickers hardness)
- ***e***
  - natural log base, 2.71828; charge of an electron

- ***E***
  - erosion rate; Young's modulus; modulus of elasticity; applied voltage; energy; activation energy
- **EAW**
  - electric arc wire (spray)
- **EB**
  - electron beam
- **EBM**
  - electron-beam machining
- **E_c**
  - Young's modulus of coating
- **E/C**
  - erosion/corrosion
- **ECCS**
  - electrolytic chromium-coated steel
- **ECD**
  - electrochemical deburring
- **ECM**
  - electrochemical machining
- **ECP**
  - electron channeling pattern
- **ECR**
  - electron cyclotron resonance
- **E_d**
  - displacement energy
- **EDM**
  - electrical discharge machining
- **EDS**
  - energy-dispersive spectrometer
- **EDX**
  - energy-dispersive spectroscopy
- **EDXA**
  - energy dispersive x-ray analysis
- **EEC**
  - erosion-enhanced corrosion
- **EELS**
  - electron energy loss spectroscopy
- **EHD**
  - elastohydrodynamic
- **EHL**
  - elastohydrodynamic lubrication
- **ELI**
  - extra-low interstitial
- **emf**
  - electromotive force
- **EP**
  - extreme pressure
- **EPA**
  - Environmental Protection Agency
- **EPMA**
  - electron probe microanalysis
- **Eq**
  - equation
- **ESCA**
  - electron spectroscopy for chemical analysis
- **ESD**
  - electrospark deposition; electron-stimulated desorption
- **ESR**

- electroslag remelting
- **et al.**
  - and others
- **ETP**
  - electrolytic tin-plated (steel strip)
- **eV**
  - electron volt
- **exp**
  - base of the natural logarithm
- ***f***
  - frequency; friction coefficient; volume fraction
- **F**
  - ferrite
- ***F***
  - load; force
- **FAA**
  - Federal Aviation Administration
- **FBC**
  - fluidized bed combustion
- **fcc**
  - face-centered cubic
- **FCC**
  - fluid catalytic cracking
- **fct**
  - face-centered tetragonal
- **FEA**
  - finite element analysis
- **Fig.**
  - figure
- **ft**
  - foot
- **FTIR**
  - Fourier transform infrared spectroscopy
- **g**
  - gram
- ***g***
  - acceleration due to gravity
- **G**
  - graphite; gauss
- **gal**
  - gallon
- **gf**
  - gram force
- **GPa**
  - gigapascal
- **GTA**
  - gas tungsten arc
- **h**
  - hour; vertical thickness; Planck's constant (6.626×10^{-27} erg · s)
- **H**
  - Henry
- ***H***
  - enthalpy; hardness; magnetic field; height; depth of wear
- **HAIM**
  - high-frequency acoustic imaging
- **HAZ**
  - heat-affected zone

- **HB**
  - Brinell hardness
- **hcp**
  - hexagonal close-packed
- **HCT**
  - high coiling temperature
- **HDPE**
  - high-density polyethylene
- **HERF**
  - high-energy-rate forming
- **HIP**
  - hot isostatic pressing
- **HK**
  - Knoop hardness
- **hp**
  - horsepower
- **HR**
  - Rockwell hardness (requires scale designation, such as HRC for Rockwell C hardness)
- **HREM**
  - high-resolution electron microscopy (microhardness)
- **HRMF**
  - Rockwell microficial (microhardness)
- **HSLA**
  - high-strength low-alloy
- **HSS**
  - high-speed steel(s)
- **HV**
  - Vickers hardness
- **HVOF**
  - high-velocity oxyfuel (thermal-spray coating)
- **Hz**
  - hertz
- ***I***
  - intensity; electrical current; bias current
- **IBAD**
  - ion-beam-assisted deposition
- **IC**
  - integrated circuit
- **ICB**
  - ionized cluster beam (deposition)
- **ID**
  - inside diameter
- **in.**
  - inch
- **IP**
  - conventional ion plating
- **IR**
  - infrared
- **ISCC**
  - intergranular stress-corrosion cracking
- **ISO**
  - International Organization for Standardization
- **ISS**
  - ion scattering spectroscopy
- **J**
  - joule
- ***J***

- ion current density
- **k**
  - Boltzmann constant
- ***k***
  - thermal conductivity; Boltzmann constant; wear factor; wear coefficient
- **K**
  - kelvin
- ***K***
  - wear coefficient; specific wear rate
- **kg**
  - kilogram
- **kgf**
  - kilogram force
- K_{Ic}
  - plane-strain fracture toughness
- K_{ISCC}
  - threshold stress intensity to produce stress-corrosion cracking
- **km**
  - kilometer
- **kN**
  - kilonewton
- **kPa**
  - kilopascal
- **ksi**
  - kips (1000 lbf) per square inch
- **kV**
  - kilovolt
- **kW**
  - kilowatt
- ***l***
  - length
- ℓ
  - length
- **L**
  - longitudinal; liter
- **lb**
  - pound
- **lbf**
  - pound force
- **LCVD**
  - laser-induced chemical vapor deposition
- **LCL**
  - lower control limit
- **LCP**
  - liquid crystal polymer
- **LCSM**
  - laser confocal scanning microscope
- **LCT**
  - low coiling temperature
- **LDPE**
  - low-density polyethylene
- **LEED**
  - low-energy electron diffraction
- **ln**
  - natural logarithm (base *e*)
- **log**
  - common logarithm (base 10)

- **LPCVD**
    - low-pressure chemical vapor deposition
- **LSI**
    - large-scale integrated (circuit)
- **LT**
    - long transverse (direction)
- **m**
    - meter
- ***m***
    - constant shear, or frictional factor; Weibull slope, for reliability above 90%; Weibull distribution; dispersion parameter; molecular weight
- **mA**
    - milliampere
- **MAS**
    - Microbeam Analysis Society
- **MBE**
    - molecular-beam epitaxy
- **mc**
    - microcracked (chromium electroplate)
- **MCM**
    - multichip module
- **MEP**
    - mean effective pressure
- **MeV**
    - megaelectronvolt
- **M_f**
    - temperature at which martensite formation finishes during cooling
- **MFP**
    - mean free path
- **mg**
    - milligram
- **Mg**
    - megagram (metric tonne, or kg × 10^3)
- **MID**
    - molded interconnect device
- **MIG**
    - metal inert gas (welding)
- **min**
    - minute; minimum
- **mL**
    - milliliter
- **mm**
    - millimeter
- **MMC**
    - metal-matrix composite
- **MOCVD**
    - metal-organic chemical vapor deposition
- **mp**
    - microporous (chromium electroplate)
- **mPa**
    - millipascal
- **MPa**
    - megapascal
- **mpg**
    - miles per gallon
- **mph**
    - miles per hour

- **MRR**
  - material removal rate
- **ms**
  - millisecond
- **M_s**
  - temperature at which martensite starts to form from austenite on cooling
- **MS**
  - megasiemens; magnetron sputtering
- **MSA**
  - methane sulfonic acid
- **MSDS**
  - material safety data sheet
- **mT**
  - millitesla
- **mV**
  - millivolt
- **MV**
  - megavolt
- **MVVA**
  - metal vapor vacuum arc
- **N**
  - newton
- ***N***
  - number of cycles; normal solution; normal force
- **NASA**
  - National Aeronautics and Space Administration
- **NBS**
  - National Bureau of Standards (former name of NIST)
- **NCCA**
  - National Coil Coaters Association
- **NDE**
  - nondestructive evaluation
- **NF**
  - nonfluoborate (tin-lead electroplating solution)
- **NIST**
  - National Institute of Standards and Technology
- **nm**
  - nanometer
- **No.**
  - number
- **ns**
  - nanosecond
- **OCG**
  - optical gas controller
- **Oe**
  - oersted
- **OFD**
  - oxyfuel detonation (spray)
- **OFP**
  - oxyfuel powder (spray)
- **OFW**
  - oxyfuel wire (spray)
- **OMCVD**
  - organo-metallic chemical vapor deposition
- **ORNL**
  - Oak Ridge National Laboratory
- **OSHA**

  - Occupational Safety and Health Administration
- **oz**
  - ounce
- **p**
  - page
- ***p***
  - pressure
- **P**
  - pearlite
- ***P***
  - specific load or unit load; pressure
- **Pa**
  - Pascal
- **PA**
  - plasma arc (spray); prealloyed; polyamide
- **PACVD**
  - plasma-assisted chemical vapor deposition
- **PAN**
  - polyacrylonitrile
- **PAO**
  - polyalphaolefin
- **PAPVD**
  - plasma-assisted physical vapor deposition
- **PBT**
  - polybutylene terephthalate
- **PCD**
  - polycrystalline diamond
- **Pe**
  - Péclet number
- **PECVD**
  - plasma-enhanced chemical vapor deposition
- **PEM**
  - plasma emission monitor
- **PES**
  - polyether sulfone
- **PFPE**
  - polyperfluoroalkylether
- **PGM**
  - platinum-group metal
- **pH**
  - negative logarithm of hydrogen-ion activity
- **PH**
  - precipitation hardenable
- **PLD**
  - pulsed-laser deposition
- **P/M**
  - powder metallurgy
- **PMMA**
  - polymethyl methacrylate
- **POP**
  - plating on plastic
- **ppb**
  - parts per billion
- **ppba**
  - parts per billion atomic
- **ppm**
  - parts per million

- **ppmm**
  - parts per million by mass
- **ppt**
  - parts per trillion
- **psi**
  - pounds per square inch
- **psia**
  - pounds per square inch absolute
- **psig**
  - gage pressure (pressure relative to ambient pressure) in pounds per square inch
- **PSII**
  - plasma-source ion implantation
- **PSZ**
  - partially stabilized zirconia
- **PTFE**
  - polytetrafluoroethylene
- **PTH**
  - plated-through-hole (printed wiring board)
- **PVC**
  - polyvinyl chloride
- **PVD**
  - physical vapor deposition
- **PWB**
  - printed wiring board
- **QWP**
  - quarter-wave plate
- ***r***
  - radius; resistivity
- **R**
  - roentgen; force vector
- ***R***
  - radius; gas constant; resistance
- R_a
  - surface roughness in terms of arithmetic average
- **RA**
  - reduction in area
- **RCRA**
  - Resource Conservation and Recovery Act
- **RE**
  - rare earth
- **Ref**
  - reference
- **rf**
  - radio frequency
- **RH**
  - relative humidity
- **RHEED**
  - reflection high-energy electron diffraction
- **RIBAD**
  - reactive ion-beam-assisted deposition
- **RIP**
  - reactive ion plating
- **rms**
  - root mean square
- **rpm**
  - revolutions per minute
- R_q

    - rms (root mean square) roughness
- **RS**
    - reactive sputtering
- **RT**
    - room temperature
- **RTP**
    - rapid thermal processing
- **s**
    - second
- ***s***
    - standard deviation
- **S**
    - sand cast; siemens
- ***S***
    - sputtering yield; Sommerfeld number; rotational speed; rms average surface roughness
- **SAD**
    - selected-area diffraction
- **SAE**
    - Society of Automotive Engineers
- **SAM**
    - scanning acoustic microscope/microscopy
- **SARA**
    - Superfund Amendments and Reauthorization Act
- **SCaM**
    - scanning capacitance microscope
- **SCC**
    - stress-corrosion cracking
- **SCE**
    - saturated calomel electrode
- **SCR**
    - selective catalytic reduction
- **SE**
    - spectroscopic ellipsometry
- **SEM**
    - scanning electron microscope/microscopy
- **sfm**
    - surface feet per minute
- **SHE**
    - standard hydrogen electrode
- **SI**
    - Système International d'Unités
- **SIMS**
    - secondary ion mass spectroscopy
- **SIP**
    - sputter ion plating
- **SLAM**
    - scanning laser acoustic microscope/microscopy
- **SMA**
    - shielded metal arc
- **SMAW**
    - shielded metal arc welding
- **SPC**
    - statistical process control
- **SPE**
    - solid particle erosion
- **sp gr**
    - specific gravity

- **SPL**
  - spent pickle liquor
- **SRM**
  - Standard Reference Materials
- **ST**
  - short transverse (direction)
- **STA**
  - solution-treated and aged
- **std**
  - standard
- **STEM**
  - scanning transmission electron microscope/microscopy
- **STLE**
  - Society of Tribologists and Lubrication Engineers (formerly ASLE)
- **STM**
  - scanning tunneling microscope/microscopy
- **SUS**
  - Saybolt Universal Seconds (viscosity)
- **SWE**
  - single-wavelength ellipsometry
- **Sv**
  - sievert
- **SZM**
  - structure-zone model
- ***t***
  - thickness; time
- **T**
  - tesla
- ***T***
  - temperature; thickness
- T_c
  - contact temperature; critical temperature; Curie temperature
- **TEM**
  - transmission electron microscope/microscopy
- **TFS**
  - tin-free steel
- **TFT**
  - thin film transistor
- **TGA**
  - thermogravimetric analysis
- **TGS**
  - threshold galling stress
- **TIG**
  - tungsten inert gas (welding)
- **TLA**
  - thin layer activation
- **TLV**
  - threshold level value
- T_m
  - mean contact temperature; melting temperature
- **TR**
  - temper rolled
- **TRS**
  - transverse rupture strength
- **TSCA**
  - Toxic Substances Control Act
- **tsi**

    - tons per square inch
- **TSM**
    - tandem scanning microscope/microscopy
- **TTT**
    - time-temperature transformation
- **UHDPE**
    - ultrahigh-density polyethylene
- **UHMWPE**
    - ultrahigh-molecular-weight polyethylene
- **UHV**
    - ultrahigh vacuum
- **UNS**
    - Unified Numbering System
- **UTS**
    - ultimate tensile strength
- ***v***
    - velocity; particle velocity
- **V**
    - volt
- ***V***
    - sliding speed; velocity; volume
- **VAR**
    - vacuum arc remelted
- **VHN**
    - Vickers microindenter hardness number
- **VI**
    - viscosity index
- **VIM-VAR**
    - vacuum induction melted-vacuum arc remelted
- **VOC**
    - volatile organic compound
- **vol**
    - volume
- **vol%**
    - volume percent
- **VPE**
    - vapor-phase epitaxy
- ***w***
    - width
- **W**
    - watt
- ***W***
    - load; weight of body; abrasive wear resistance; wear volume
- **WDS**
    - wavelength-dispersive spectrometer
- **WPC**
    - wear particle concentration
- **WRP**
    - work removal parameter
- **wt%**
    - weight percent
- **XPS**
    - x-ray photoelectron spectroscopy
- **XRD**
    - x-ray diffraction
- **XRF**
    - x-ray fluorescence

- **XTEM**
    - cross-sectional transmission electron microscopy
- ***Y***
    - yield stress in tension
- **YAG**
    - yttrium-aluminum-garnet
- **yr**
    - year
- **ZTA**
    - zirconia-toughened alumina
- °
    - angular measure; degree
- **°C**
    - degree Celsius (centigrade)
- **°F**
    - degree Fahrenheit
- **!**
    - direction of reaction
- ÷
    - divided by
- =
    - equals
- ≅
    - approximately equals
- ≠
    - not equal to
- ≡
    - identical with
- >
    - greater than
- >>
    - much greater than
- ≥
    - greater than or equal to
- ∞
    - infinity
- ∝
    - is proportional to; varies as
- ∫
    - integral of
- <
    - less than
- <<
    - much less than
- ≤
    - less than or equal to
- ±
    - maximum deviation
- -
    - minus; negative ion charge
- ×
    - diameters (magnification); multiplied by
- ·
    - multiplied by
- /
    - per
- %

- percent
- **+**
  - plus; positive ion charge
- $\sqrt{}$
  - square root of
- **~**
  - approximately; similar to
- ∂
  - partial derivative
- **α**
  - nominal contact angle; thermal diffusivity; taper angle; angle of incidence
- **β**
  - coefficient of friction
- **γ**
  - shear strain rate
- **δ**
  - film width
- Δ
  - change in quantity; an increment; a range; critical amplitude
- **ε**
  - lubricant film thickness; tribocontact parameter; emissivity; strain
- $\dot{e}$
  - strain rate
- **η**
  - lubricant viscosity; efficiency of material removal; degree of wear; abrasive fraction
- **θ**
  - angle
- **λ**
  - wavelength; pressure coefficient of viscosity; film thickness-to-roughness ratio; lambda ratio; specific film thickness
- Λ
  - specific film thickness; compressibility number; film thickness parameter
- **μ**
  - friction coefficient; magnetic permeability
- **μF**
  - microfarads
- **μin.**
  - microinch
- **μm**
  - micrometer (micron)
- **μs**
  - microsecond
- *u*
  - Poisson's ratio
- *x*
  - Poisson's ratio
- **π**
  - pi (3.141592)
- **ρ**
  - density
- **σ**
  - stress; standard deviation; root-mean-square roughness; Stefan-Boltzmann constant
- σ_s
  - shear stress
- Σ
  - summation of
- *t*

- applied stress
- *f*
  - standard normal distribution
- Φ
  - energy rate; work function
- **ψ**
  - rolling angle
- **ω**
  - angular velocity; frequency
- **Ω**
  - ohm

Greek Alphabet

- **A, α**
  - alpha
- **B, β**
  - beta
- Γ**, γ**
  - gamma
- Δ**, δ**
  - delta
- **E, ε**
  - epsilon
- **Z,** *z*
  - zeta
- **H, η**
  - eta
- Θ**, θ**
  - theta
- **I,** *i*
  - iota
- **K, κ**
  - kappa
- Λ**, Lambda;**
  - lambda
- **M, μ**
  - mu
- **N,** *u*
  - nu
- Ξ**,** *x*
  - xi
- **O, o**
  - omicron
- Π**, π**
  - pi
- **P, ρ**
  - rho
- Σ**, σ**
  - sigma
- **T,** *t*
  - tau
- ϒ**,** *u*
  - upsilon
- Φ**,** *f*
  - phi
- **X, χ**

- chi
- **ψ,**
  - psi
- **Ω, ω**
  - omega

o **Tradenames**
- **Amplate**
  - is a tradename of Amorphous Technologies International
- **Argental**
  - is a tradename of Ingold Me β technik GmbH
- **Falex**
  - is a trademark of Falex Corporation
- **Ferrostan**
  - is a trademark of USX Corporation
- **Galvalume**
  - is a trademark of Bethlehem Steel Corporation
- **Galvan**
  - is a trademark of USX Corporation
- **Inconel, Incoloy, and Nimonic**
  - are trademarks of Inco Alloys International, Inc.
- **Haynes and Hastelloy**
  - are trademarks of Haynes International, Inc.
- **Scotch-Brite and Scotch-Weld**
  - are trademarks of 3M Company
- **Super D-Gun**
  - is a tradename of Praxair Surface Technologies, Inc.
- **Taber Abraser**
  - is a trademark of Taber Industries

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